Министерство общего и профессионального образования

Российской Федерации

Южно-Уральский государственный университет

Д. Г. Ким

ОРГАНИЧЕСКИЕ РЕАКЦИИ

Учебное пособие

Челябинск 1999

В учебном пособии систематизированы схемы реакций алифатических и ароматических соединений и содержит сведения о более чем 1000 реакциях. Учебное пособие носит информационно-справочный характер, является дополнением к известным учебникам.

Учебное пособие предназначено для студентов, изучающих органическую химию и органический синтез. Оно может быть полезно также для преподавателей ВУЗов, аспирантов и научных работников.

Библиогр.: 13 назв.

ВВЕДЕНИЕ

Органическая химия бурно развивается. Открываются новые реакции, новые методы синтеза ещё недавно мало доступных веществ. Новой информации об органических синтезах становится настолько много, что вузовские учебники не успевают их полностью отразить.

В настоящем учебном пособии в соответствии с программой общего курса по органической химии для химических факультетов классических университетов систематизированы основные методы синтезов и реакций алифатических и ароматических соединений. Такая систематизация особенно важна для подготовки к экзаменам и семинарским занятиям. В пособии также приведены названия наиболее важных именных реакций и названия некоторых сложных органических соединений.

Материалы, включенные в данное пособие в основном предназначены для студентов, начинающих изучать органическую химию в вузах, но могут быть полезны и для старшекурсников, изучающих дисциплину “Органический синтез”.

В этом учебном пособии рассматриваются исключительно схемы органических реакций, а знания о механизмах химических реакций, стереохимии и реакционной способности органических соединений можно найти в литературе, список которой приведён в конце данного учебного пособия.

Следует отметить, чтобы найти некоторые схемы реакций, необходимо просмотреть несколько разделов. Так, например, схема получения сложного эфира может быть приведена не только в разделе “Синтезы сложных эфиров”, но и в разделах “Свойства спиртов” и “Свойства кислот”.

Предложенные схемы реакций могут быть использованы для составления различных синтетических схем, для построения сложных молекулярных структур.

1. Алканы

1.1. Синтезы

1. $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$
2. $CS_2 + 2H_2S + 8Cu \longrightarrow CH_4 + 4Cu_2S$
3. $RCOONa + NaOH \longrightarrow RH + Na_2CO_3$
4. $RMgX + H_2O \longrightarrow R–H + Mg(OH)X$
5. $2RX + 2Na \longrightarrow R–R + 2NaX$ (Вюрц)
6. $RX + R_2CuLi \longrightarrow R–R$
7. $RI + HI \longrightarrow RH + I_2$
8. $R_3B + RCO_2H \longrightarrow R–H$
9. $2RCOO^- + 2e^- \longrightarrow 2RCOO^\bullet \longrightarrow R–R + 2CO_2$ (Кольбе)
10. $C_nH_{2n} + H_2 \xrightarrow{Ni} C_nH_{2n+2}$
11. $RCOR^1 \xrightarrow[\text{или } NH_2NH_2/KOH]{Zn,\ HX} RCH_2R^1$
12. $nC + (n+1)H_2 \xrightarrow[Fe]{P,\ t^\circ} C_nH_{2n+2}$
13. $nCO + (2n+1)H_2 \xrightarrow[Co]{P,\ t^\circ} C_nH_{2n+2} + nH_2O$ (Фишер-Тропш)

1.2. Реакции

1. $RH + X_2 \xrightarrow{h\nu} RX + HX$ X = Cl, Br
2. $RH + HNO_3 \longrightarrow RNO_2 + H_2O$
3. $RH + SO_2 + Cl_2 \xrightarrow{h\nu} RSO_2Cl + HCl$ (сульфохлорирование)
4. $RH + SO_2 + O_2 \xrightarrow{h\nu} RSO_2OH$ (сульфоокисление)
5. $RH + CH_2N_2 \xrightarrow{h\nu} RCH_3 + N_2$
6. $2CH_4 \xrightarrow{t^\circ} C_2H_2 + 3H_2$
7. $CH_3CH_3 \xrightarrow{t^\circ} C_2H_2 + C_2H_4 + H_2$
8. $CH_3(CH_2)_3CH_3 \rightleftharpoons[AlX_3]{} CH_3CH(CH_3)CH_2CH_3 + CH_3C(CH_3)_2CH_3$
9. $RCH_2CH_3 \xrightarrow{t^\circ} RCH{=}CH_2 + CH_4 + RCH_3 + C_2H_4 + RCH{=}CHCH_3 + H_2$
10. $CH_4 + O_2 \xrightarrow{t^\circ} HCOH$
11. $C_4H_{10} + O_2 \xrightarrow{t^\circ} CH_3COOH$

12. $CH_4 + S \xrightarrow[>500\,^\circ C]{SiO_2} CS_2$

13. $CH_4 + N_2 \xrightarrow{t^\circ} HCN$

2. Алкены

2.1. Синтезы

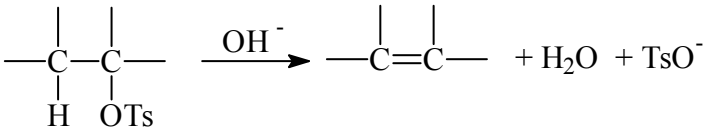
1. $R–C\equiv C–R + H_2 \xrightarrow{Pd/PbCO_3} RCH=CHR$

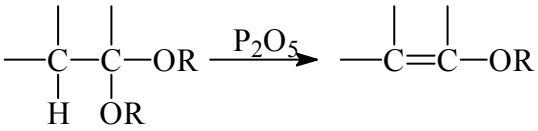
2. $R_2CH–CR_2Cl \xrightarrow[ROH]{NaOH} R_2C=CR_2 + HCl$

3. $R_2XC–CR_2X + Zn \longrightarrow R_2C=CR_2$

4. $CH_3CH_2CH_2OH \xrightarrow[>300^\circ C]{Al_2O_3} CH_3CH=CH_2$

5. $R_2CH–CR_2OH \xrightarrow{H^+} R_2C=CR_2$

6. 

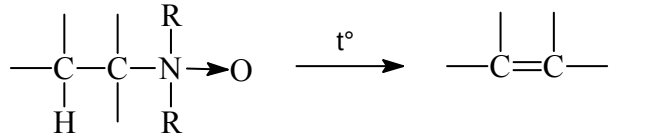
7. 

8. $R_2CO + H_2C=PR_3 \longrightarrow R_2C=CH_2 + R_3PO$ (Виттиг)

9. $RCHO + ZCH_2Z \longrightarrow RCH=CZ_2$ (Z = CN, COR, COOR) (Кневенагель)

10. $H_3C–CH_2SO_2–CHX–CH_3 \xrightarrow[H_2O]{NaOH} H_3C–CH=CH–CH_3$ (Рамберг-Беклунд)

11. $[R_3NCH_2CH_2CH_2CH_3]\,OH \longrightarrow CH_3CH_2CH=CH_2 + R_3N + H_2O$ (Гофман)

12. 

13. $C_2H_5–O–C(S)–SCH_3 \xrightarrow{t^\circ} CH_2=CH_2 + COS + CH_3SH$ (Чугаев)

2.2. Реакции

2.2.1. Реакции присоединения и циклоприсоединения

1. $RCH=CH_2 + X_2 \longrightarrow RCHXCH_2X$

2. $RCH=CH_2 + HX \longrightarrow RCHXCH_3$ (Правило Марковникова)

3. $(CH_3)_2CHCH=CH_2 + HX \longrightarrow (CH_3)_2CX–CH_2CH_3$

4. $CF_3CH=CH_2 + HX \longrightarrow CF_3CH_2–CH_2X$

5. $RCH{=}CH_2 + ROH \xrightarrow{H^+} RCH(OR)CH_3$

6. $RCH{=}CH_2 + H_2O \xrightarrow{H^+} RCH(OH)CH_3$

7. $RCH{=}CH_2 + RCOOH \xrightarrow{H^+} RCH(CH_3){-}OOCR$

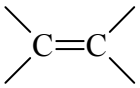
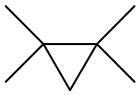
8. $RCH{=}CH_2 + NOCl \longrightarrow RCHCl{-}CH_2NO$

9. $RCH{=}CH_2 + RSCl \longrightarrow RCHCl{-}CH_2SR$

10. $RCH{=}CH_2 + INCO \longrightarrow RCHI{-}CH_2NCO$

11. $RCH{=}CH_2 + R_2NCl \xrightarrow[CH_3COOH]{H_2SO_4} RCHCl{-}CH_2NR_2$

12. $RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2)_3B$

13.  $+ CH_2N_2 \xrightarrow{h\nu}$  $+ N_2$

14. $2CH_2{=}CH_2 \xrightarrow{h\nu}$ 

15. $RCH{=}CH_2 + BH_3 \longrightarrow \xrightarrow{CO} \xrightarrow[OH^-]{H_2O_2} (RCH_2CH_2)_3COH$

16. $RCH{=}CH_2 + Hg(OAc)_2 + R^1OH \longrightarrow RCH(OR^1)CH_2HgOAc$

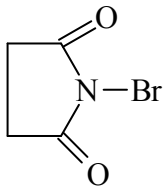
17. $RCH{=}CH_2 + X_2 + H_2O \longrightarrow RCH(OH)CH_2X$

18. $RCH{=}CH_2 + HX \xrightarrow{h\nu \text{ или } R\bullet} RCH_2CH_2X$

19. $RCH{=}CH_2 + R^1SH \xrightarrow{h\nu \text{ или } R\bullet} RCH_2CH_2SR^1$

2.2.2. Реакции в аллильное положение

1. $RCH_2CH{=}CH_2 + Cl_2 \xrightarrow{500^\circ C} RCHClCH{=}CH_2$ (Львов)

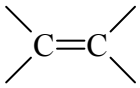
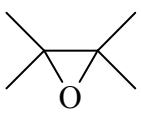
2. $RCH_2CH{=}CH_2 +$  $\longrightarrow RCHBrCH{=}CH_2$

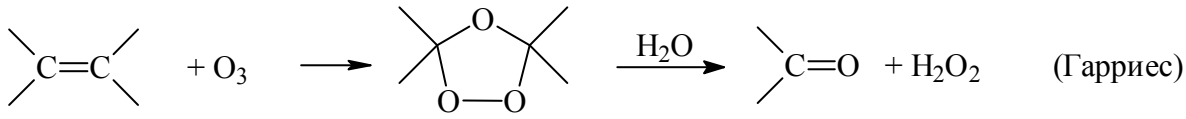
2.2.3. Реакции окисления и оксосинтез

1. $RCH{=}CH_2 + 2KMnO_4 + 4H_2O \longrightarrow RCH(OH)CH_2OH + 2KOH + 2MnO_2$ (Вагнер)

2. $RCH{=}CH_2 + KMnO_4 \xrightarrow{H^+} RCO_2H + CO_2$

3. $R_2C{=}CHR \xrightarrow{CrO_3} R_2C{=}O + RCOH$

4.  $+ RCO_3H \longrightarrow$  $+ RCO_2H$ (Прилежаев)

5.  (Гарриес)

6. $CH_2{=}CH_2 + CO + H_2 \xrightarrow{HCo(CO)_4} CH_3CH_2CHO$ (гидроформилирование)

7. $CH_3CH_2CH{=}CH_2 + CO + H_2 \xrightarrow{Co} CH_3CH_2CH_2CHO + (CH_3)_2CHCHO$

8. $CH_2{=}CH_2 + CO + H_2O \xrightarrow{Co} CH_3CH_2CO_2H$

9. $CH_2{=}CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$

2.2.4. Другие реакции

1. $CH_3{-}CH_2{-}CH{=}CH_2 \xrightarrow{t^\circ} CH_3{-}CH{=}CH{-}CH_3 + (CH_3)_2C{=}CH_2$

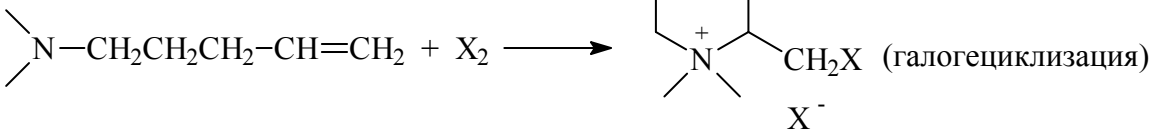
2. $R{-}Z{-}CH_2{-}CH{=}CH_2 \xrightarrow{OH^-} R{-}Z{-}CH{=}CH{-}CH_3$ Z = O, S, NR

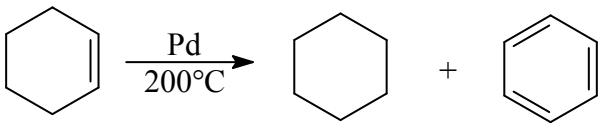
3. $R\text{-}CH{=}CH\text{-}R + R^1\text{-}CH{=}CH\text{-}R^1 \underset{}{\overset{Re_2O_7/Al_2O_3}{\rightleftharpoons}} 2R\text{-}CH{=}CH\text{-}R^1$ (метатезис)

4. $nCH_2{=}CH_2 + R_3Al + TiCl_4 \longrightarrow R{-}(CH_2{-}CH_2{-})_nTiCl_3$ (Циглер-Натта)

5. $nCH_2{=}CH_2 + CCl_4 \longrightarrow Cl{-}(CH_2{-}CH_2)_n{-}CCl_3$

6. $nRCH{=}CH_2 \longrightarrow (-CHR{-}CH_2-)_n$

7.  (галогециклизация)

8.  (Зелинский)

9. $CH_2{=}CH_2 + PdCl_2 \longrightarrow CH_2{=}CH_2{\bullet}PdCl_2$ π-комплекс

10. $CH_2{=}CH_2 + K_2[PtCl_4] \longrightarrow KCl + K[C_2H_4PtCl_3]$ соль Цейзе

3. Алкины

3.1. Синтезы

1. $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

2. $Mg_2C_3 + 4H_2O \longrightarrow CH_3C{\equiv}CH + Mg(OH)_2$

3. $2CH_4 \xrightarrow{t^\circ} C_2H_2 + 3H_2$

4. $RCH_2CHBr_2 + KOH + EtOH \xrightarrow{NaNH_2} RC{\equiv}CH$

5. $RCBr_2CHBr_2 + Zn \longrightarrow RC{\equiv}CH$

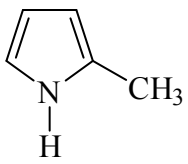
6. $RCCl_2CH_3 + NaOH + EtOH \longrightarrow RC{\equiv}CH$

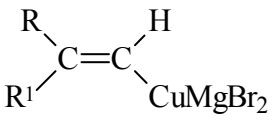
3.2. Реакции

3.2.1. Реакции с сохранением тройной связи

1. $RC{\equiv}CH + [Ag(NH_3)_2]^+ \longrightarrow RC{\equiv}CAg$
2. $RC{\equiv}CH + NaNH_2 \longrightarrow RC{\equiv}CNa$
3. $HC{\equiv}CH \xrightarrow{RONa} \xrightarrow{R^1X} HC{\equiv}CR$
4. $R{-}C{\equiv}CH + NaNH_2 \longrightarrow R{-}C{\equiv}CNa + NH_3$
5. $R{-}C{\equiv}CH + RMgX \longrightarrow R{-}C{\equiv}CMgX + RH$ (Иоцич)
6. $R{-}C{\equiv}CH + NaOH \rightleftharpoons R{-}C{\equiv}CNa + H_2O$
7. $R{-}C{\equiv}CH + Cu^+ \longrightarrow R{-}C{\equiv}CCu + H^+$
8. $R{-}C{\equiv}C{-}Cu + ArI \longrightarrow R{-}C{\equiv}C{-}Ar$
9. $R{-}C{\equiv}CH + Ag^+ \longrightarrow R{-}C{\equiv}CAg + H^+$
10. $R{-}C{\equiv}C{-}CH_3 + NaNH_2 \longrightarrow R{-}CH_2{-}C{\equiv}CNa$
11. $HC{\equiv}CH + RCHO \xrightarrow{Cu_2C_2} RCH(OH){-}\ C{\equiv}CH$ (Реппе)
12. $HC{\equiv}CH + R^1COR^2 \xrightarrow{KOH} R^1R^2C(OH){-}\ C{\equiv}CH$ (Фаворский)
13. $RCH_2{-}C{\equiv}CH \xrightarrow[170^\circ C]{KOH} RCH{=}C{=}CH_2 \longrightarrow RC{\equiv}C{-}CH_3$ (Фаворский)
14. $RC{\equiv}CH + X_2 \xrightarrow{NaOH} RC{\equiv}CX$

3.2.2. Реакции присоединения

1. $RC{\equiv}CH + X_2 \longrightarrow RCX{=}CHX$
2. $RC{\equiv}CH + HX \longrightarrow RCX{=}CH_2$
3. $HC{\equiv}CH + HCN \longrightarrow CH_2{=}CH{-}CN$
4. $RC{\equiv}CH + H_2O \xrightarrow{H^+ + Hg2+} [R{-}C(OH){=}CH_2] \longrightarrow RCOCH_3$ (Кучеров)
5. $HC{\equiv}CH + ROH \xrightarrow{KOH} ROCH{=}CH_2$
6. $HC{\equiv}CH + RSH \xrightarrow{KOH} RSCH{=}CH_2$
7. $HC{\equiv}CH + (CH_3)_2C{=}NOH \xrightarrow{KOH + ДМСО}$  (Трофимов)
8. $HC{\equiv}CH + RNH_2 \xrightarrow{KOH} R{-}N{=}CH{-}CH_3$
9. $HC{\equiv}CH + H_2S \xrightarrow{KOH + ДМСО} CH_2{=}CH{-}S{-}CH{=}CH_2$
10. $HC{\equiv}CH + RCO_2H \xrightarrow{H^+ + Hg2+} H_2C{=}CH{-}O{-}COCH_3$

11. $RC{\equiv}CH + R^1CuMgBr_2 \longrightarrow$ 

12. $RC{\equiv}CR \xrightarrow{Na + NH_3} RCH{=}CHR$ (*транс*-изомер)

13. $RC{\equiv}CR \xrightarrow{H_2 + Pd} RCH{=}CHR$ (*цис*-изомер)

14. $RC{\equiv}CR \xrightarrow{BH_3} \xrightarrow{CH_3CO_2H} RCH{=}CHR$ (*цис*-изомер)

3.2.3. Другие реакции

1. $HC{\equiv}CH + KMnO_4 \longrightarrow KO_2C{-}CO_2K$

2. $RC{\equiv}CR^1 \xrightarrow{[O]} RCOOH + R^1COOH$

3. $HC{\equiv}CH + CO + HX \xrightarrow{Ni(CO)_4} CH_2{=}CH{-}COX$ X = OH, OR, NH_2

4. $2HC{\equiv}CH \xrightarrow{Cu^+} CH_2{=}CH{-}C{\equiv}CH$

5. $2RC{\equiv}CH + O_2 \xrightarrow{Cu^+} R{-}C{\equiv}C{-}C{\equiv}C{-}H$

6. $nHC{\equiv}CH + O_2 \xrightarrow{Cu^+} H{-}[{-}C{\equiv}C{-}]_n{-}H$

7. $3HC{\equiv}CH \xrightarrow{kat.} C_6H_6$

4. 1,3-Диены

4.1. Синтезы

1. $2C_2H_5OH \xrightarrow{Al_2O_3 + ZnO} CH_2{=}CH{-}CH{=}CH_2$ (Лебедев)

2. $CH_3CH(OH)\,CH_2CH_2OH \xrightarrow{H^+,\ t^\circ} CH_2{=}CH{-}CH{=}CH_2$

3. $HOCH_2CH_2\,CH_2CH_2OH \xrightarrow{H^+} CH_2{=}CH{-}CH{=}CH_2$

4. $CH_3CH_2CH_2CH_3 \xrightarrow{Cr_2O_3} CH_2{=}CH{-}CH{=}CH_2$

5. $C_4H_8 \xrightarrow[CrO_3]{t^\circ} CH_2{=}CH{-}CH{=}CH_2$

4.2. Реакции

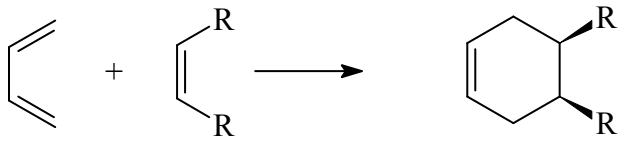
1. $CH_2{=}CH{-}CH{=}CH_2 + H_2 \xrightarrow{Ni} CH_3{-}CH{=}CH{-}CH_3$

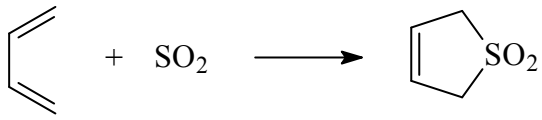
2. $CH_2{=}CH{-}CH{=}CH_2 + Br_2 \longrightarrow BrCH_2{-}CH{=}CH{-}CH_2Br + BrCH_2{-}CHBr{-}CH{=}CH_2$

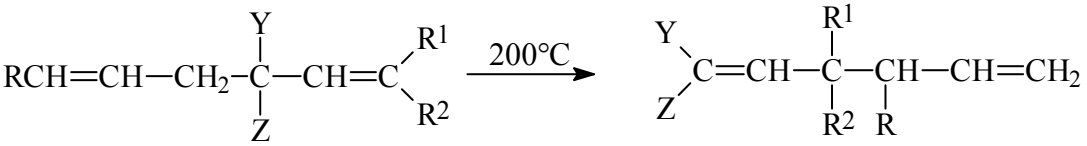
3. $CH_2{=}CH{-}CH{=}CH_2 + HBr \longrightarrow CH_3{-}CHBr{-}CH{=}CH_2 + CH_3{-}CH{=}CH{-}CH_2Br$

4. $nCH_2{=}CH{-}CH{=}CH_2 \xrightarrow{R\bullet} (-CH_2{-}CH{=}CH{-}CH_2-)n$

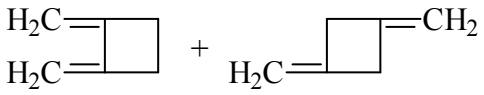
5. $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{h\nu}$ 

6.  (Дильс-Альдер)

7. 

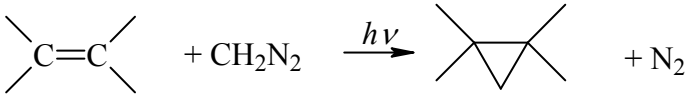
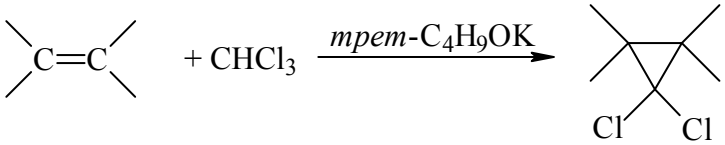
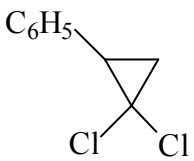
8.  (Коуп)

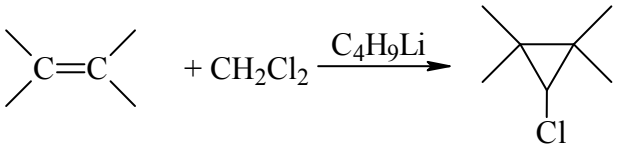
5. Синтезы и реакции алленов

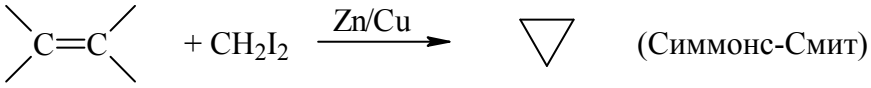
1. $CH_2=CBr–CH_2Br + Zn \longrightarrow CH_2=C=CH_2$
2. $CH_2=C=CH_2 + NaNH_2 \longrightarrow CH_3C\equiv CH$
3. $CH_2=C=CH_2 + H_2 \xrightarrow{Ni} CH_3CH=CH_2$
4. $CH_2=C=CH_2 + H_2O \xrightarrow{H^+} CH_3C(OH)=CH_2 \longrightarrow (CH_3)_2CO$ (правило Эльтекова-Эрленмейера)
5. $2\ CH_2=C=CH_2 \longrightarrow$ 

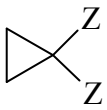
6. Циклопропан и его производные

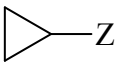
6.1. Синтезы

1. $BrCH_2–CH_2–CH_2Br + Na \longrightarrow$ 
2. 
3. 
4. $C_6H_5CH=CH_2 + CHCl_3 \xrightarrow{50\%\ NaOH\ -\ ТЭБАХ}$  межфазный катализ (Макоша)

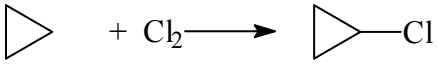
5. 

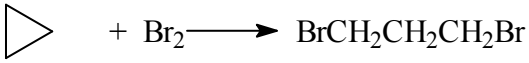
6.  (Симмонс-Смит)

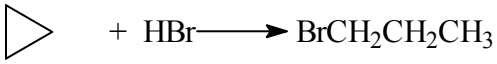
7. $Z_2CH_2 + BrCH_2CH_2Br \xrightarrow{RO^-}$  Z – CN, COR, COOR

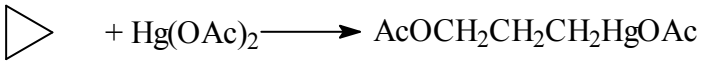
8. $XCH_2CH_2CH_2Z \xrightarrow{KOH}$ 

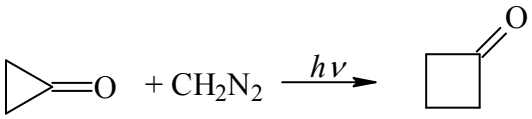
6.2. Реакции

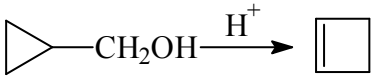
1. 

2. 

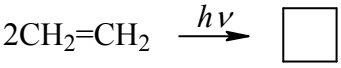
3. 

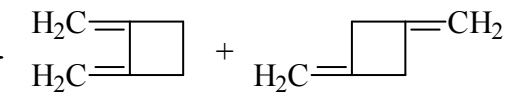
4. 

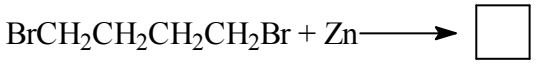
5. 

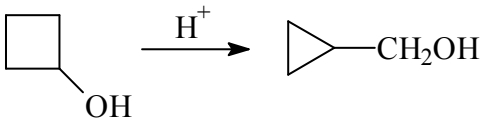
6. 

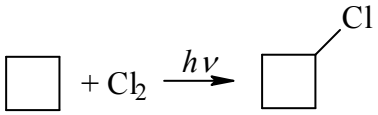
7. Циклобутан и его производные

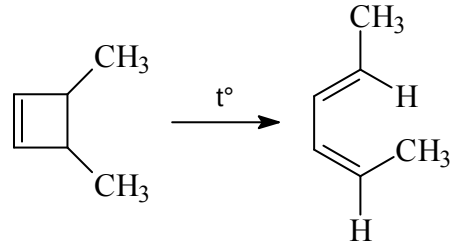
1. 

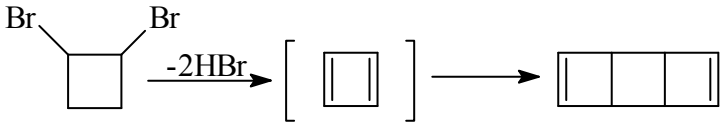
2. 

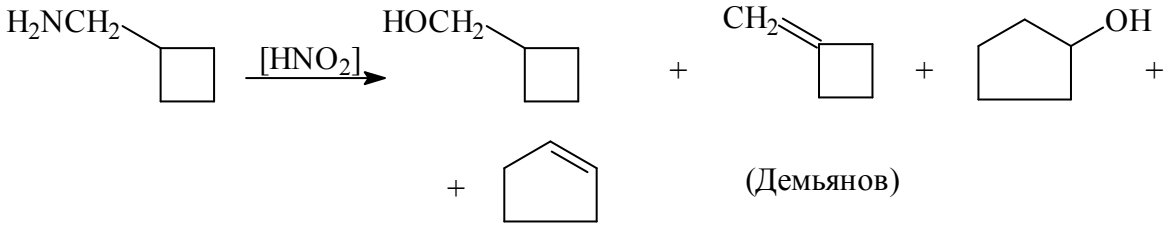
3. 

4. 

5. 

6. 

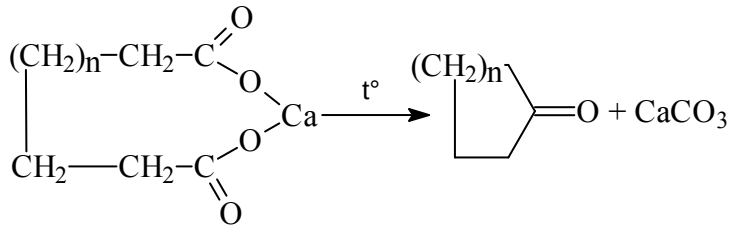
7. 

8. 

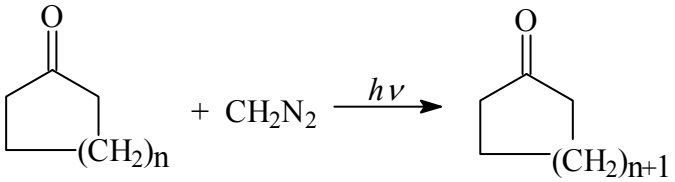
(Демьянов)

8. Циклопентан, циклогексан и средние циклы

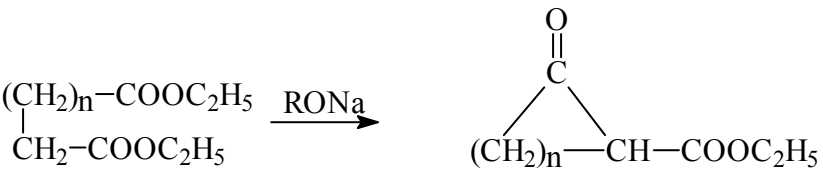
8.1. Общие методы синтеза

1. 

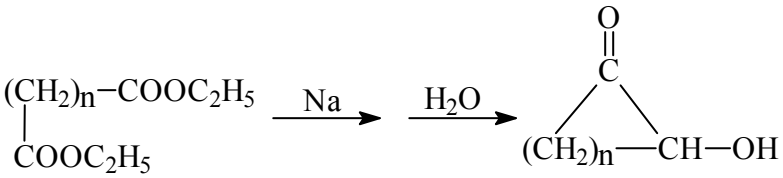
n = 1 - 31 (Ружичка)

2. 

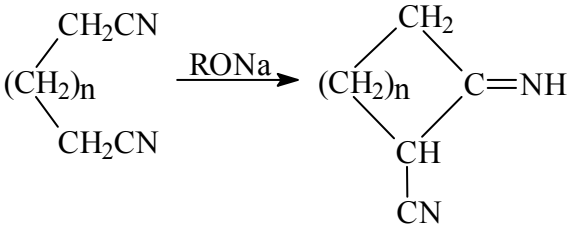
n = 1, 2, 3

3. 

n = 3, 4 (Дикман)

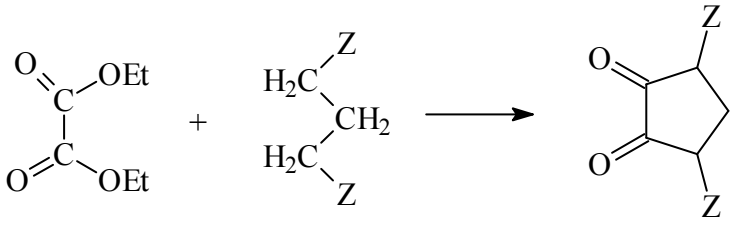
4. 

n = 3, 4, 5

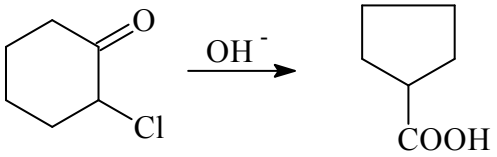
5. 

n = 2 – 5 (Торп)

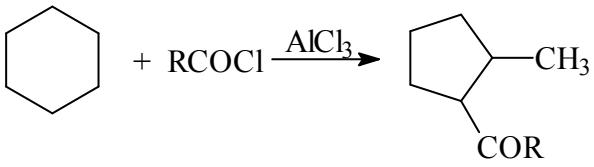
8.2. Циклопентан и его производные

1. 

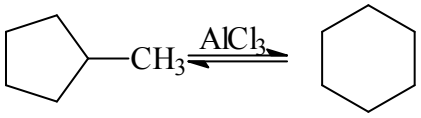
Z = CN, COR, COOR

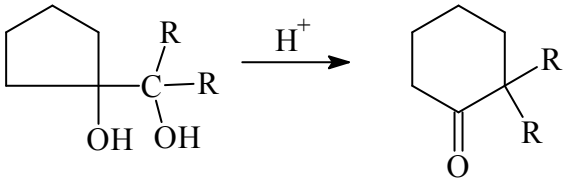
2. 

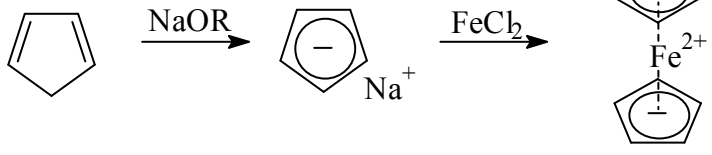
(Фаворский)

3. 

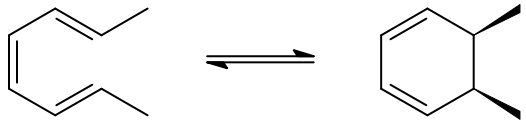
(Неницеску)

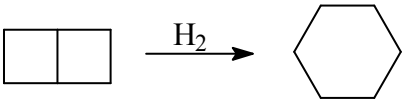
4. 

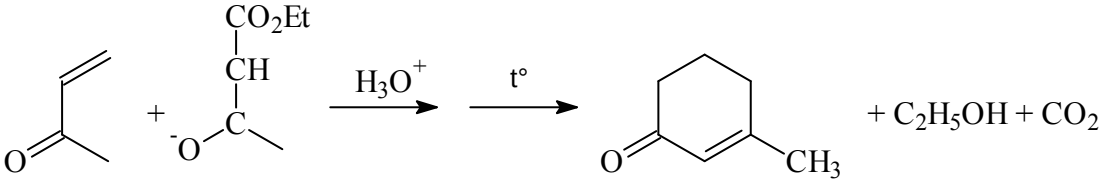
5. 

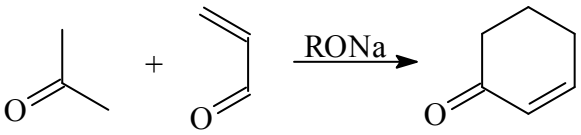
6. 

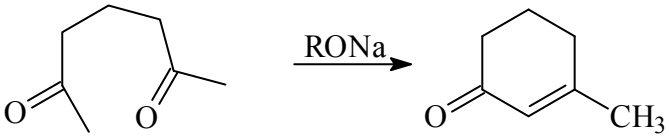
8.3. Циклогексан и его производные

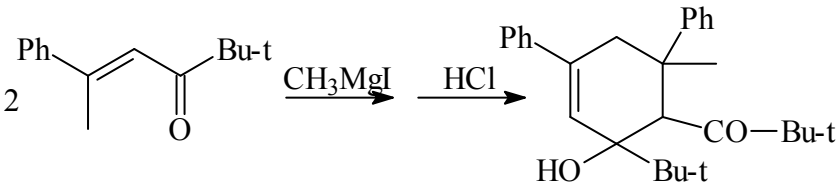
1. 

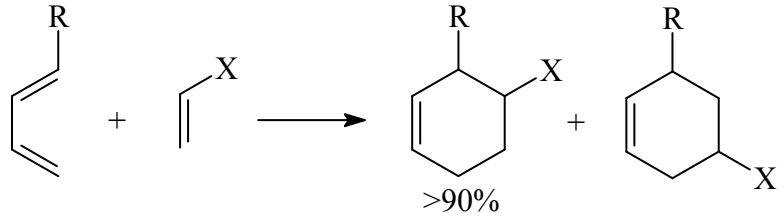
2. 

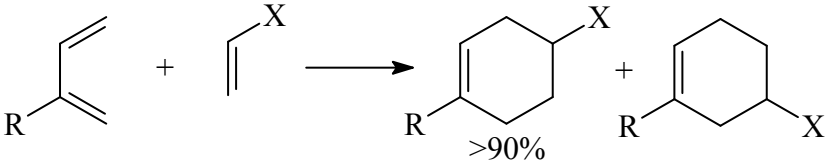
3. 

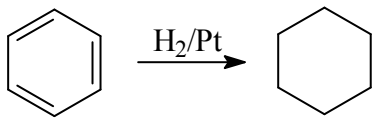
4. 

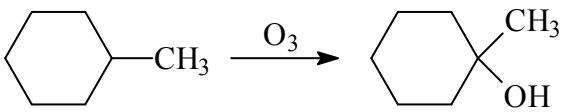
5. 

6. 

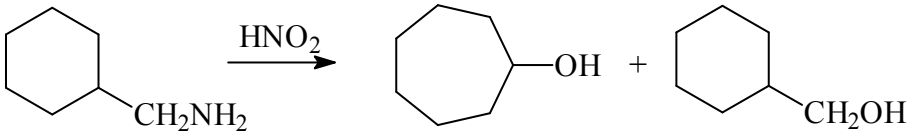
7. 

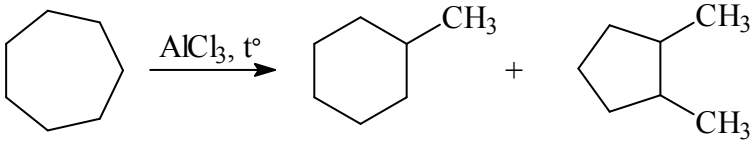
8. 

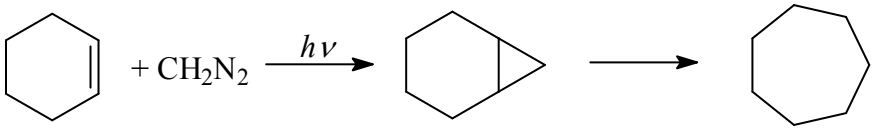
9. 

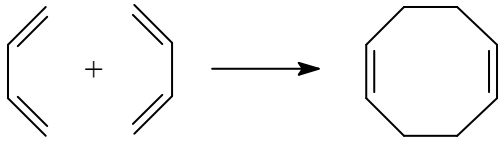
10. 

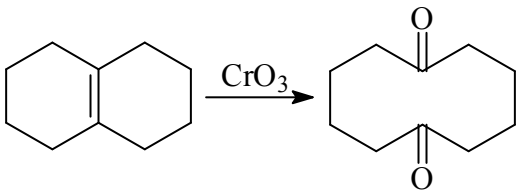
8.4. Средние циклы и их производные

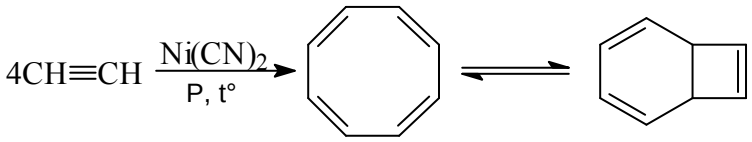
1. 

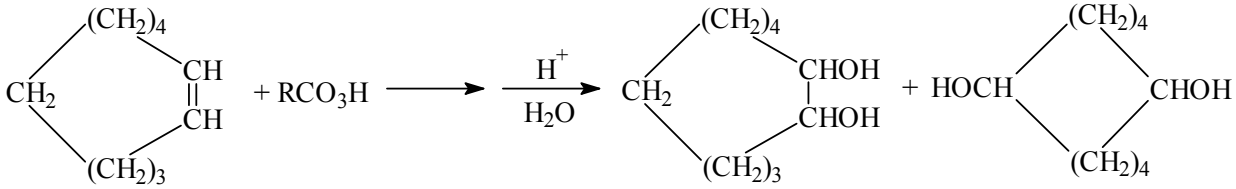
2. 

3. 

4. 

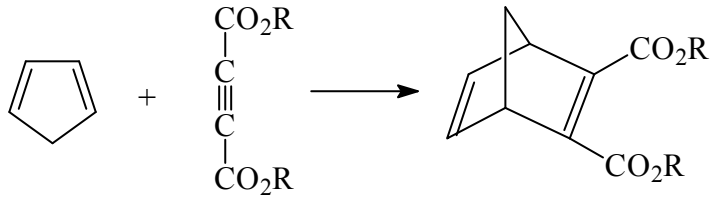
5. 

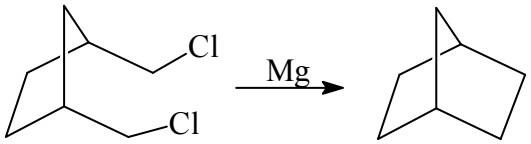
6. 

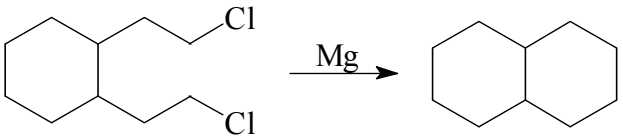
7. 

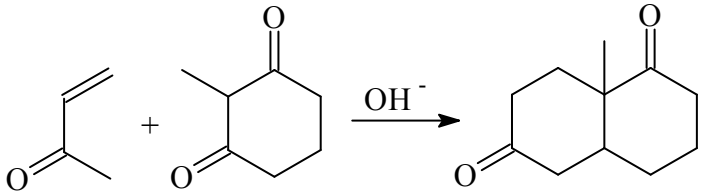
(трансаннулярная реакция)

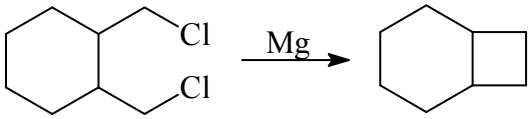
9. Би- и полициклы. Спираны

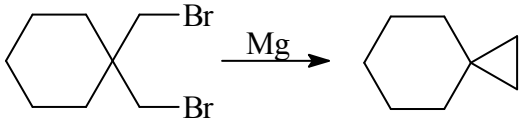
1. 

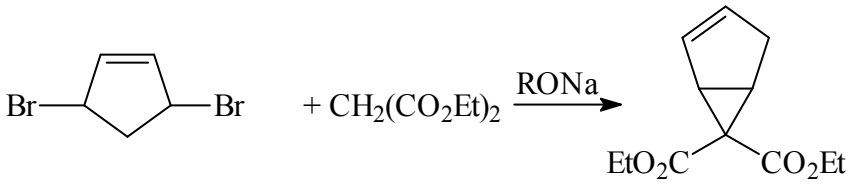
2. 
норборнан

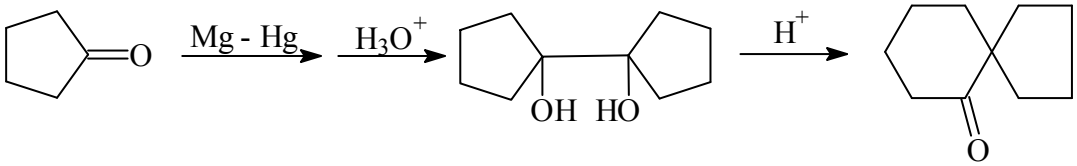
3. 
декалин

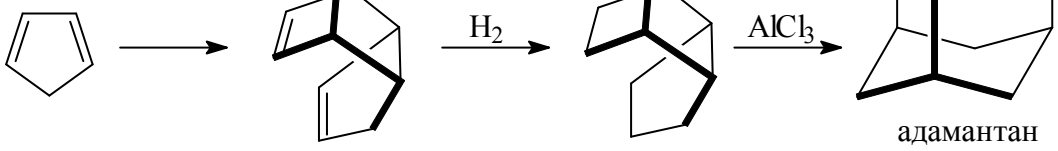
4. 
(Робинсон)
(декалин)

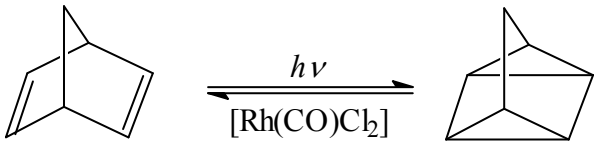
5. 
бицикло[4.2.0]октан

6. 
спиро[2.5]октан

7. 
(Ипатьев)

8. 

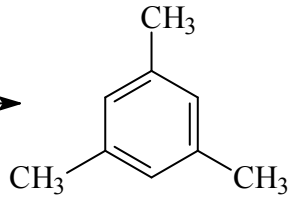
9. 2 
адамантан

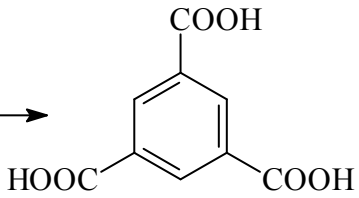
10.  квадрициклан

10. Бензол и его гомологи

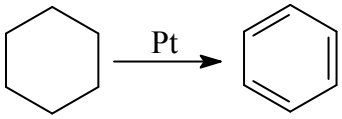
10.1. Синтезы

1. $3HC{\equiv}CH \xrightarrow[600^\circ C]{C} C_6H_6$

2. $3CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{H^+}$  мезитилен

3. $3HOOCCH_2COOH \longrightarrow$  тримезиновая кислота

4. $C_6H_{14} \xrightarrow[>450^\circ C]{Cr_2O_3/Al_2O_3} C_6H_6$

5. 

10.2. Реакции

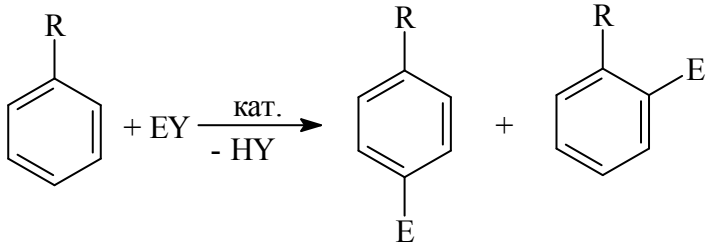
1. $C_6H_6 + HNO_3 + H_2SO_4 \longrightarrow C_6H_5NO_2$
2. $C_6H_6 + SO_3 \longrightarrow C_6H_5SO_3H$
3. $C_6H_6 + X_2 \xrightarrow{FeX_3} C_6H_5X$ X = Cl, Br
4. $C_6H_6 + AgF_2 \longrightarrow C_6H_5F + Ag + HF$
5. $C_6H_6 + RX \xrightarrow{AlX_3} C_6H_5R$ (Фридель-Крафтс)
6. $C_6H_6 + ROH \xrightarrow{H_3PO_4} C_6H_5R$
7. $C_6H_6 + RCH{=}CH_2 \xrightarrow{H_3PO_4} C_6H_5CHR{-}CH_3$
8. $2\ C_6H_6 + CH_2Cl_2 \xrightarrow{AlCl_3} C_6H_5{-}CH_2{-}C_6H_5$
9. $3\ C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} (C_6H_5)_3CH$
10. $3\ C_6H_6 + CCl_4 \xrightarrow{AlCl_3} (C_6H_5)_3CCl$

11. $C_6H_6 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2C_6H_5$

12. $C_6H_6 + C_6H_5CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5$

13. $C_6H_6 + RCOX \xrightarrow{AlX_3} C_6H_5COR$ (Фридель-Крафтс)

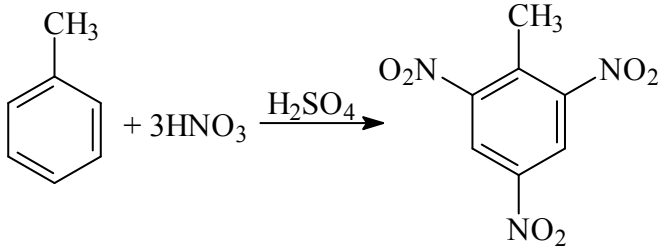
14. $C_6H_6 + COCl_2 \longrightarrow C_6H_5COCl$

15. 

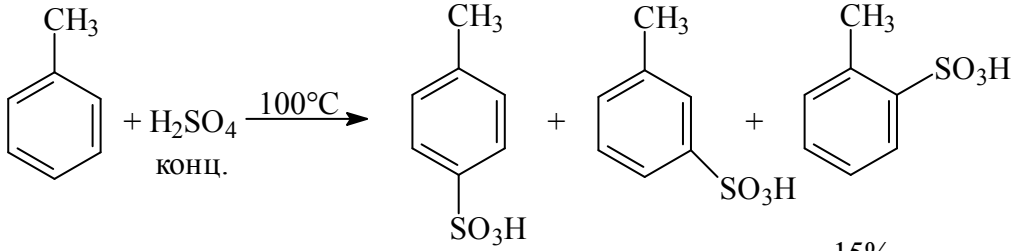
R = Alk

E = NO_2, SO_3, X, R, RCO

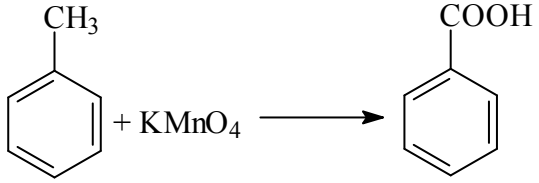
16. $C_6H_5CH_3 \xrightarrow{диоксан \cdot Br_2} 4\text{-}Br\text{-}C_6H_4\text{–}CH_3$

17. 

тротил, тол

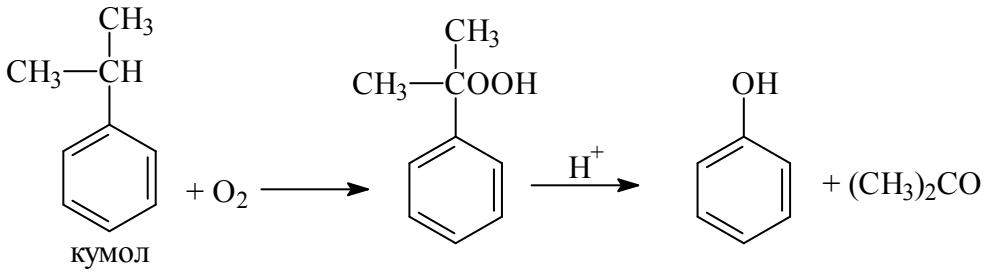
18. 

80% 5% 15%

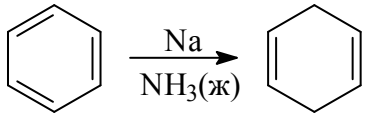
19. 

20. $C_6H_5CH_3 + Cl_2 \xrightarrow{h\nu} C_6H_5CH_2Cl + C_6H_5CHCl_2 + C_6H_5CCl_3$

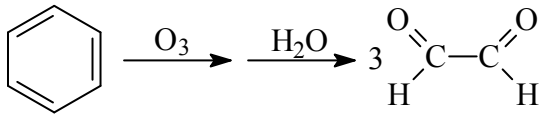
21. $C_6H_5CH_2CH_3 \xrightarrow[t°]{Ni} C_6H_5CH{=}CH_2$ стирол

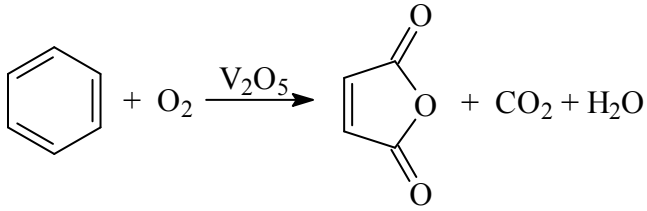
22. 

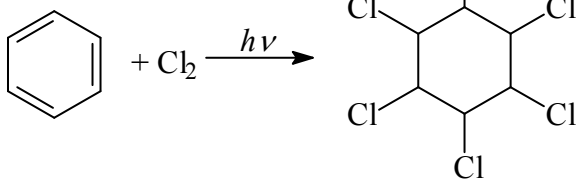
10.3. Реакции бензола приводящих к неароматическим системам

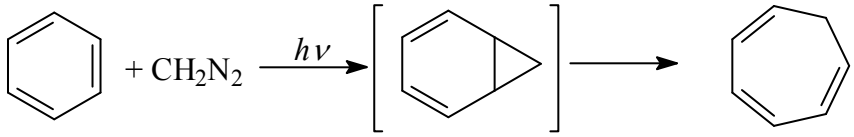
1. 

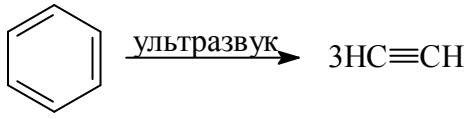
(Бёрч)

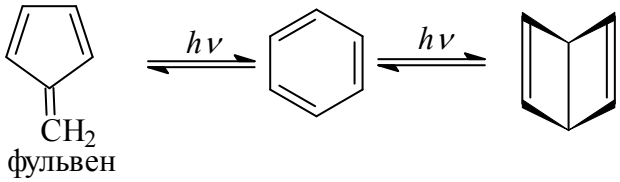
2. 

3. 

4. 

5. 

6. 

7. 

11. Дифенил (бифенил) и его производные

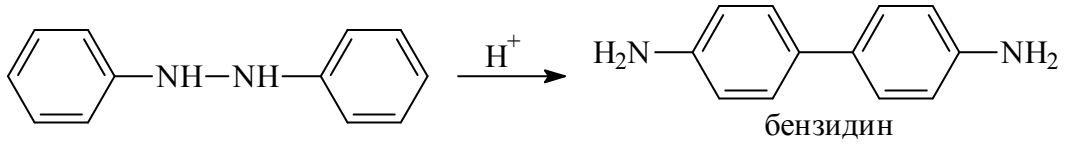
11.1. Синтезы

1. $2\ C_6H_6 \xrightarrow{t^\circ} C_6H_5 - C_6H_5$

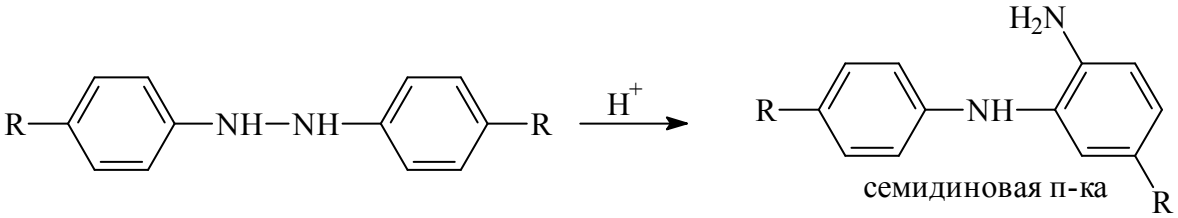
2. $C_6H_5Br + Na \longrightarrow C_6H_5 - C_6H_5$

3. $C_6H_5I + Cu \xrightarrow{t^\circ} C_6H_5 - C_6H_5 + CuI$ (Ульман)

4. $C_6H_6 + PdX_2 \longrightarrow C_6H_5 - C_6H_5 + Pd + HX$

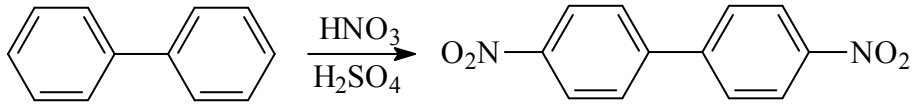
5. 

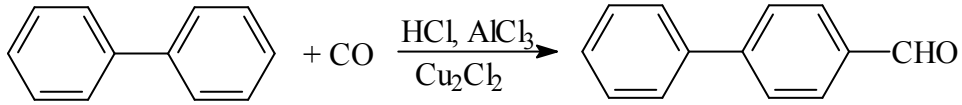
бензидин

6. 

семидиновая п-ка

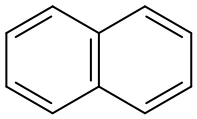
11.2. Реакции

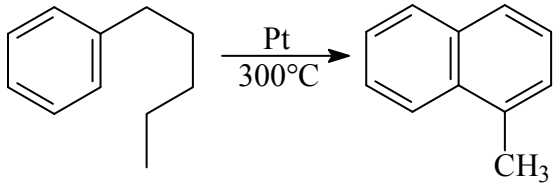
1. 

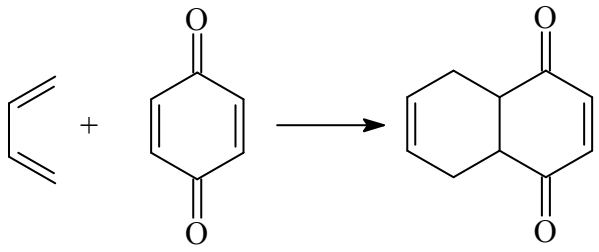
2. 

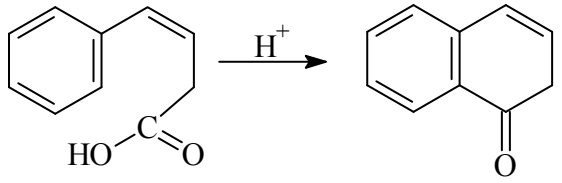
12. Нафталин и его производные

12.1. Синтезы

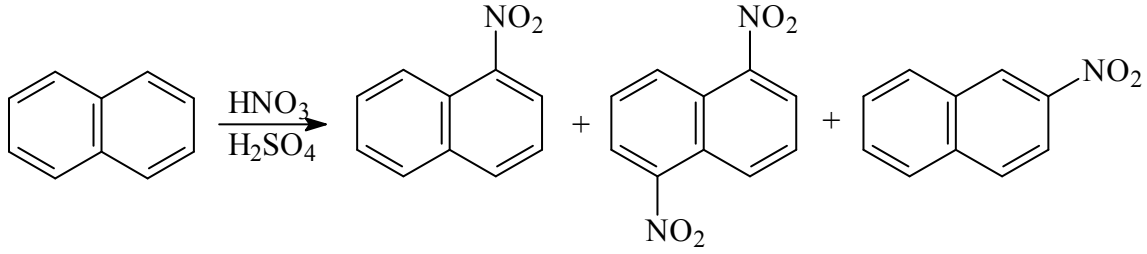
1. $5\ HC{\equiv}CH \xrightarrow[400°C]{C}$ 

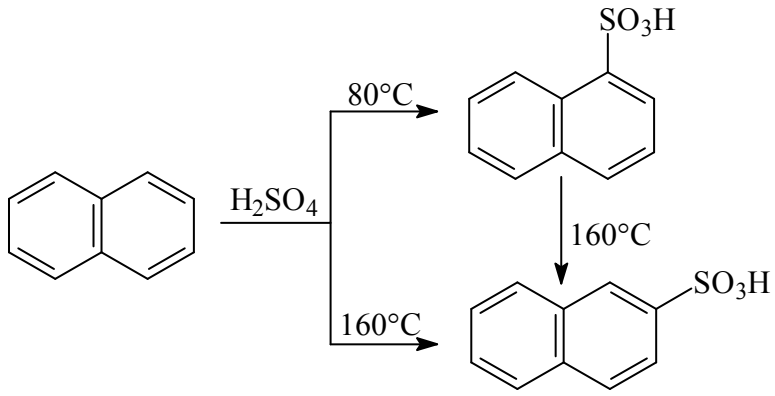
2. 

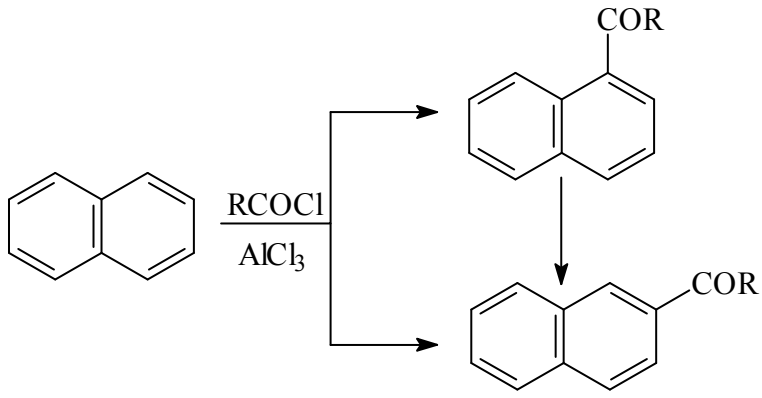
3. 

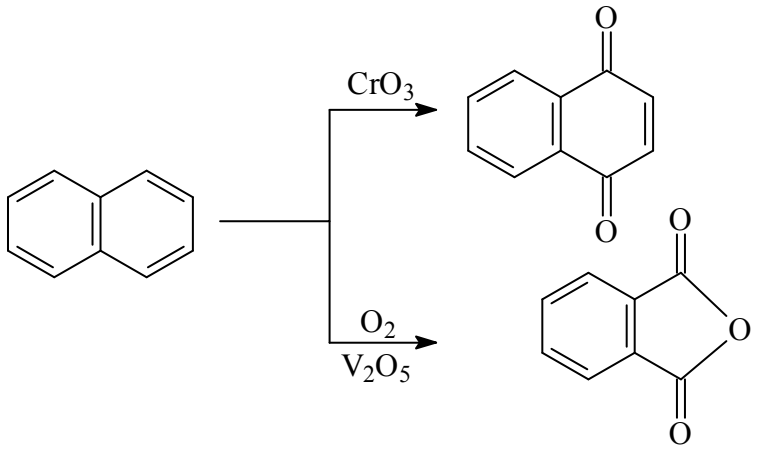
4. 

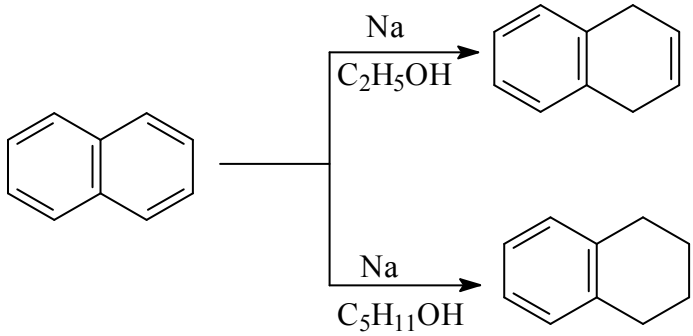
12.2. Реакции

1. 

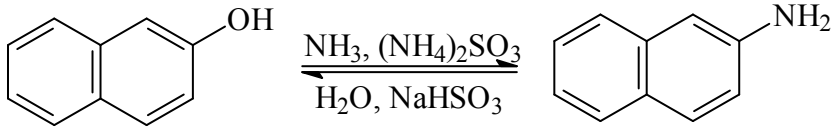
2. 

3. 

4. 

5. 

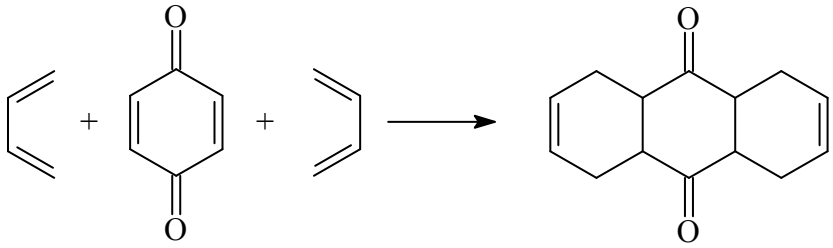
тетралин

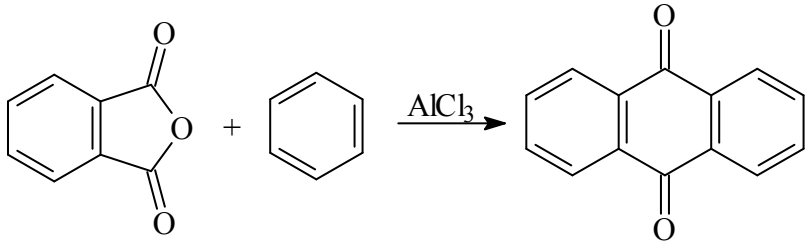
6. 

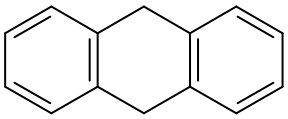
(Бухерер)

13. Антрацен и его производные

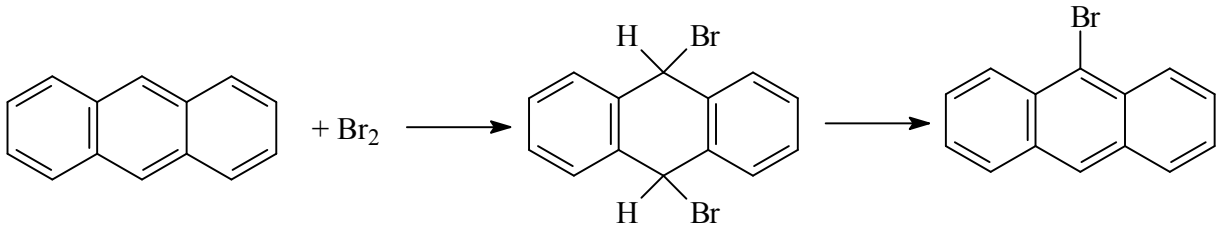
13.1. Синтезы

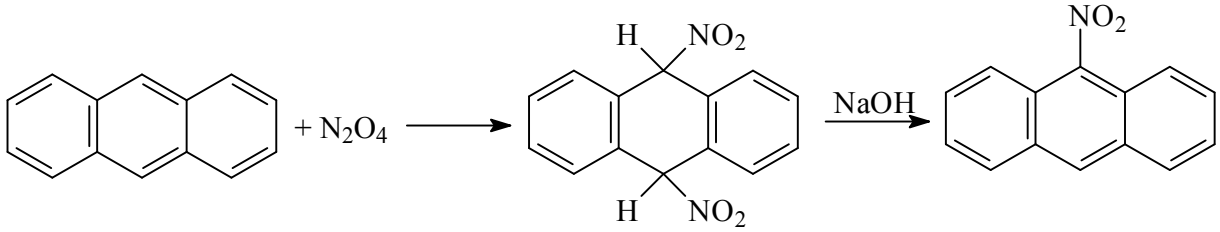
1. 

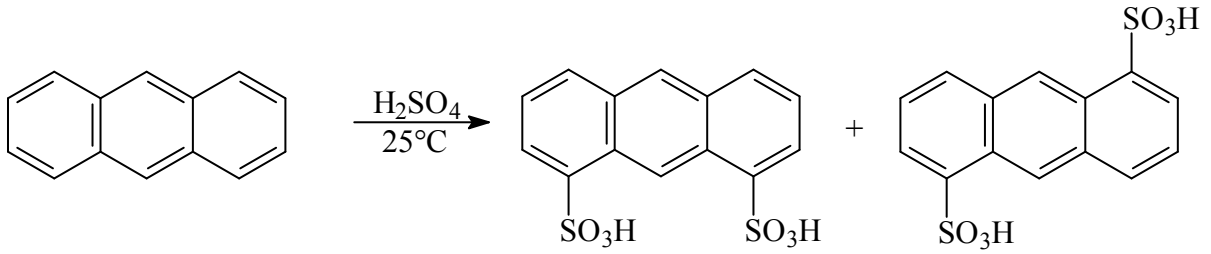
2. 

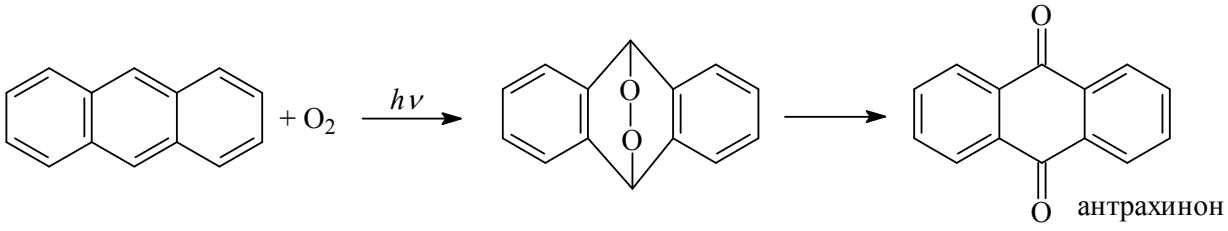
3. $2C_6H_5CH_2Cl \xrightarrow{AlCl_3}$ 

13.2. Реакции

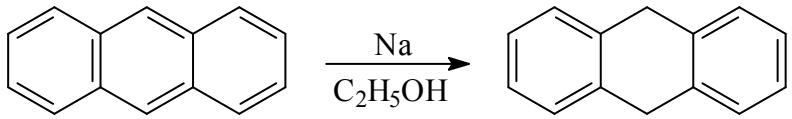
1. 

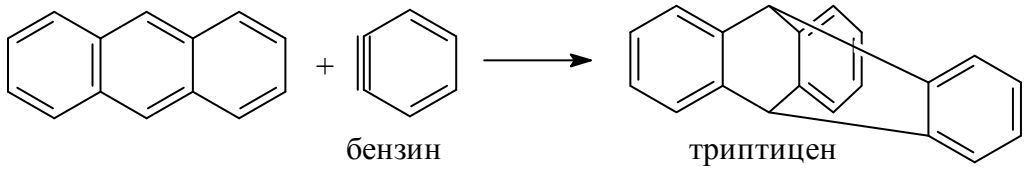
2. 

3. 

4. 

антрахинон

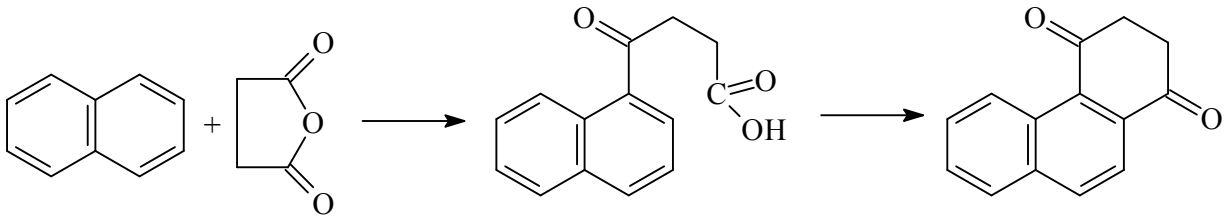
5. 

6. 

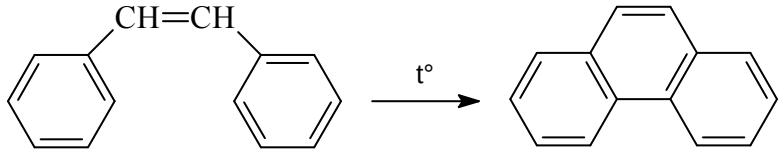
бензин триптицен

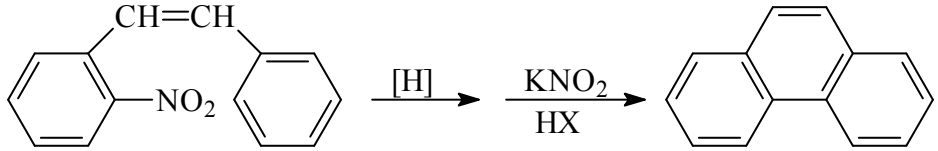
14. Фенантрен и его производные

14.1. Синтезы

1. 

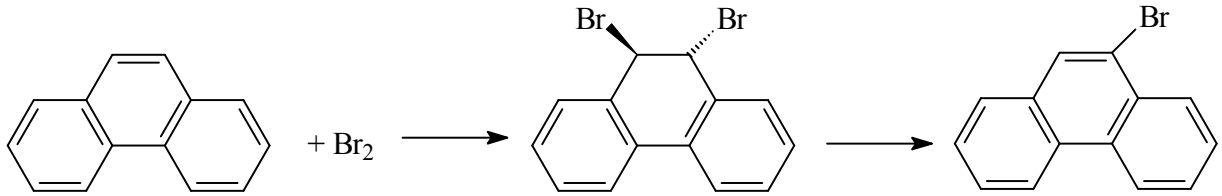
(Хеуорс)

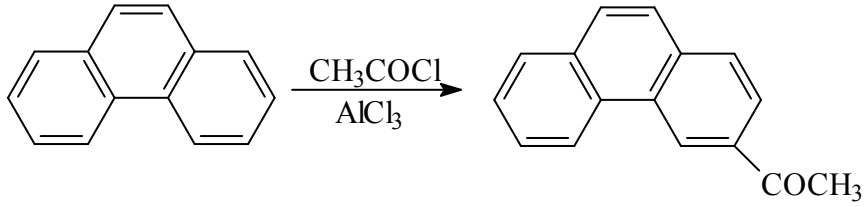
2. 

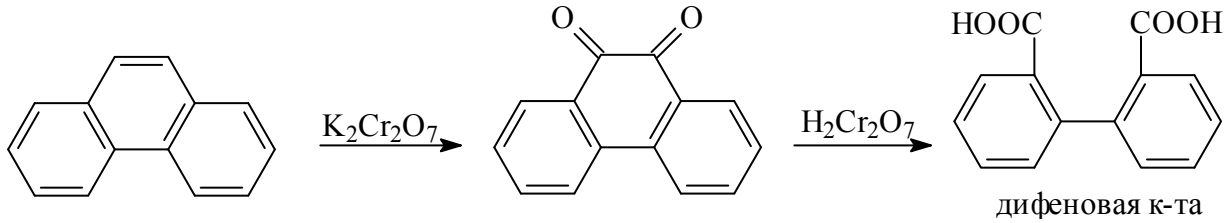
3. 

(Пшорр)

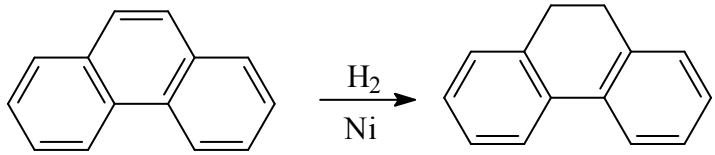
14.2. Реакции

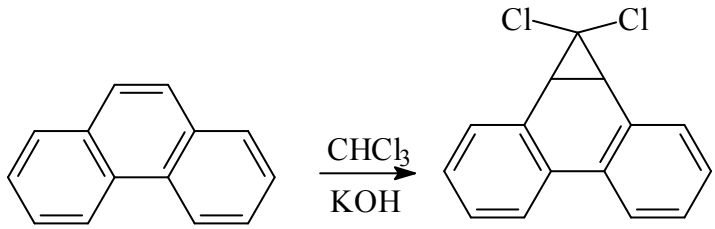
1. 

2. 

3. 

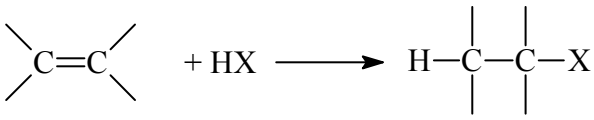
дифеновая к-та

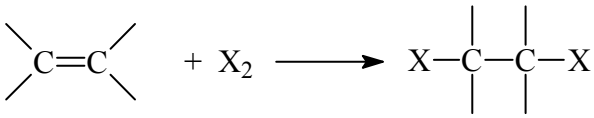
4. 

5. 

15. Галогеналканы

15.1. Синтезы

1. $RH + X_2 \xrightarrow{h\nu} RX$
2. $ROH + HX \longrightarrow RX$
3. $ROH \xrightarrow{PX_3;\ PX_5;\ SOCl_2} RX$
4. 

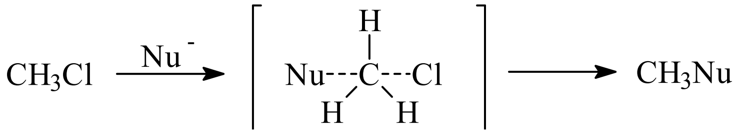
5. 

6. $CH_3–CH=CH_2 + CCl_4 \xrightarrow{R\bullet} CH_3–CHCl–CH_2–CCl_3$
7.  $+ Br_2 \longrightarrow BrCH_2CH_2CH_2Br$
8.  $+ HBr \longrightarrow BrCH_2CH_2CH_3$
9. $RCOR^1 \xrightarrow{PCl_5} RCCl_2R^1 + POCl_3$
10. $RCO_2Ag + Br_2 \longrightarrow RBr + CO_2 + AgBr$ (Бородин-Хунсдикер)
11. $RCOR^1 + SF_4 \xrightarrow{t^\circ} RCF_2R^1$
12. $RCOOH + HgO + Br_2 \longrightarrow RBr + CO_2 + HgBr_2 + H_2O$
13. $RCOOH + SF_4 \xrightarrow{t^\circ} RCF_3$
14. $RCOCl + PCl_5 \xrightarrow{t^\circ} RCCl_3$

15.2. Реакции галогеналканов

Реакции нуклеофильного замещения

1. $RX + H_2O \longrightarrow ROH$
2. $CH_2=CHCH_2Cl \longrightarrow CH_2=CH–\overset{+}{C}H_2 \xrightarrow{Nu^-} CH_2=CHCH_2Nu$ (S_N1)

3.  (S_N2)

4. $RX + R^1ONa \longrightarrow ROR^1$ (Вильямсон)

5. $RX + R^1COONa \longrightarrow R^1COOR$

6. $RX + NaSH \longrightarrow RSH$

7. $RX + Na_2S \longrightarrow RSR$

8. $RX + R^1SNa \longrightarrow RSR^1$

9. $RX + Na \longrightarrow RNa \longrightarrow R–R$

10. $RX + R^1Na \longrightarrow R–R^1$

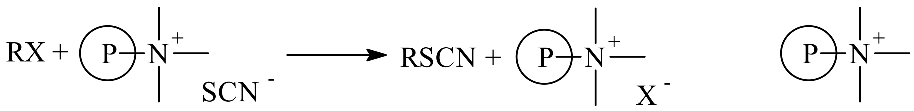
11. $RX + Mg \longrightarrow RMgX \longrightarrow R–R$

12. $RX + R^1MgX \longrightarrow R–R^1$

13. $RX + NaCN \longrightarrow R–CN + R–NC$

14. $RX + NaNO_2 \longrightarrow R–NO_2 + RONO$

15. $RX + NaN_3 \xrightarrow{\text{аликват 336}} RN_3$ межфазный катализ

16.  - полимерный носитель

17. $RX + CH_2Z_2 \xrightarrow{OH^-} R–CHZ_2$ $Z = CN, COR, COOR$

18. $RX + NH_3 \longrightarrow R–NH_2 + NH_4X$

19. $RX + R^1NH_2 \longrightarrow RR^1NH_2X$

20. $RX + (R^1)_2NH \longrightarrow R(R^1)_2NHX$

21. $RX + (R^1)_3N \longrightarrow [R(R^1)_3N]X$ (Меншуткин)

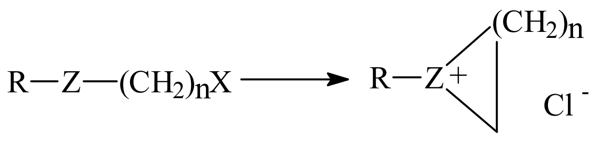
22. $RX + (R^1)_3P \longrightarrow [R(R^1)_3P]X$

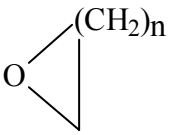
23. $RCCl_2R^1 + H_2O \xrightarrow{H^+} RCOR^1$

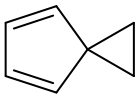
24. $RCCl_3 + H_2O \xrightarrow{H^+} RCOOH$

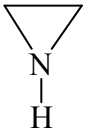
25. $RX + KI \xrightarrow{\text{ацетон}} RI$ (Финкельштейн)

26. $RCl + KF \xrightarrow[160^\circ\ C]{\text{ТБГДФБ}, H_2O} RF$ межфазный катализ

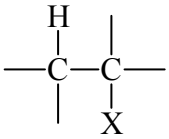
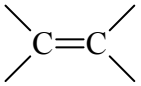
27.  $n = 1, 2, 3, 4$
$Z = NH, NR$

28. $HO—(CH_2)_nCH_2X \longrightarrow$  n = 1, 2, 3, 4

29. $Br(CH_2)_2Br$ +  $\xrightarrow{ТЭБАХ + NaOH + H_2O}$ 

30. $ClCH_2–CH_2Cl + NH_3 \xrightarrow{CaO} CaCl_2 + H_2O +$  азиридин

Реакции элиминирования

1.  $\xrightarrow{OH^-}$ 

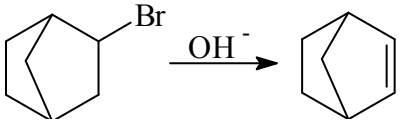
2. $CH_3CH_2CHXCH_3 \xrightarrow{OH^-} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$

(правила Зайцева и Гофмана)

3. $(CH_3)_2CCl–CH_2CH_3 + H_2O \xrightarrow{OH^-} (CH_3)_2C=CHCH_3 + (CH_3)_2C(OH)–CH_2CH_3$

4. $DCCl_2–CF_3 \xrightarrow[D_2O]{OD^-} Cl_2C=CF_2$ ($E1_{cb}$)

5. $CH_3CHBrCH_2CH_3 \xrightarrow{EtO^-} CH_3CH=CHCH_3 + CH_2=CHCH_2CH_3$ (E2)

6.  правило Бредта

7. $XCH_2CH_2X \xrightarrow[ацетон]{NaI} CH_2=CH_2 + NaX + I_2$

Другие реакции

1. $RX + ArH \xrightarrow{AlX_3} Ar–R$
2. $RCH_2X + H_2 \xrightarrow{Ni} RCH_3$
3. $RCH_2I + HI \longrightarrow RCH_3$
4. $RCH_2X + (CH_3)_2SO \xrightarrow{ТЭА} RCHO$ (Корнблюм)
5. $CHCl_3 \xrightarrow{OH^-} :CCl_2 + Cl^- + H_2O$

16. Галогеналкены, галогеналкадиены и галогеналкины

1. $RCHXCH_2X \xrightarrow{OH^-} RCH=CHX$

2. $HOCH_2CH_2Cl \xrightarrow{H^+} CH_2=CHCl$

3. $HCCl_2–CHCl_2 \xrightarrow{t°} CCl_2=CHCl$

4. $CHF_2Cl \xrightarrow{t°} CF_2=CF_2$

5. $HC\equiv C–CH=CH_2 + HCl \xrightarrow{kat.} CH_2=CCl\text{-}CH=CH_2$

6. $RC\equiv CH + HX \longrightarrow RCX=CH_2$

7. $R–C\equiv CH + NaOH + Br_2 \longrightarrow R–C\equiv CBr$

8. $HCX=CHX \xrightarrow{OH^-} HC\equiv CX$

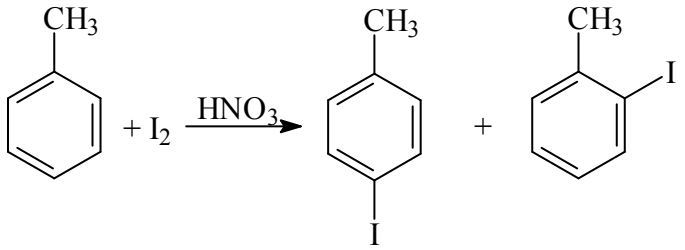
9. $HCX=CHCl + HCl \xrightarrow[OH^-]{t°} CH_2=CCl_2$

10. $R–C\equiv CCl + H_2O \xrightarrow{kat.} RCO–CH_2Cl$

17. Galogenarene

17.1. Sinteze

1. $ArH + X_2 \xrightarrow{FeX_3} ArX$ X = Cl, Br

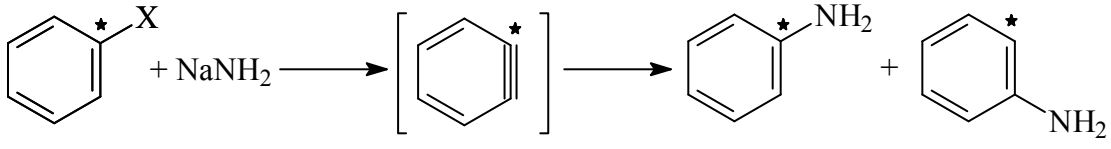
2. 

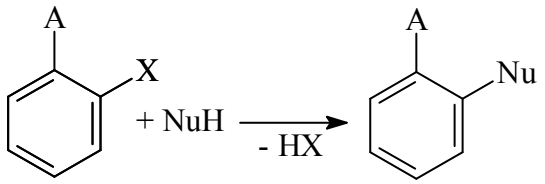
3. $ArN_2X + CuX \longrightarrow ArX$ X = Cl, Br

4. $ArN_2X + KI \longrightarrow ArI$

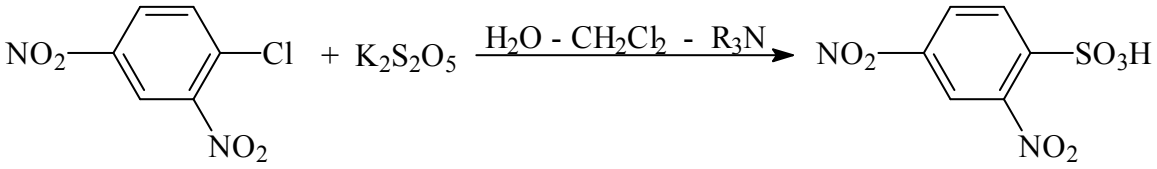
5. $ArN_2BF_4 \xrightarrow{t°} ArF + N_2 + BF_3$ (Шиман)

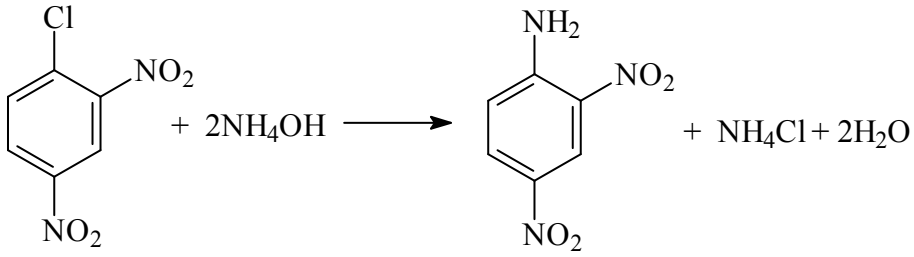
17.2. Reakcii

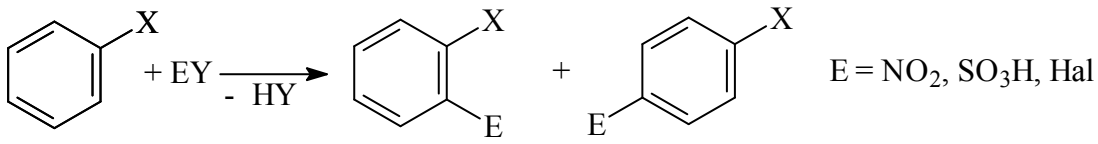
1. 

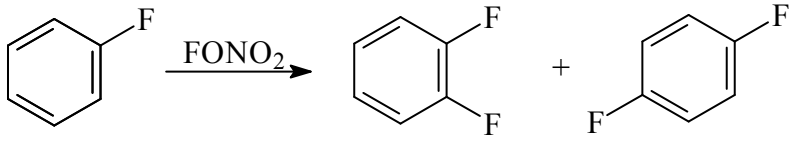
2. 

A = акцепторная група
Nu = OH , RO , NH_2

3. 

4. 

5. 

6. 

7. $4\text{-Br–C}_6\text{H}_4\text{–OCH}_3 + \text{HNO}_3 \longrightarrow 4\text{-NO}_2\text{–C}_6\text{H}_4\text{–OCH}_3$ (ипсо-замещение)

8. $\text{C}_6\text{H}_5\text{X} + \text{Mg} \longrightarrow \text{C}_6\text{H}_5\text{MgX}$

9. $\text{ArX} + \text{CO} + \text{NaOH} \xrightarrow[\text{ТЭБАХ}]{\text{NaOH - H}_2\text{O - ксилол}} \text{Ar–COONa} + \text{NaX} + \text{H}_2\text{O}$

18. Галогенониевые соединения

1. $\text{ArX} + \text{ArN}_2\text{BF}_4 \longrightarrow [\text{Ar–X–Ar}]\text{BF}_4$
2. $\text{ArI} + \text{Cl}_2 \xrightarrow{\text{CHCl}_3} \text{ArICl}_2$
3. $2\ \text{ArH} + \text{KIO}_3 + \text{H}_2\text{SO}_4 \longrightarrow [\text{Ar–I–Ar}]\text{HSO}_4$
4. $\text{R–I} + \text{R–F} + \text{SbF}_5 \longrightarrow [\text{R–I–R}]\text{SbF}_6$
5. $\text{ArICl}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \longrightarrow \text{Ar–I=O}$
6. $[\text{Ar–I–Ar}]\text{Cl} \longrightarrow \text{Ar–Cl} + \text{Ar–I}$
7. $[\text{Ar–I–Ar}]\text{Cl} + \text{CH}_3\text{OH} \longrightarrow \text{Ar–OCH}_3 + \text{Ar–I} + \text{HCl}$

19. Литий- и натрийорганические соединения

1. $\text{R–X} + \text{M} \longrightarrow \text{R–M}$ M = Li, Na
2. $(\text{CH}_3)_2\text{Hg} + \text{Na} \longrightarrow \text{CH}_3\text{Na} + \text{Hg}$
3. $\text{RH} + \text{Na} \longrightarrow \text{RNa} + \text{H}_2$ R = $\text{HC}\equiv\text{C–}$, $(\text{C}_6\text{H}_5)_3\text{C–}$

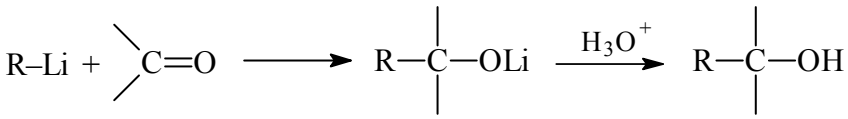
4. $R–M + R^1X \longrightarrow R–R^1 + MX$

5. $R–M + H_2O \longrightarrow R–H + MOH$

6. $R–Li + O_2 \longrightarrow \xrightarrow{H_3O^+} R–OH$

7. $R–Li + CuX \longrightarrow R–Cu + LiX$

8. $R–Li + R–Cu \longrightarrow Li[CuR_2]$ диалкилкупрат лития

9. 

10. $R–Li + R^1CN \longrightarrow RR^1C{=}N–Li \xrightarrow{H_3O^+} RR^1CO$

11. $R–Li + CH_2{=}CH–CH{=}CH_2 \longrightarrow RCH_2CH{=}CHCH_2Li \longrightarrow$ полимер

12. $(CH_3)_3C–Li + SiCl_4 \longrightarrow (CH_3)_3C–SiCl_3 + LiCl$

20. Магний- и цинкорганические соединения

1. $R–X + Mg \longrightarrow R–MgX \longrightarrow R–Mg–R$ (Гриньяр)

2. $C_2H_5I + Zn \longrightarrow R–Zn–R + ZnI_2$ (Франклад)

3. $R–Li + ZnCl_2 \longrightarrow R–Zn–R + LiCl$

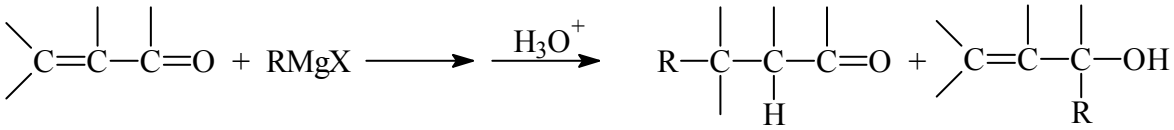
4. $RMgX + R_2NH \longrightarrow RH + R_2N–MgX$

5. $RMgX + I_2 \longrightarrow RI + MgXI$

6. $RMgX + O_2 \longrightarrow ROOMgX$

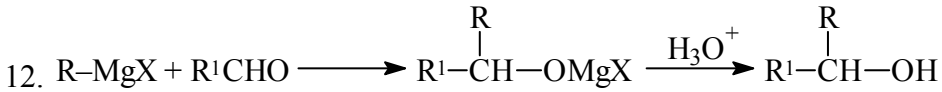
7. $RMgX + S \longrightarrow RSMgX$

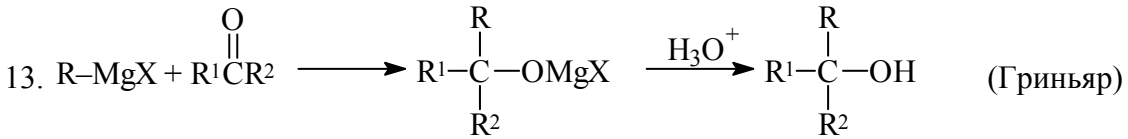
8. 

9. 

10. $R–MgX + R^1X \longrightarrow R–R^1$

11. $R–MgX + R^1OH \longrightarrow R–H + Mg(OR^1)X$

12. 

13.  (Гриньяр)

14.R– MgX + R^1COOR^2 ⟶ R^1–CO–R + Mg(OR^2)X

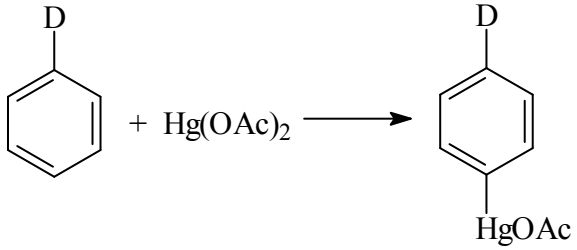
15.R– MgX + CO_2 ⟶ R—C(=O)—OMgX $\xrightarrow{H_3O^+}$ R—COOH + Mg(OH)X

16.R– MgX + $R^1C{\equiv}N$ ⟶ R^1–CR=N–MgX $\xrightarrow{H_3O^+}$ R^1–CR=NH $\xrightarrow{H_3O^+}$ R^1–CO–R

17.R–Zn–R + R^1COCl ⟶ $RCOR^1$

18.R–Zn–R + BCl_3 ⟶ R_3B + $ZnCl_2$

21. Другие металлорганические соединения

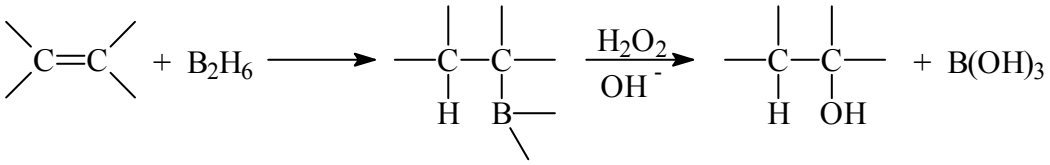
1. R–I + Hg $\xrightarrow{h\nu}$ R–HgI ⟶ R–Hg–R
2. 2RHgI + 2KI ⟶ R_2Hg + K_2HgI_4
3. R_2Hg + HgX_2 ⟶ 2RHgX
4. R–X + Hg(Na) ⟶ R–Hg–R
5. R–MgX + $HgCl_2$ ⟶ R–Hg–R
6. HC≡CH + $HgCl_2$ ⟶ Cl–CH=CH–HgCl
7. CH_2=CH_2 + Hg($OAc)_2$ + H_2O ⟶ HO–CH_2–HgOAc
8.  D – электронодонорная группа
9. ArN_2Cl + $HgCl_2$ ⟶ ArN_2HgCl_3 $\xrightarrow{Hg}$ ArHgCl + N_2 + $HgCl_2$ (Несмеянов)
10. [R–Cu–R]Li + R^1X ⟶ R–R^1 + R–Cu + LiX
11. R–Hg–R + Al ⟶ R_3Al + Hg
12. R–Li + $AlCl_3$ ⟶ R_3Al + LiCl
13. R–MgX + $AlCl_3$ ⟶ R_3Al + MgXCl
14. 3CH_2=CH_2 + AlH_3 ⟶ $(C_2H_5)_3Al$
15. $(C_2H_5)_3Al$ $\xrightarrow{t°}$ $(C_2H_5)_2AlH$ + CH_2=CH_2
16. $(C_2H_5)_3Al$ + C_2H_5Li ⟶ $[(C_2H_5)_4Al]Li$
17. R_3Al + CH_2=CH_2 ⟶ $R_2AlCH_2CH_2R$ $\xrightarrow{C_2H_4}$ $R_2AlCH_2CH_2CH_2CH_2R$ $\xrightarrow{C_2H_4}$ полимер
18. MCl_4 + 4CH_3Li ⟶ $(CH_3)_4M$ M = Ge, Sn, Pb
19. 2$PbCl_2$ + 4C_2H_5MgCl ⟶ $(C_2H_5)_4Pb$ + 4MgCl
20. 4C_2H_5Cl + Pb(Na) ⟶ $(C_2H_5)_4Pb$

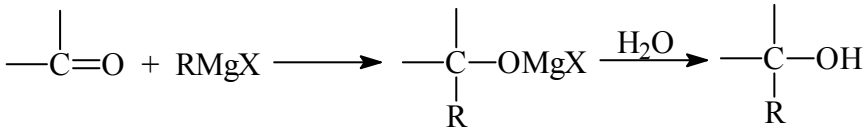
22. Алканолы

22.1. Синтезы

1. $R–X + H_2O \xrightarrow{OH^-} R–OH$

2. $CH_2=CH_2 + H_2SO_4 \longrightarrow CH_3–CH_2–O–SO_3H \xrightarrow{H_2O} CH_3–CH_2–OH$

3. 

4. 

5. $R–CHO + H_2 \xrightarrow{kat.} R–CH_2–OH$

6. $R–COOR^1 + LiAlH_4 \longrightarrow R–CH_2–OH + R^1OH$

7. $CO + 2\,H_2 \xrightarrow[t°]{ZnO + ZnCr_2O_4} CH_3OH$

8. $C_6H_{12}O_6 \xrightarrow{фермент} 2\,C_2H_5OH + 2\,CO_2$

22.2. Реакции

22.2.1. Реакции замещения с разрывом связи O–H

1. $ROH + Na \longrightarrow RONa + H_2$

2. $ROH + Al \longrightarrow (RO)_3Al + H_2$

3. $ROH + H_2SO_4 \longrightarrow ROSO_3H \longrightarrow ROSO_2OR$

4. $ROH + HNO_3 \longrightarrow RONO_2$

5. $ROH + NaNO_2 \xrightarrow[0°C]{H_2SO_4} RO–N=O$

6. $ROH + B(OH)_3 \xrightarrow{H^+} (RO)_3B$

7. $ROH + ClSO_2–OH \longrightarrow ROSO_2–OH$

8. $ROH + R^1SO_2Cl \longrightarrow ROSO_2R^1$

9. $ROH + Me_3SiCl \xrightarrow{OH^-} ROSiMe_3$

10. $ROH + R^1COCl \xrightarrow{Py} R^1COOR$

11. $ROH + Ac_2O \xrightarrow{Py} ROAc$

12. $ROH + R^1COOH \xrightarrow{H^+} R^1COOR$

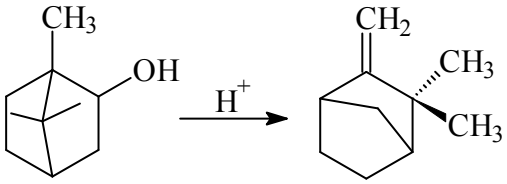
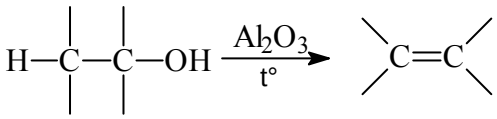
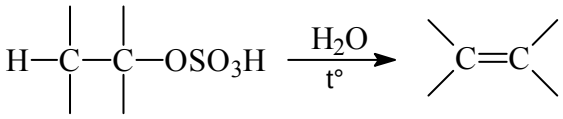
13. $ROH + R^1X \xrightarrow{OH^-} ROR^1$

14. $ROH + R^1CCl_3 \xrightarrow{OH^-} R^1C(OR)_3$

22.2.2. Реакции замещения с разрывом связи C–O

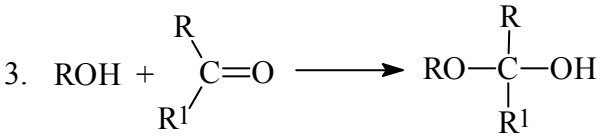
1. $ROH + HX \longrightarrow RX + H_2O$
2. $(CH_3)_3COH + HBr \longrightarrow (CH_3)_3CBr \qquad (S_N1)$
3. $(CH_3)_3C–CH(OH)CH_3 + HCl \longrightarrow (CH_3)_3C–CH(Cl)CH_3 + (CH_3)_2CCl–CH_2CH_3$
4. $3C_2H_5OH + PCl_3 \longrightarrow C_2H_5Cl + (C_2H_5O)_2POH$
5. $3C_2H_5OH + POCl_3 \longrightarrow C_2H_5Cl + H_3PO_4$
6. $ROH + PX_5 \longrightarrow RX + POX_3$
7. $ROH + SOCl_2 \longrightarrow ROSOCl \longrightarrow RCl + SO_2$
8. $ROH \xrightarrow{H^+} ROR$
9. $ROH + ArH \xrightarrow{BF_3} ArR$

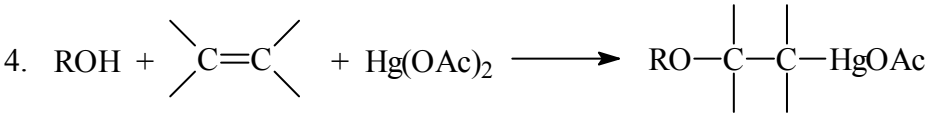
22.2.3. Реакции элиминирования

1. $CH_3CH_2CH_2OH \xrightarrow{H^+} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$
2. $(CH_3)_3C–CH(OH)CH_3 \longrightarrow (CH_3)_2C=C(CH_3)_2 + (CH_3)_3C–CH=CH_2$
3. $(CH_3)_3C–CH(OH)–CH_3 \xrightarrow{H^+} (CH_3)_2C=C(CH_3)_2$ (ретропинаколиновая п-ка)
4. $(CH_3)_3COH \xrightarrow{H^+} (CH_3)_2C=CH_2$
5.  (Вагнер-Мейервейн)
6. 
7. 

22.2.4. Реакции присоединения к кратным связям

1. $ROH + HC\equiv CH \xrightarrow{OH^-} ROC=CH_2$
2. $ROH + (CH_3)_2C=CH_2 \xrightarrow{H^+} ROC(CH_3)_3$

3. 

4. 

5. $ROH + Ph–N=C=O \longrightarrow ROCONHPh$

6. $RONa + CS_2 \longrightarrow ROCSSNa$ ксантогенат

7. $RONa + CO_2 \longrightarrow ROCOONa$

22.2.5. Другие реакции

1. $R–CH_2–OH \xrightarrow{kat.} R–CHO + H_2$ kat. = CrO_3, CuO

2. $ROH + H_2O_2 \xrightarrow{H^+} ROOH + H_2O$

3. $ROH + ROOH \xrightarrow{H^+} ROOR + H_2O$

4. $2CH_3OH + O_2 \xrightarrow{Cu,\ t°} 2HCHO + H_2O$

5. $R–CH_2–OH + KMnO_4 + KOH \longrightarrow R–COOH$

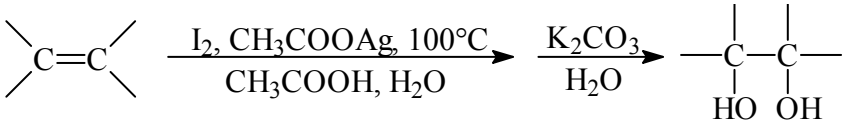
6. $ROH + CO \xrightarrow{HCo(CO)_4} RCOOH$

7. $CH_3OH + CO + 2H_2 \xrightarrow{kat.} CH_3CH_2OH + H_2O$

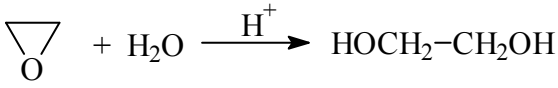
23. Многоатомные спирты

23.1. Синтезы

1. $RCH=CH_2 + KMnO_4 + H_2O \longrightarrow RCH(OH)–CH_2OH$

2.  (Вудворд)

3. $XCH_2–CH_2X + H_2O \xrightarrow{OH^-} HOCH_2–CH_2OH$

4. 

23.2. Реакции

1. $HOCH_2–CH_2OH + HCl \xrightarrow{t°} HOCH_2–CH_2Cl$

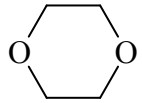
2. $HOCH_2–CH_2OH \xrightarrow{P,\ t°} [CH_2=CH_2OH] \longrightarrow CH_3–CHO$

3. $HOCH_2–CH_2OH + HNO_3(разб.) \longrightarrow HOCH_2–CHO$

4. $HOCH_2–CH_2OH + HNO_3(конц.) \longrightarrow HOC–COOH$

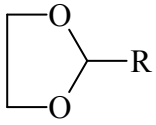
5. $HOCH_2–CH(OH)–CH_2OH + HNO_3 + H_2SO_4 \longrightarrow O_2NOCH_2–CH(ONO_2)–CH_2ONO_2$

6. $(CH_3)_2C(OH)–C(CH_3)_2(OH) \xrightarrow{H^+} CH_3–CO–C(CH_3)_3$ (пинаколиновая п-ка)

7. $2\ HOCH_2–CH_2OH \xrightarrow{H^+}$ 

8. $HO–CH_2–CH(OH)–CH_2OH \xrightarrow{H^+} \xrightarrow{H^+} CH_2=CH–CHO$ акролеин

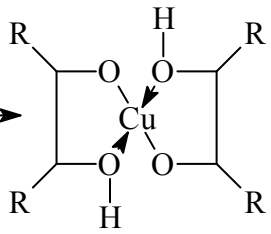
9. $HOCH_2–CH_2OH +$  $\xrightarrow{H^+} (HOCH_2CH_2)_2O$ диэтиленгликоль

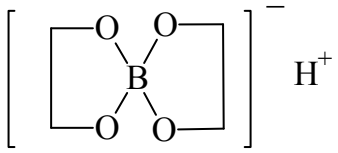
10. $HOCH_2–CH_2OH + RCHO \xrightarrow{H^+}$ 

11. $RCHOH–CH(OH)R + HIO_4 \longrightarrow 2RCHO + H_2O + HIO_3$ (Малопрад)

12. $HOCH_2–CH_2OH + H_2O_2 \xrightarrow{Fe2+} HOCH_2–CHO$

13. $R_2COH–C(OH)R_2 + Pb(OAc)_4 \longrightarrow 2R_2CO + Pb(OAc)_2 + 2AcOH$ (Криге)

14. $RCHOH–CH(OH)R + Cu(OH)_2 \longrightarrow$ 

15. $HOCH_2–CH_2OH + B(OH)_3 \longrightarrow$ 

24. Фенолы

24.1. Синтезы

1. $3NaO_3S–C_6H_4–SO_3Na + NaOH \xrightarrow{t°} \xrightarrow{H^+} 3HO–C_6H_4–OH$ резорцин

2. $ArCl + NaOH \xrightarrow{t°} ArONa$

3. $ArN_2X + H_2O \longrightarrow ArOH + N_2 + HX$

4. $C_6H_6 + H_2O_2 \xrightarrow{V_2O_5} C_6H_5OH$

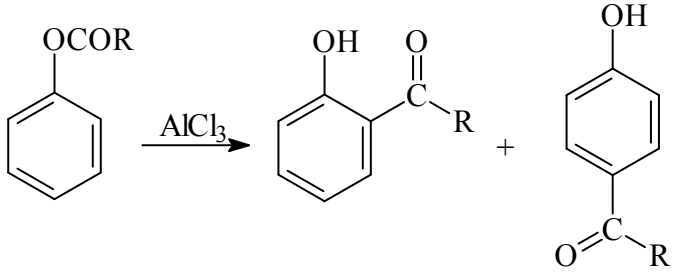
5. $C_6H_5CH_3 \xrightarrow{H_2O_2/BF_3} 4\text{-}CH_3–C_6H_4–OH + 2\text{-}CH_3–C_6H_4–OH$ крезолы

6. $C_6H_6 + O_2 \xrightarrow{Co/AgNO_3} C_6H_5OH$

7. $Ph–C(CH_3)_2–OOH \xrightarrow{H^+} Ph–OH + (CH_3)_2CO$ (Сергеев-Удрис)

8. $C_6H_5NHOH \xrightarrow{H^+} 4\text{-}NH_2–C_6H_4–OH$ (Бамбергер)

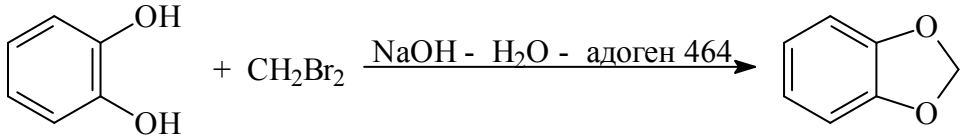
9. $C_6H_5N(O)=N–C_6H_5 \xrightarrow{H^+} 4\text{-}HO–C_6H_4–N=N–C_6H_5$

10. 

(Фрис)

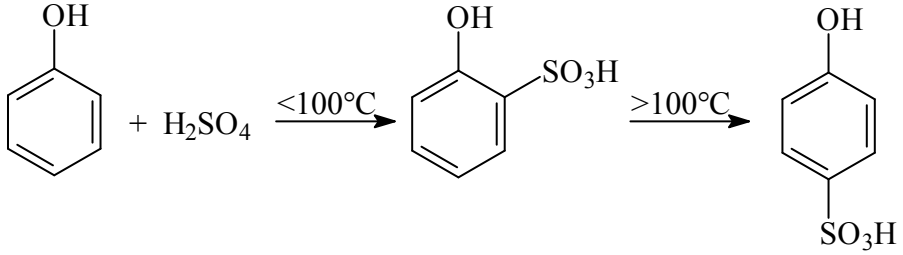
24.2. Реакции

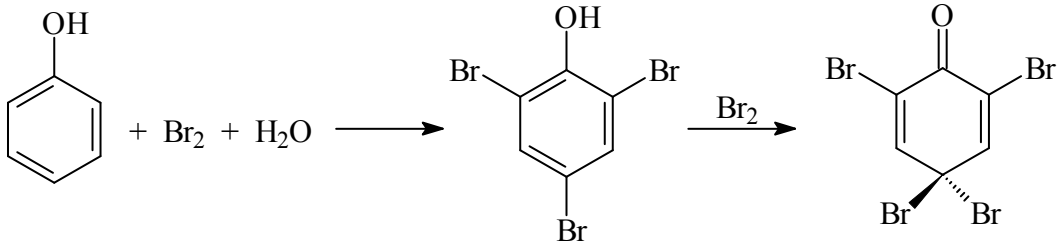
24.2.1. Реакции с участием гидроксильной группы

1. $ArOH + EtONa \longrightarrow ArONa$
2. $ArOH + PCl_3 \longrightarrow P(OAr)_3$
3. $ArOH + POCl_3 \longrightarrow O=P(OAr)_3$
4. $ArO^- + RX \longrightarrow ArOR + X^-$
5. 

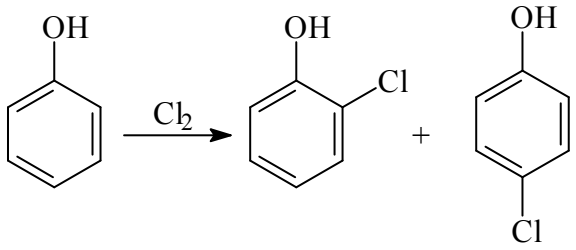
6. $ArO^- + RCOCl \longrightarrow ArOCR + Cl^-$
7. $ArOH + HC\equiv CH \xrightarrow{OH^-} ArOCH=CH_2$

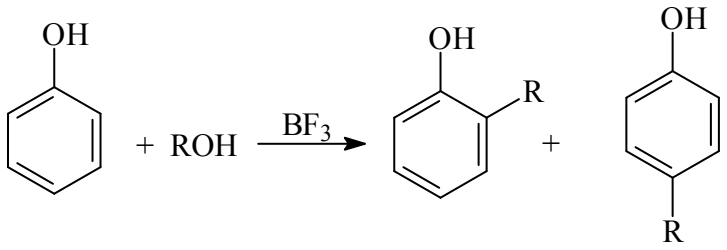
24.2.2. Реакции электрофильного замещения

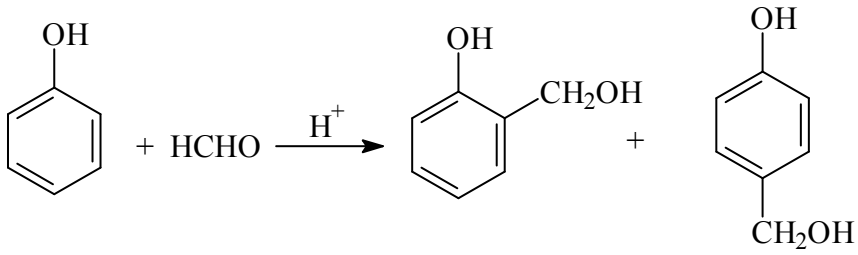
1. 

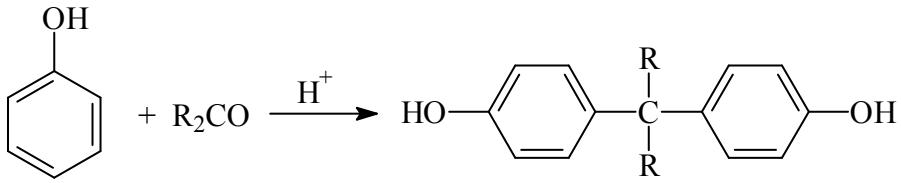
2. 

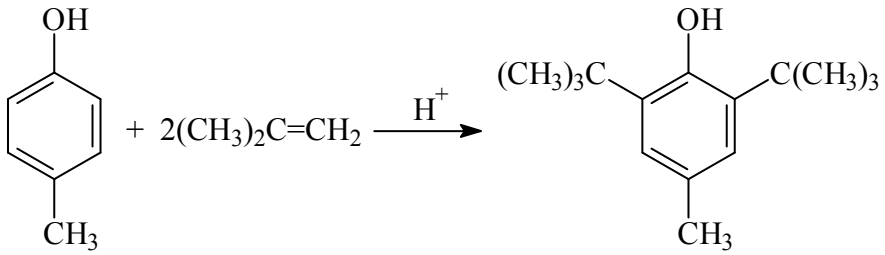
3. $C_6H_5OH \xrightarrow[Br_2]{\text{диоксан}} 4\text{-}Br–C_6H_4–OH$
4. $C_6H_5OH + SO_2Cl_2 \longrightarrow 4\text{-}Cl–C_6H_4–OH$

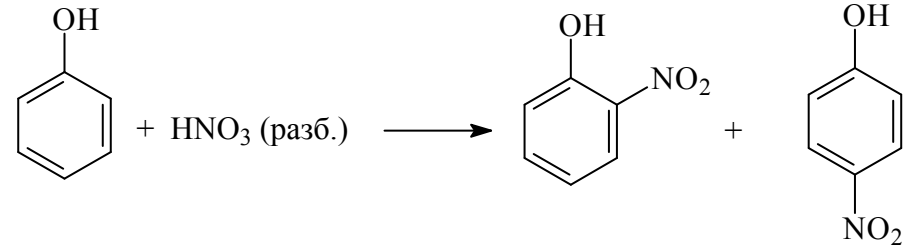
5. 
OH
Cl2
OH
Cl
+
OH
Cl

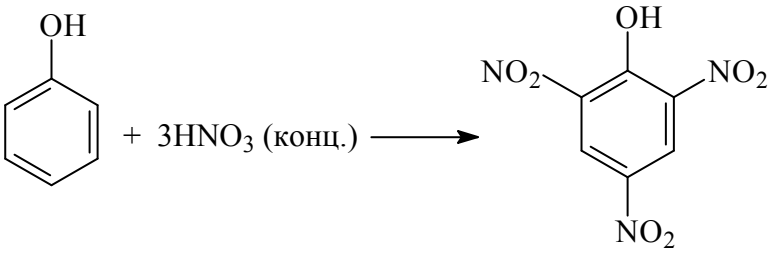
6. 
OH
+ ROH
BF3
OH
R
+
OH
R

7. 
OH
+ HCHO
H+
OH
CH2OH
+
OH
CH2OH

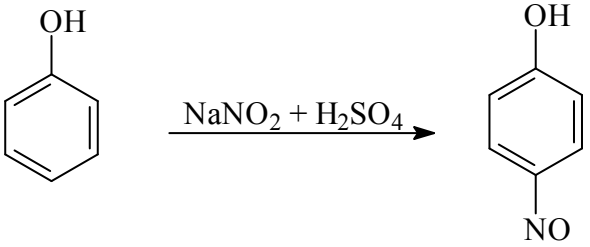
8. 
OH
+ R2CO
H+
HO
R
C
R
OH

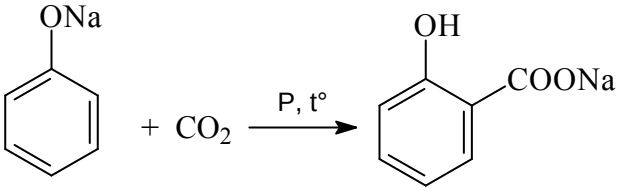
9. 
OH
+ 2(CH3)2C=CH2
H+
(CH3)3C
OH
C(CH3)3
CH3

10. 
OH
+ HNO3 (разб.)
OH
NO2
+
OH
NO2

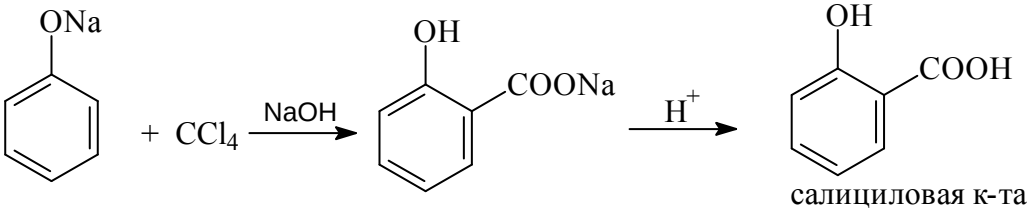
11. 

пикриновая кислота

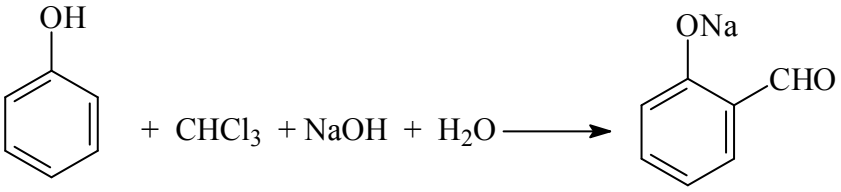
12. 

13. 

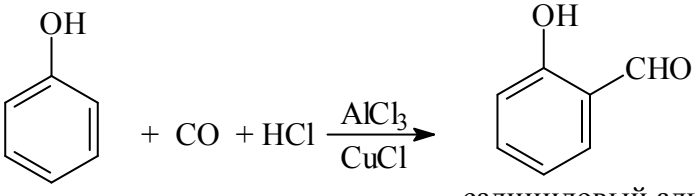
(Кольбе)

14. 

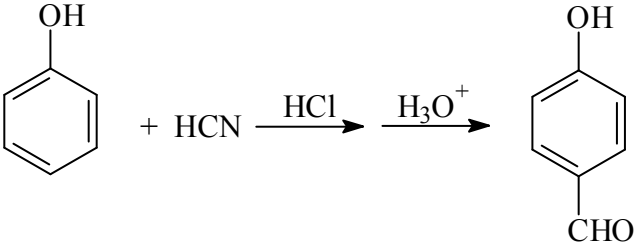
салициловая к-та

15. 

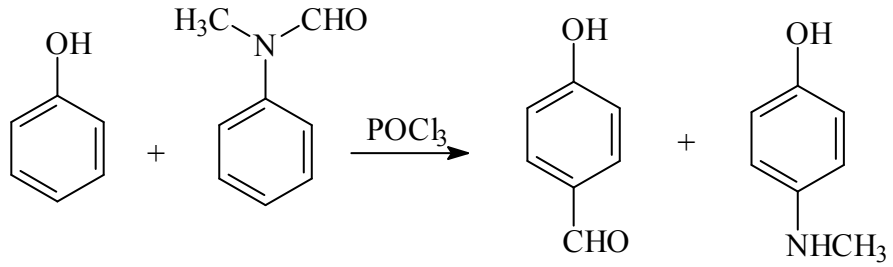
(Реймер-Тиман)

16. 

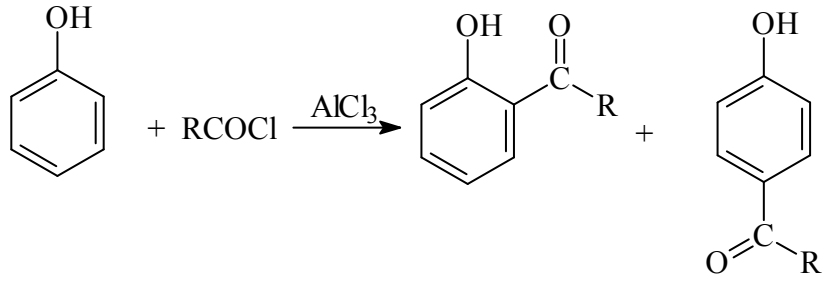
салициловый альдегид
(Гатерман-Кох)

17. 

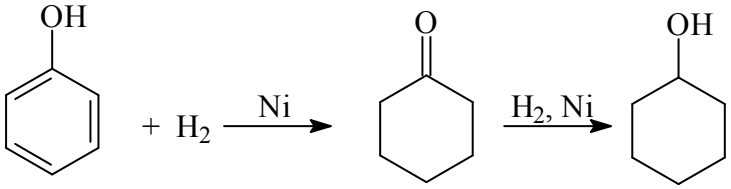
(Геш)

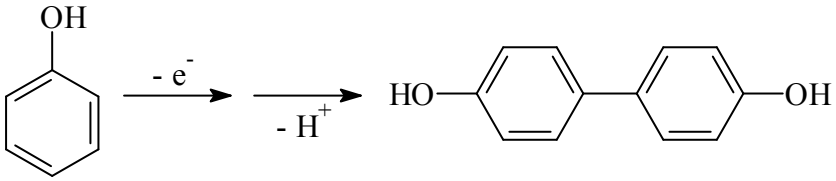
18. 

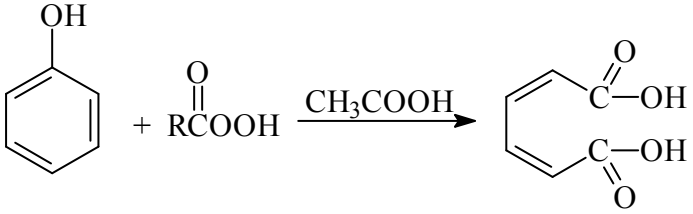
(Вильсмейер)

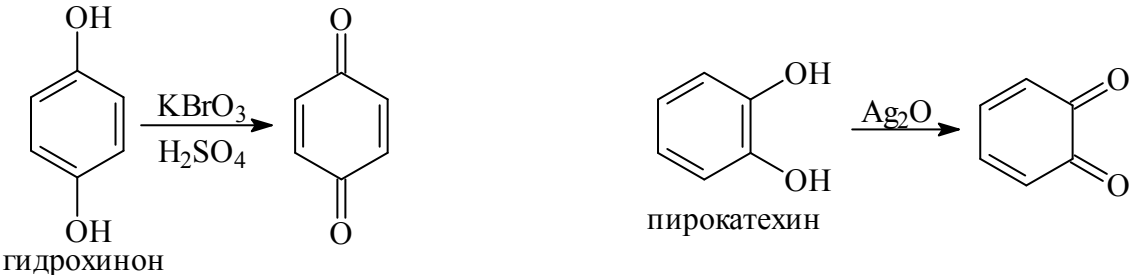
19. 

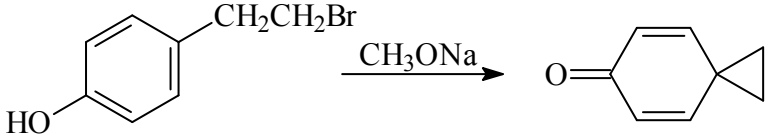
24.2.3. Другие реакции

1. 

2. 

3. 

4. 

5. 

25. Простые эфиры

25.1. Синтезы

1. $C_2H_5OH \xrightarrow[250^\circ C]{Al_2O_3} C_2H_5–O–C_2H_5$

2. $C_2H_5OH + H_2SO_4 \xrightarrow{130^\circ C} C_2H_5–O–SO_3H \xrightarrow[140^\circ C]{ROH} C_2H_5–O–R$

3. $ROH \xrightarrow{BF_3} R–O–R$

4. $RONa + R^1X \longrightarrow R–O–R^1$

5. $C_6H_5OH + C_6H_5Br \xrightarrow[230^\circ C]{Cu,\ K_2CO_3} C_6H_5–O–C_6H_5$

6. $ROH + H_2C{=}CH–R^1 \xrightarrow{H^+} H_3C–CH(OR)–R^1$

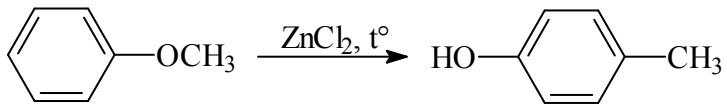
7. $RCH{=}CH_2 + Hg(OAc)_2 + R^1OH \longrightarrow RCH(OR^1)CH_2HgOAc \xrightarrow{NaBH_4} RCH(OR^1)CH_3$

8. $ROH + HC{\equiv}CH \xrightarrow{OH^-} R–O–CH{=}CH_2$

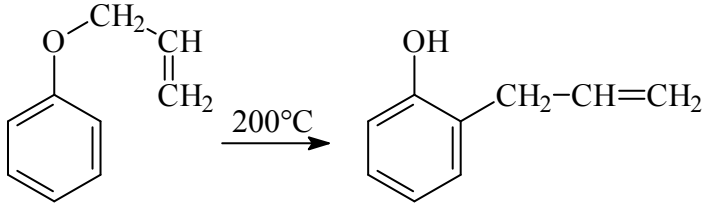
25.2. Реакции

1. $R–O–R + HX \rightleftharpoons R–\overset{+}{O}(H)–R\ X^- \longrightarrow ROH + RX$

2. $CH_3CH_2–O–CH_2CH_3 + O_2 \longrightarrow CH_3–CH(O–OH)–O–CH_2CH_3$

3. 

4. $C_6H_5OR + CH_3COONO_2 \longrightarrow 2\text{-}NO_2–C_6H_4–OR\ (>90\%) + 4\text{-}NO_2–C_6H_4–OR$

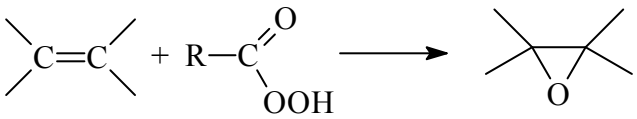
5. 

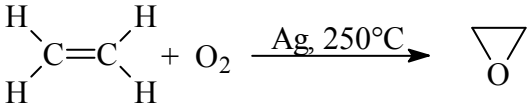
(п-ка Кляйзена)

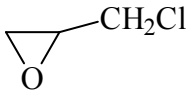
6. $R–O–CH{=}CH_2 + H_2O \xrightarrow{H^+} ROH + CH_3CHO$

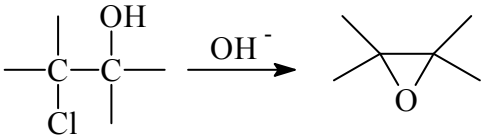
26. Циклические эфиры

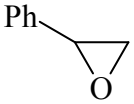
26.1. Синтезы

1. 

2. 

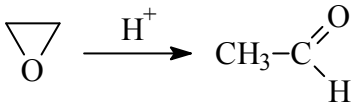
3. $CH_2{=}CHCH_2Cl \xrightarrow{Cl_2 + H_2O} \xrightarrow{NaOH}$  эпихлоргидрин

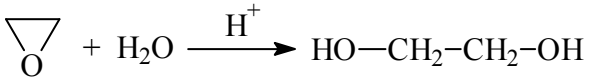
4. 

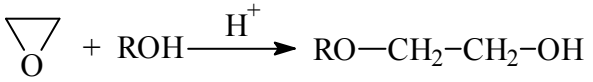
5. $PhCHO + C_{12}H_{25}S^+Me_2I^- \xrightarrow{NaOH - H_2O - C_6H_6}$  (Кори)

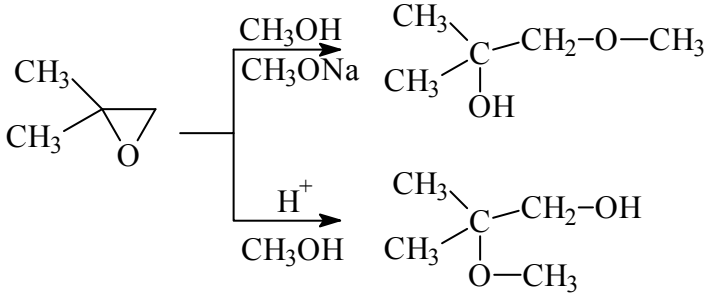
6. $HOCH_2CH_2OH + (CH_2CH_2Cl)_2O \longrightarrow$ [18]краун-6

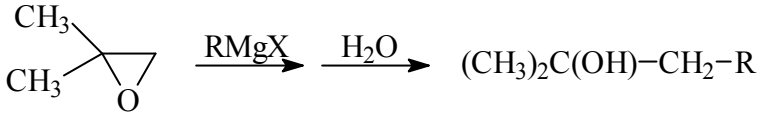
26.2. Реакции

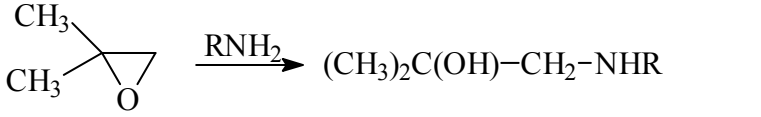
1. 

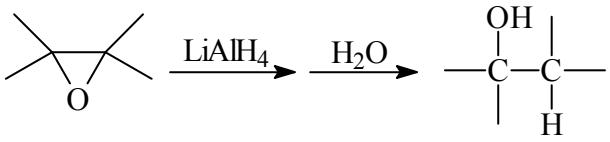
2.  этиленгликоль

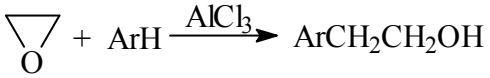
3.  целлозольвы

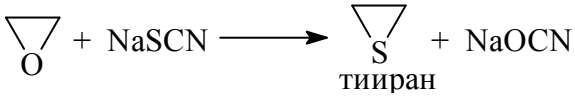
4. 

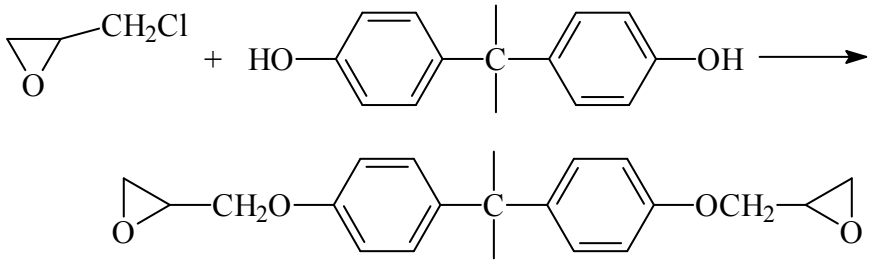
5. 

6. 

7. 

8. 

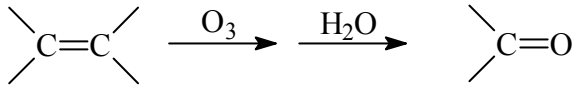
9. 

10. 

27. Алифатические монокарбонильные соединения

27.1. Синтезы

1. $CH_4 + O_2 \xrightarrow[t^\circ]{Cu\,/\,Zn} HCHO$

2. 

3. $RCH_2OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} RCHO$

4. $R_2CHOH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} R_2CO$

5. $RCH(OH)–C(OH)R_2 \xrightarrow{NaIO_4 \text{ или } Pb(OAc)_4} RCHO + R_2CO$

6. $RCOCl + H_2 \xrightarrow{Pd} RCHO$

7. $RC{\equiv}CH + H_2O \xrightarrow{H^+ + Hg2+} RCO–CH_3$

8. $RMgX + HCOONa \longrightarrow RCHO + NaX + MgO$

9. $RMgX + R^1–C{\equiv}N \longrightarrow \xrightarrow{H_2O} R^1COR + NH_3 + Mg(OH)Br$

10. $R_2C(OH)–C(OH)R_2 \xrightarrow{H^+} R_3C–CO–R$

11. $Ar–CR_2–OOH \xrightarrow{H^+} R_2CO + ArOH$

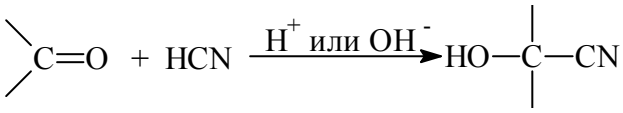
12. $RCX_2R^1 + H_2O \longrightarrow RR^1CO$

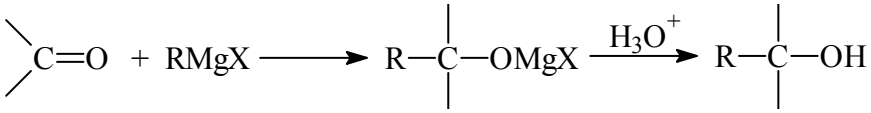
13. $R_2CBr–CH(Br)–R^1 \xrightarrow[t^\circ]{H_2O,\,PbO} \xrightarrow{H^+} R_2CH–COR^1$ (Эльтеков)

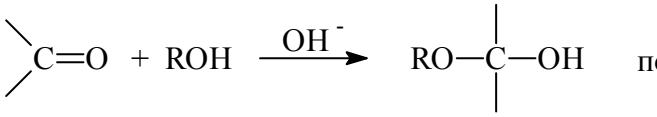
14. $(RCOO)_2Ca \xrightarrow{t^\circ} RCOR + CaCO_3$ (Пириа)

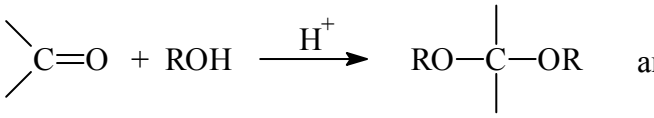
27.2. Реакции

27.2.1. Реакции присоединения

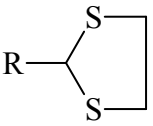
1.  циангидрин

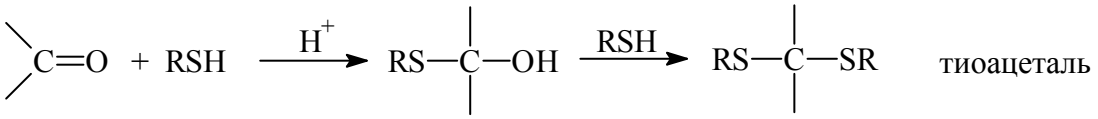
2. 

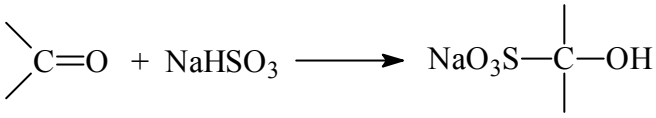
3.  полуацеталь

4.  ацеталь

5. $HCHO + ROH \xrightarrow{HCl} ROCH_2Cl$

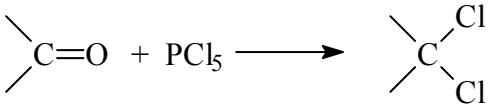
6. $RCHO + HS–CH_2–CH_2–SH \xrightarrow{H^+}$  Защита карбонильной группы

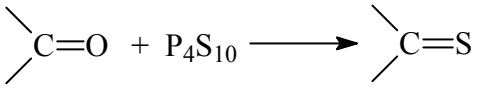
7.  тиоацеталь

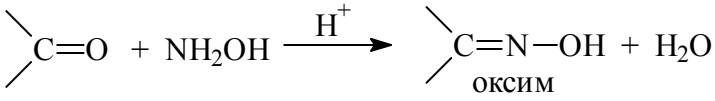
8. 

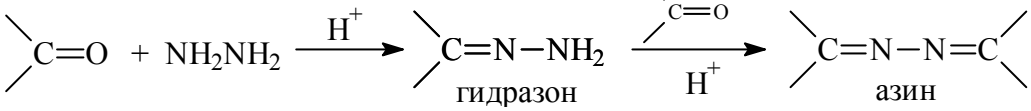
9. $CCl_3–CHO + H_2O \longrightarrow CCl_3–CH(OH)_2$

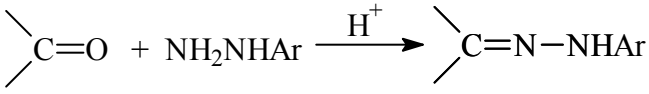
27.2.2. Реакции присоединения-элиминирования

1. 

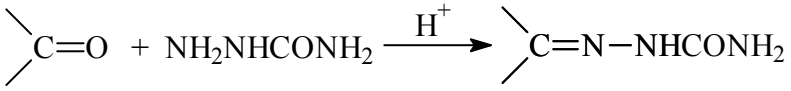
2. 

3. 
оксим

4. 
гидразон азин

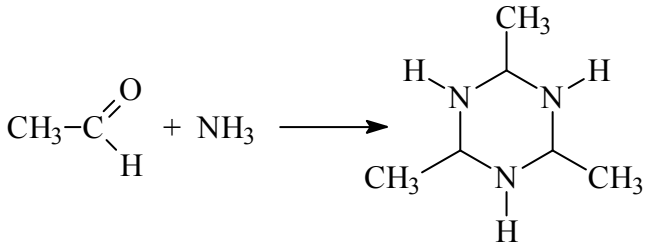
5. 

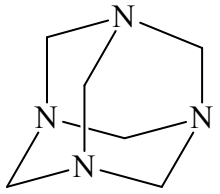
6. $RCH(OH)–CHO + ArNH–NH_2 \bullet HCl \longrightarrow RC(=N–NH–Ar)–CH=N–NH–Ar$

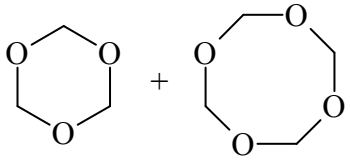
7. 

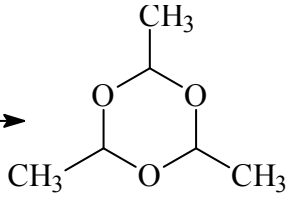
семикарбазон

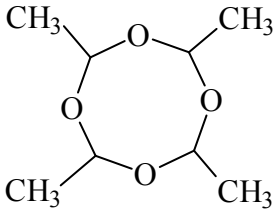
27.2.3. Реакции циклизации

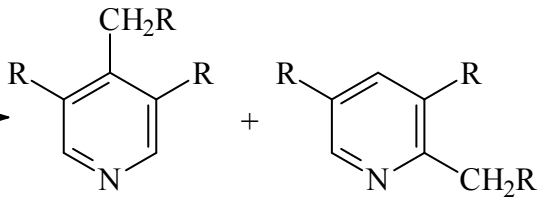
1. 

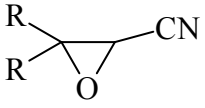
2. $HCHO + NH_3 \longrightarrow$  уротропин

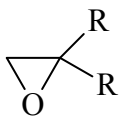
3. $HCHO \longrightarrow$ 

4. $3CH_3CHO \xrightarrow[20°C]{H_2SO_4}$  паральдегид

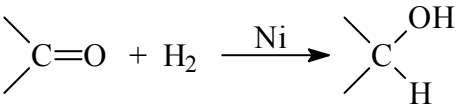
5. $4CH_3CHO \xrightarrow[0°C]{H_2SO_4}$  метальдегид

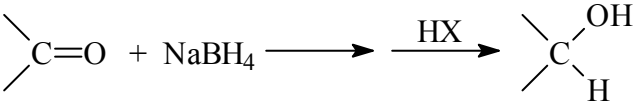
6. $3RCH_2COH + NH_3 \xrightarrow[P,\ t°]{Al_2O_3}$  (Чичибабин)

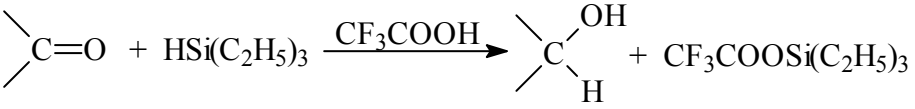
7. $R_2CO + ClCH_2CN \xrightarrow{50\%NaOH - ТЭБАХ}$  (Дарзан)

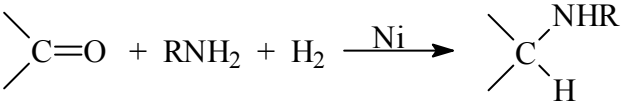
8. $R_2CO + (CH_3)_2S=CH_2 \xrightarrow[0°C]{ДМСО}$  (Кори)

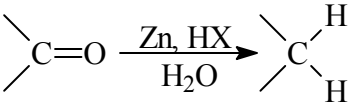
27.2.4. Реакции окисления и восстановления

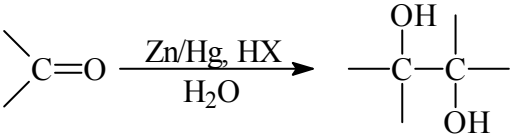
1. 

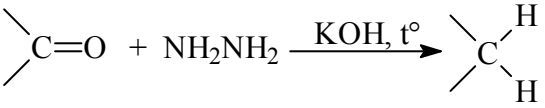
2. 

3. 

4. 

5. 
(Клемменсен)

6. 

7. 
(Кижнер-Вольф)

8. $RCHO + 2Ag(NH_3)_2OH \longrightarrow RCOONH_4 + Ag + H_2O + NH_3$

9. $RCHO + Cu(OH)_2 \longrightarrow RCOOH + Cu_2O + H_2O$

10. $RCHO + O_2 \longrightarrow RCOOH$

11. $RCH_2COCH_2R^1 \xrightarrow{KMnO_4} RCOOH + RCH_2COOH + R^1COOH + R^1CH_2COOH$

12. $RCH_2CHO \xrightarrow[CH_3COOH]{SeO_2} RCO–CHO$

13. $2HCHO \xrightarrow{NaOH} CH_3OH + HCOONa$ (Канниццаро)

14. $2CH_3CHO + Al(OCH_3)_3 \longrightarrow CH_3COOCH_2CH_3$ (Тищенко)

15. $3R_2CO + Al[OCH(CH_3)_2]_3 \rightleftharpoons (R_2CHO)_3Al + 3(CH_3)_2CO$

(Меервейен-Понндорф-Верлей)

27.2.5. Другие реакции

1. $RCH_2–COR^1 + X_2 \xrightarrow{H^+ \text{ или } OH^-} RCHXCOR^1$

2. $R–CO–CH_3 + X_2 \xrightarrow{OH^-} R–CO–CX_3 \xrightarrow{OH^-} R–COO^- + CHX_3$

3. $CH_3CHO \xrightarrow{OH^-} CH_3–CH(OH)–CH_2–CHO$ (альдольная конденсация)

4. $CH_3CHO \xrightarrow{H^+} CH_3–CH=CH–CHO$ кротоновый альдегид

5. $(CH_3)_3C–CO–CH_3 + RX \xrightarrow{KNH_2} (CH_3)_3C–CO–CH_2–R + (CH_3)_3C–C(OR)=CH_2$

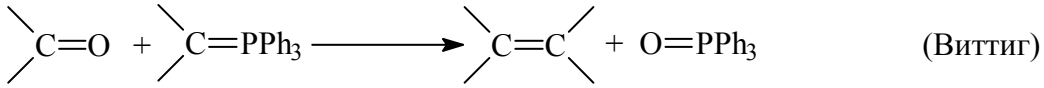
6. $(n+1)HCHO + H_2O \longrightarrow HO–CH_2–(CH_2)_n–OH$ параформ

7. $HCOH + CH_3–CH=CH_2 \xrightarrow{H^+} \begin{cases} \longrightarrow CH_2=CH—CH_2CHOH \\ \longrightarrow CH_3CH(OH)—CH_2CH_2OH \end{cases}$ (Принс)

8. $R_2CO + R^1X \xrightarrow{Zn,\ t°} \xrightarrow{H_3O^+} R^2C(OH)R^1$ (Зайцев)

9. $2HCHO \xrightarrow[H_2O]{Ca(OH)_2} HOCH_2–CHO \xrightarrow{HCHO} \longrightarrow (C_6H_{10}O_5)_n$ (Бутлеров)

10. $R_2CO \xrightarrow{Mg} \xrightarrow{H_3O^+} R_2C(OH)–C(OH)R_2$

11.  (Виттиг)

28. Ароматические монокарбонильные соединения

28.1. Синтезы

1. $ArCH_3 + Cl_2 \xrightarrow{h\nu} ArCHCl_2 \xrightarrow{H_2O} ArCHO$

2. $ArCOCl \xrightarrow[Pd]{H_2} ArCHO$

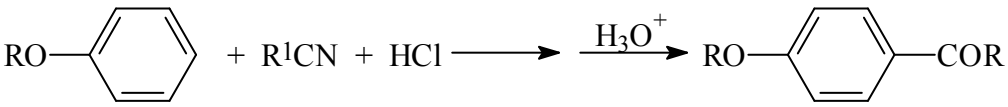
3. $PhCH_2CH_3 + O_2 \longrightarrow PhCH(CH_3)–OOH \longrightarrow H_2O + PhCOCH_3$ ацетофенон

4. $ArCH_2Cl + C_6H_{12}N_4 \longrightarrow ArCHO + NH_3 + HCHO + [CH_3NH_3]Cl$ (Соммле)

5. $ArH + CO + HCl \xrightarrow{CuCl} ArCHO$

6. $ArH + RCO–Cl \xrightarrow{AlCl_3} ArCOR$

7. $C_6H_6 + C_6H_5CO–Cl \xrightarrow{AlCl_3} C_6H_5COC_6H_5$ бензофенон

8. 

9. $ArCN + RMgBr \longrightarrow ArCR=N–MgBr \xrightarrow{H_3O^+} ArCOR$

10. $ArMgBr + HCOOR \longrightarrow ArCHO + Mg(OR)Br$

28.2. Реакции

1. $ArCHO + Cl_2 \longrightarrow ArCOCl$

2. $ArCHO + O_2 \xrightarrow{Fe(III)} ArCOOH$

3. $ArCHO + H_2N–Ar \longrightarrow Ar–CH=N–Ar + H_2O$

4. $2ArCHO \xrightarrow{KCN} ArCH(OH)–CO–Ar$ бензоин

5. $ArCHO + NaOH \longrightarrow ArCOONa + ArCH_2OH$ (Канниццаро)

6. $ArCHO + CH_3CHO \xrightarrow{OH^-} ArCH(OH)–CH_2CHO$

7. $ArCHO + (CH_3)_2CO \xrightarrow{OH^-} ArCH=CH–CO–CH_3$ (кротоновая конденсация)

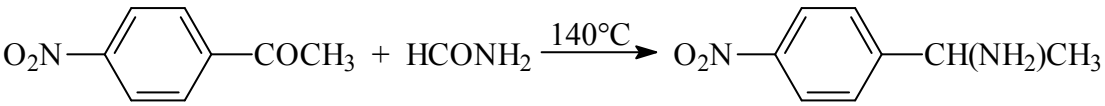
8. $2ArCOCH_3 \xrightarrow{H^+} ArC(CH_3)=CH–CO–Ar + H_2O$

9. $C_6H_6COCH_3 + RCOOR^1 + Na \longrightarrow R–CO–CH_2–CO–C_6H_5 + R^1ONa$

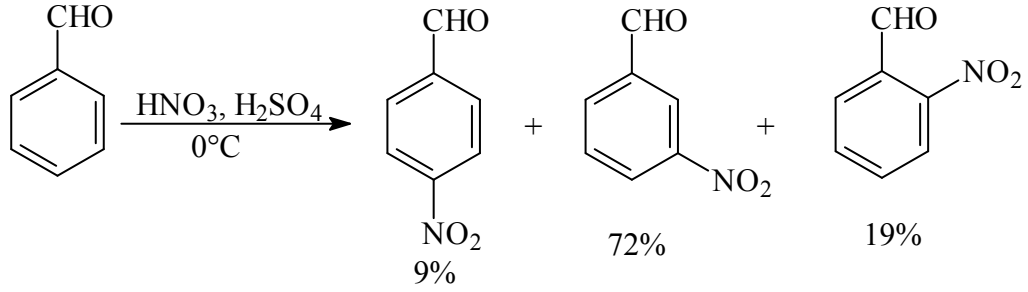
10. $C_6H_6COCH_3 + (CH_3CO)_2O \xrightarrow{BF_3} CH_3–CO–CH_2–CO–C_6H_5 + CH_3COOH$

11. $ArCHO + (RCH_2CO)_2O \xrightarrow{OH^-} ArCH=CR–COOH$

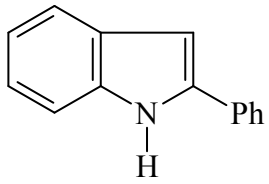
12. $C_6H_6COCH_3 + HCHO + HNR_2 + HCl \longrightarrow C_6H_5COCH_2CH_2NR_2 \bullet HCl$ (Манних)

13. 

14. $(C_6H_5)_2CO + NaOH \longrightarrow C_6H_5CONa + C_6H_6$

15. 

16. $(C_6H_5)_2CO \xrightarrow{h\nu} \xrightarrow{(CH_3)_2CHOH} (C_6H_5)_2C(OH)–C(C_6H_5)_2–OH$

17. $C_6H_5COCH_3 + PhNH–NH_2 \xrightarrow[100°C]{ПФК}$  (Фишер)

29. Непредельные альдегиды и кетоны

29.1. Синтезы

1. $CH_2{=}CH{-}CH_3 + O_2 \xrightarrow[400^\circ C]{CuO} CH_2{=}CH{-}CHO$

2. $CH_3CHO \xrightarrow{H^+ \text{ или } OH^-} CH_3{-}CH{=}CH{-}CHO$ кротоновый альдегид

3. $(CH_3)_2CO \xrightarrow{H^+ \text{ или } OH^-} CH_3{-}CO{-}CH{=}C(CH_3)_2$ окись мезитила

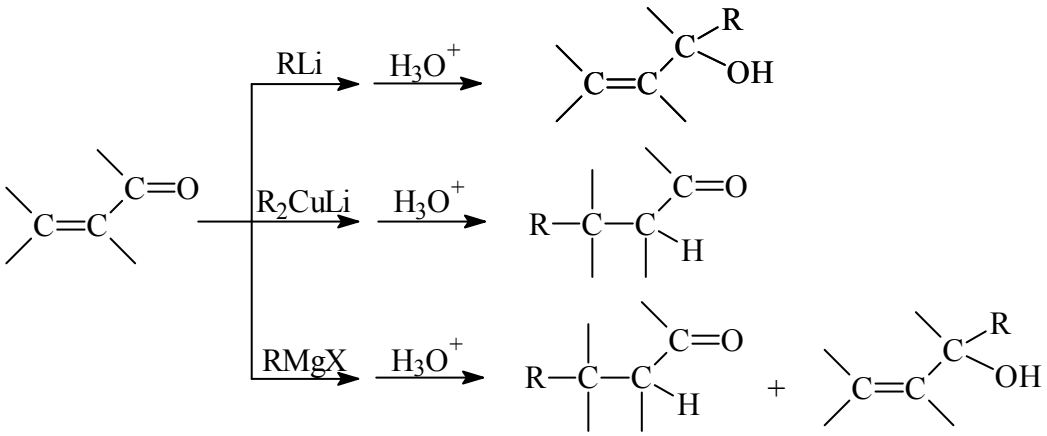
4. $CH_3COCH_3 + HCHO \xrightarrow{H^+ \text{ или } OH^-} CH_2{=}CH{-}CO{-}CH_3$

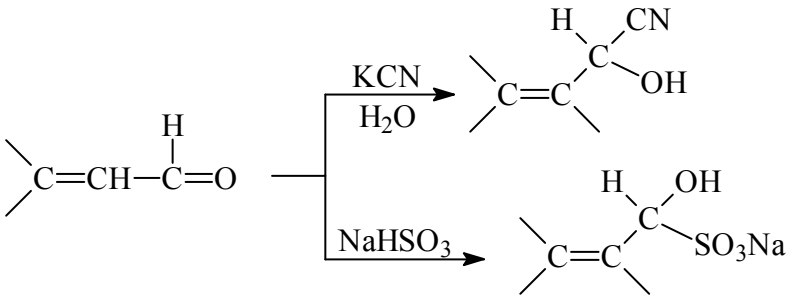
5. $C_6H_5CHO + CH_3CHO \xrightarrow{OH^-} C_6H_5CH{=}CH{-}CHO$ коричный альдегид

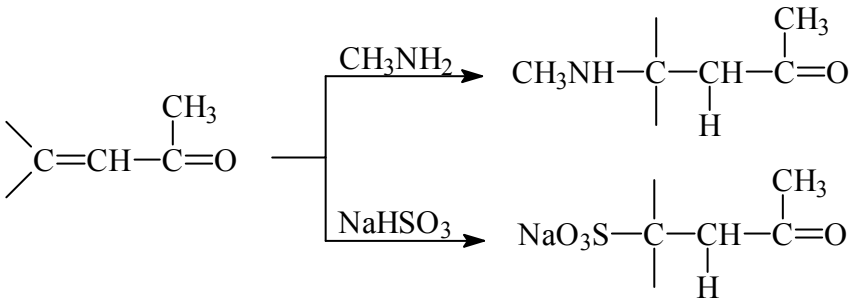
6. $C_6H_5CHO + C_6H_5COCH_3 \xrightarrow{OH^-} C_6H_5{-}CH{=}CH{-}CO{-}C_6H_5$ халкон

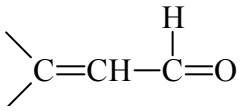
7. $2HOCH_2{-}CHOH{-}CH_2OH \xrightarrow[-\,2H_2O]{H^+} CH_2{=}CH{-}CHO$

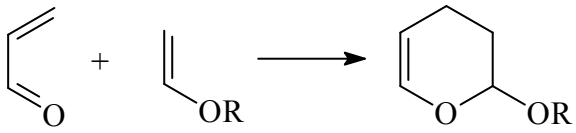
29.2. Реакции

1. 

2. 

3. 

4.  + HX ⟶ ClCH$_2$CH$_2$CHO

5. 

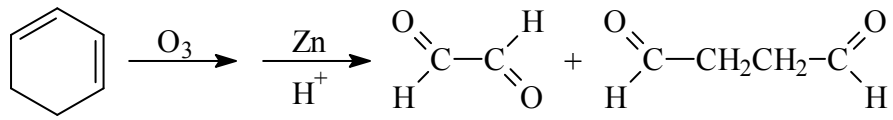
6. CH_2=CH–CHO $\xrightarrow{H_2O_2,\ H_2O}$ HOCH$_2$–CHOH–CH$_2$OH

30. Кетены

1. $R_2CBr–COBr + Zn \longrightarrow R_2C=C=O$
2. $(CH_3)_2CO \xrightarrow{750°C} CH_2=C=O + CH_4$
3. $CH_3COOH \xrightarrow[700°C]{AlPO_4} CH_2=C=O + H_2O$
4. $RCOCHN_2 \xrightarrow{Cu,\ t°} R–CH=C=O$ (Вольф)
5. $R_2C=C=O + H_2O \longrightarrow R_2CHCOOH$
6. $R_2C=C=O + ROH \longrightarrow R_2CHCOOR$
7. $R_2C=C=O + CH_3COOH \longrightarrow R_2CHCOOCOR$
8. $R_2C=C=O + CH_3NH_2 \longrightarrow R_2CHCONHCH_3$

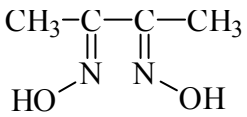
31. Дикарбонильные соединения

31.1. Синтезы

1. $CH_3CHO + SeO_2 \longrightarrow OHC–CHO$
2. $CH_3COCH_2CH_3 + SeO_2 \longrightarrow CH_3CO–CO–CH_3$ диацетил
3. $HOCH_2CH_2OH \xrightarrow{[O]} OHC–CHO$
4. $C_6H_5–CH(OH)–CO–C_6H_5 \xrightarrow{[O]} C_6H_5–CO–CO–C_6H_5$ бензил
5. $CH_3COCH_3 + (CH_3CO)_2O \xrightarrow{BF_3} CH_3CO–CH_2–CO–CH_3$ ацетилацетон
6. $RCOCH_2R^1 + R^2COOC_2H_5 \xrightarrow{C_2H_5ONa} \xrightarrow{HX} RCOCHR^1–COR^2$ (Кляйзен)
7. 

31.2. Реакции

1. $2OHC–CHO \xrightarrow{OH^-} CH_2(OH)–COO^-$

2. $CH_3CO–COCH_3 + NH_2OH \longrightarrow$  диметилглиоксим

3. $C_6H_5CO–COC_6H_5 + NaOH \longrightarrow (C_6H_5)_2C(OH)–COONa$ (Бензиловая п-ка)

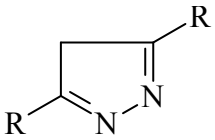
4. $CH_3CO–CH_2–COCH_3 \xrightarrow[NaOH]{RX} CH_3CO–CHR–COCH_3 + CH_3CO–CH=C(OR)CH_3$

5. $CH_3COCH_2COCH_3 + RCHO \longrightarrow CH_3CO–CH(COCH_3)–CHR–CH(COCH_3)–COCH_3$

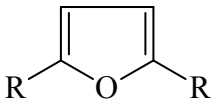
6. $RCOCH_2COR + R^1NH_2 \longrightarrow RCO–CH_2–C(R)=N–R^1$

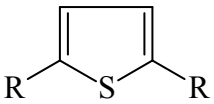
7. $RCOCH_2COR \xrightarrow[-\ HY]{EY} RCO–CH(E)–COR$ $\quad E = NO, NO_2, ArN_2, SO_3H, Hal$

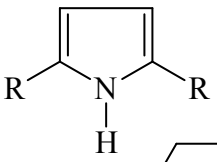
8. $RCOCH_2COR \xrightarrow[H_2O]{NaOH} RCOCH_3 + RCOONa$

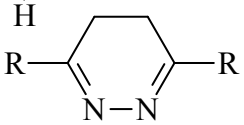
9. $RCOCH_2COR + NH_2NH_2 \xrightarrow{H^+}$  пиразолы

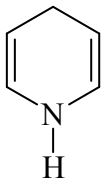
10. $RCOCH_2CH_2COR$

$\xrightarrow[t°]{H^+}$  (Пааль-Кнорр)

$\xrightarrow[t°]{H_2S}$ 

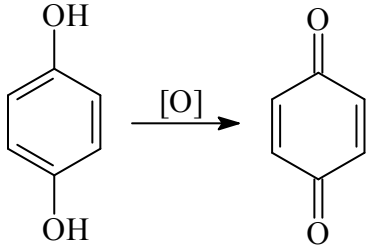
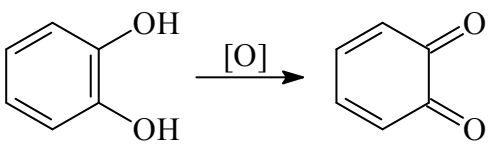
$\xrightarrow[t°]{NH_3}$ 

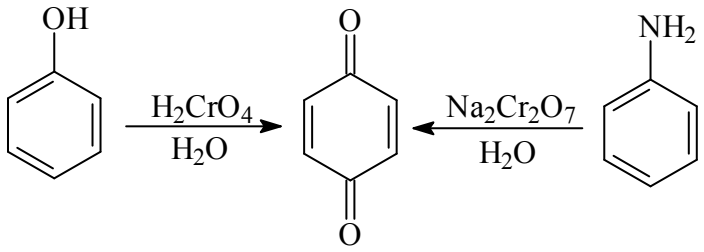
$\xrightarrow[t°]{NH_2NH_2}$ 

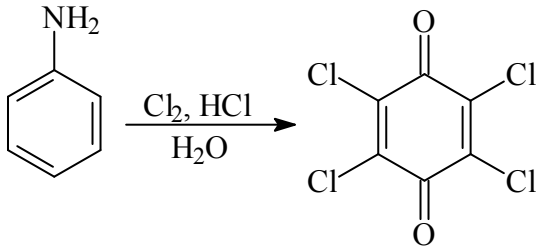
11. $RCOCH_2CH_2CH_2COR + NH_3 \longrightarrow$ 

32. Хиноны

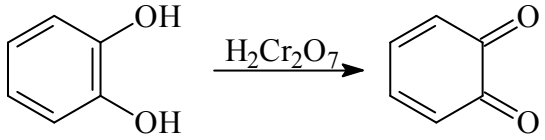
32.1. Синтезы

1. 


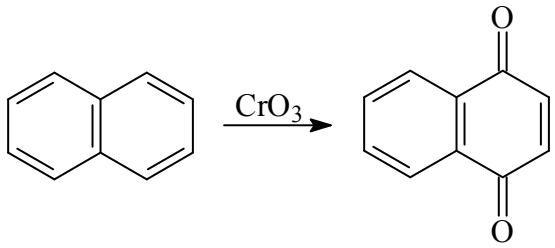
2. 

3. 

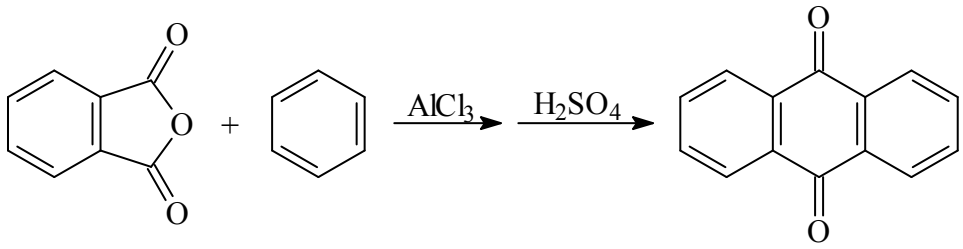
хлоранил

4. 

о-бензохинон

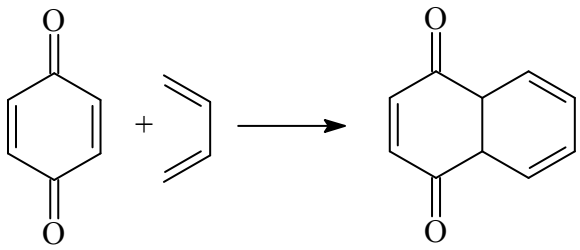
5. 

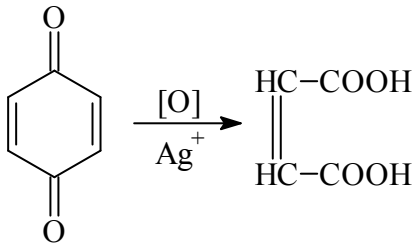
нафтохинон

6. 

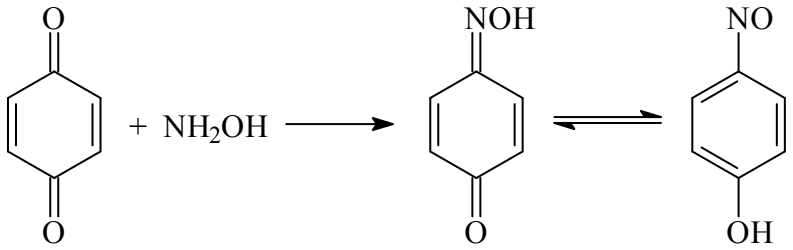
антрахинон

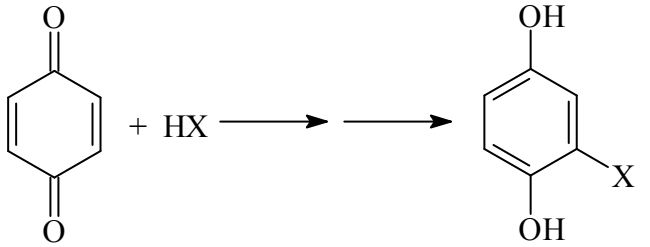
32.2. Реакции

1. 

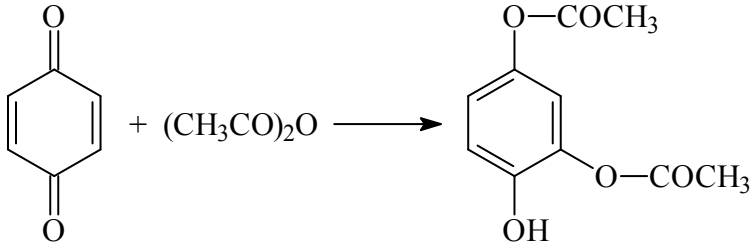
2. 

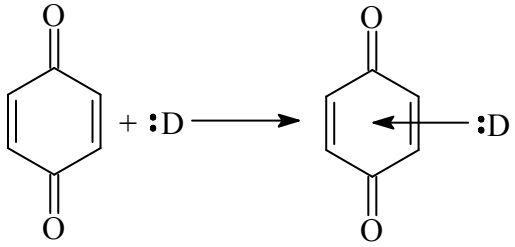
малеиновая кислота

3. 

4. 

X = Cl, HNR, OR

5. 

6. 

D = фенолы, ариламины и арены

КПЗ

33. Нитроалканы

33.1. Синтезы

1. $RH + HNO_3 \xrightarrow{150°C} RNO_2$ (Коновалов)
2. $CH_3CH_2CH_3 + HNO_3 \xrightarrow{420°C} CH_3NO_2 + CH_3CH_2NO_2 + C_3H_7NO_2$ (Гесс)
3. $RX + AgNO_2 \longrightarrow RNO_2 + RONO + AgX$
4. $RX + NaNO_2 \longrightarrow RNO_2 + NaX$
5. $RNO + O_2 \longrightarrow RNO_2$

33.2. Реакции

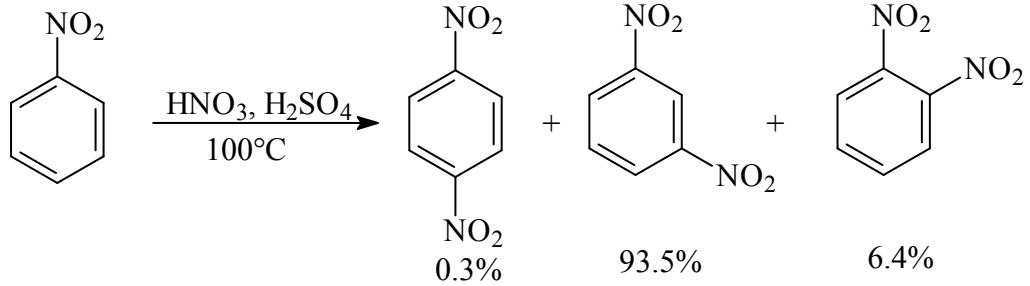
1. $RCH_2NO_2 + X_2 \xrightarrow{OH^-} RCH(X)–NO_2$
2. $RCH_2NO_2 + R^1X \xrightarrow{OH^-} RCH(R^1)–NO_2 + R_2CH=N(O)–OR^1$
3. $R_2CHNO_2 + [HNO_2] \longrightarrow R_2C(NO)–NO_2$
4. $R_2CHNO_2 + R^1R^2CO \xrightarrow{OH^-} R_2C(NO_2)–C(OH)R^1R^2$
5. $RCH_2NO_2 + H_2SO_4(конц.) + H_2O \longrightarrow RCOOH + [H_3NOH]HSO_4$ (Бамбергер)
6. $R_2CHNO_2 + H_2SO_4(разб.) \longrightarrow R_2CO + NO + H_2O$ (Неф)
7. $RCH_2NO_2 + PCl_5 \xrightarrow{Py} R–CN$
8. $RNO_2 + H_2S \longrightarrow RNH_2 + S + H_2O$
9. $RNO_2 + LiAlH_4 \longrightarrow RNH_2$
10. $RNO_2 + 3Fe + 6HCl \longrightarrow RNH_2 + 2FeCl_2 + 2H_2O$

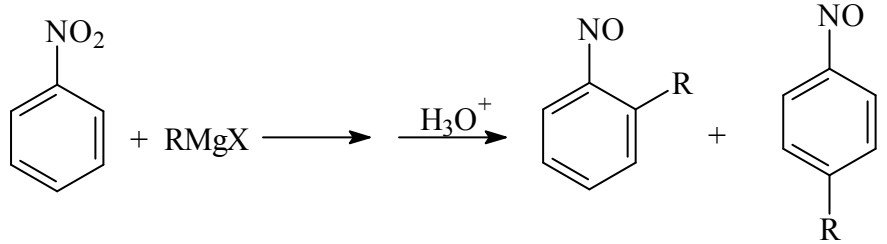
34. Нитроарены

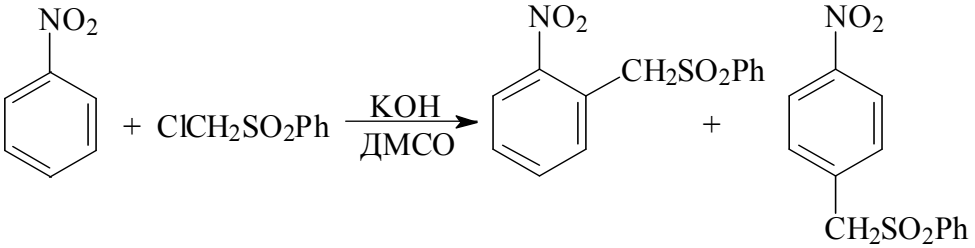
34.1. Синтезы

1. $ArH + HNO_3 + H_2SO_4 \longrightarrow ArNO_2$
2. $ArNO \xrightarrow{[O]} ArNO_2$
3. $ArN_2X \xrightarrow{CuNO_2} ArNO_2$
4. $ArNH_2 + H_2O_2 \longrightarrow ArNO_2$

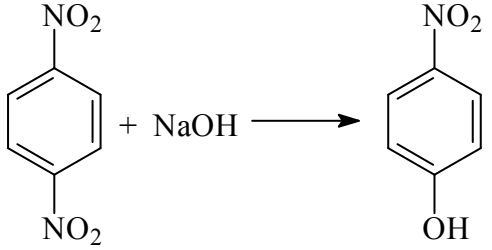
34.2. Реакции

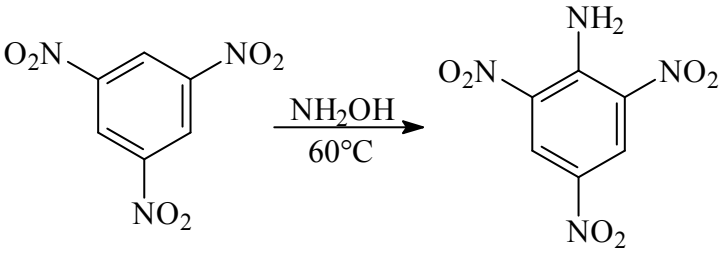
1. 

2. 

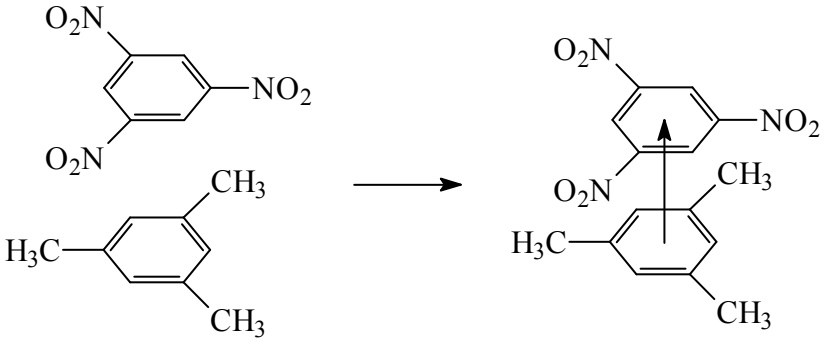
3. 

Викариозное нуклеофильное замещение

4. 

5. 

6. $ArNO_2 + NaOH + CH_3OH \longrightarrow Ar–N=N(O)–Ar$
7. $ArNO_2 + NaOH + SnCl_2 \longrightarrow Ar–N=N–Ar$
8. $ArNO_2 + NaOH + Zn \longrightarrow Ar–NH–NH–Ar$
9. $ArNO_2 + Zn + NH_4Cl \longrightarrow ArNHOH$
10. $ArNO_2 + Zn + HCl \longrightarrow ArNH_2$

11. 

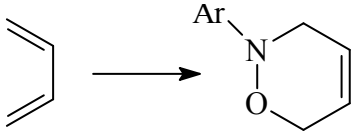
комплекс с переносом заряда (КПЗ)

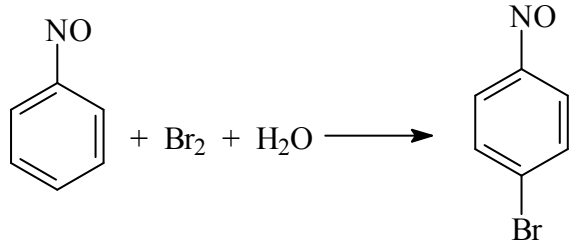
35. Нитрозоарены

1. $ArNHOH + K_2Cr_2O_7 + H_2SO_4 \xrightarrow{0°C} ArNO$
2. $ArMgCl + O=N–Cl \longrightarrow ArNO$
3. $ArNO + PhNH_2 \longrightarrow Ar–N=N–Ph$

4. $ArNO + PhNHOH \xrightarrow{NaOH} Ar–N=N(O)–Ph$

5. $ArNO + H_2C(COR)_2 \longrightarrow Ar–N=C(COR)_2$

6. $ArNO +$ 

7. 

36. Алифатические амины

36.1. Синтезы

1. $RX + NH_3 \longrightarrow RNH_2 + NH_4X$

2. $CH_3OH + NH_3 \xrightarrow[300^\circ C]{ZnCl_2} CH_3NH_2$

3. $ROH + NH_3 \xrightarrow[300^\circ C]{Al_2O_3} RNH_2$

4. $2ROH + NH_3 \xrightarrow[300^\circ C]{Al_2O_3} R_2NH$

5. $3ROH + NH_3 \xrightarrow[300^\circ C]{Al_2O_3} R_3N$

6. $ROH + RNH_2 \xrightarrow[300^\circ C]{Al_2O_3} R_2NH$

7. $RCN \xrightarrow{[H]} RCH_2NH_2$

8. $RNC \xrightarrow{[H]} RNHCH_3$

9. $RNO_2 \xrightarrow{[H]} RNH_2$

10. $CH_3COCH_3 + NH_3 + H_2 \xrightarrow{Ni} CH_3CH(NH_2)CH_3$

11. $NH_3 +$  $\longrightarrow HOCH_2CH_2NH_2$ моноэтаноламин

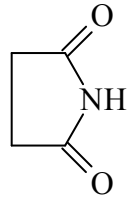
12. $R–N=C=O + H_2O \xrightarrow{H^+ \text{ или } OH^-} RNH_2$

13. $R–CO–NH_2 + NaOH + Br_2 \longrightarrow RNH_2$ (Гофман)

14. $RCO–NHOH \xrightarrow[Ac_2O]{P_2O_5} RNH_2 + CO_2$ (Лоссен)

15. $R–CO–N_3 \longrightarrow R–N=C=O \xrightarrow{H_3O^+} RNH_2$ (Курциус)

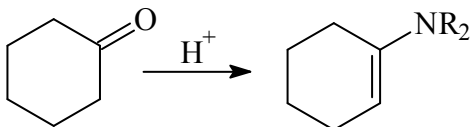
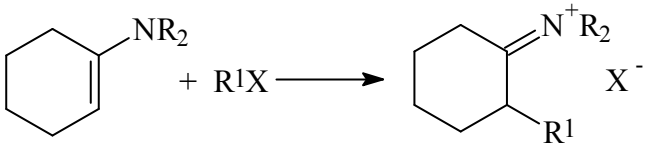
16. $(CH_3)_3COH + H_2SO_4 \xrightarrow{RCN} \xrightarrow{H_3O^+} (CH_3)_3CNH_2$ (Риттер)

17.  $\xrightarrow{RX} \xrightarrow[OH^-]{H_2O} RNH_2$ (Габриэль)

сукцинимид

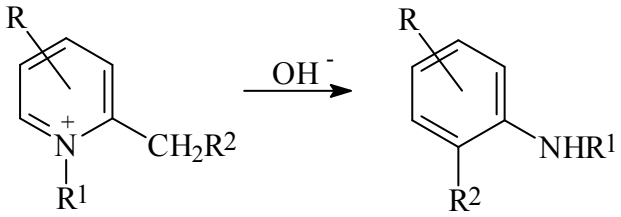
18. $RCOOH + HN_3 \xrightarrow{H^+} RNH_2 + N_2 + CO_2$ (Шмидт)

36.2. Реакции

1. $RNH_2 + HX \longrightarrow RNH_3X$
2. $RNH_2 + R^1X \longrightarrow RR^1NH_2X$
3. $RNH_2 + R^1COCl \longrightarrow RNHCOR^1$
4. $R_2NH + ArSO_2Cl \longrightarrow ArSO_2NR_2$
5. $RNH_2 + X_2 \longrightarrow \longrightarrow RNHX + HX$
6. $R_2NH + SO_3 \longrightarrow R_2N–SO_3H$
7. $R_3N + H_2O_2 \longrightarrow R_3N \rightarrow O$
8. $RNH_2 + [NO]X \longrightarrow \xrightarrow{H_2O} ROH + N_2 + HX + RX +$ алкен
9. $R_2NH + [NO]X \longrightarrow R_2N–N=O + HX$
10. $R_3N + [NO]X \longrightarrow [R_3N–N=O]X$ X = Hal, ONO, O_3SOH
11. $RNH_2 + CHCl_3 + NaOH \longrightarrow RNC + NaCl + H_2O$ (Гофман)
12. $R_2NH + CO_2 \longrightarrow R_2NCOO^-[R_2NH_2]^+$
13. $R_2NH + CS_2 \longrightarrow R_2NCSS^-[R_2NH_2]^+$
14. $R_2NH + ClCN \longrightarrow R_2N–CN$
15. $RNH_2 +$  $\longrightarrow RNHCH_2CH_2OH$
16. $RNH_2 + CH_2=CH–CHO \longrightarrow RNHCH_2CH_2CHO$
17. $R_2NH + HC\equiv CH \xrightarrow{OH^-} R_2N–CH=CH_2$
18. $R_2NH +$ 
19.  (Сторк)

37. Ароматические амины

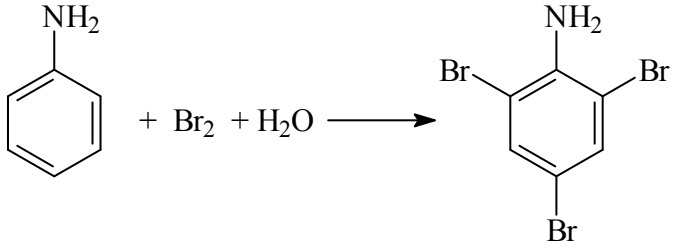
37.1. Синтезы

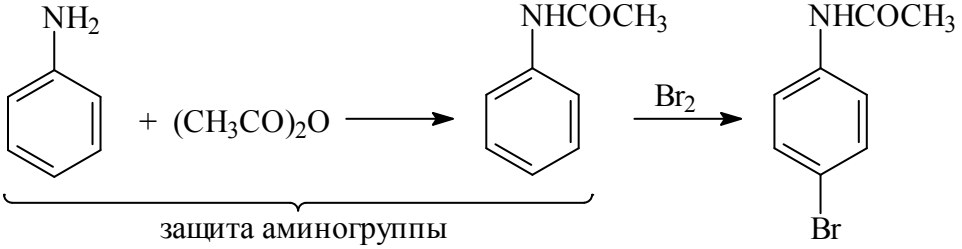
1. $ArNO_2 + 3(NH_4)_2S \longrightarrow ArNH_2 + 3S + 6NH_3 + 2H_2O$ (Зинин)
2. $C_6H_5NO_2 + H_2S \longrightarrow C_6H_5NH_2$
3. $C_6H_5NO_2 + 3SnCl_2 + 6HCl \longrightarrow C_6H_5NH_2 + 3SnCl_4 + 2H_2O$
4. $4C_6H_5NO_2 + 9Fe + 4H_2O \longrightarrow 4C_6H_5NH_2 + 3Fe_3O_4$
5. $C_6H_5N{=}N{-}C_6H_5 + 2SnCl_2 + 4HCl \longrightarrow 2C_6H_5NH_2 + 2SnCl_4$
6. $ArX + NH_3 \xrightarrow{t^\circ} ArNH_2$
7. 

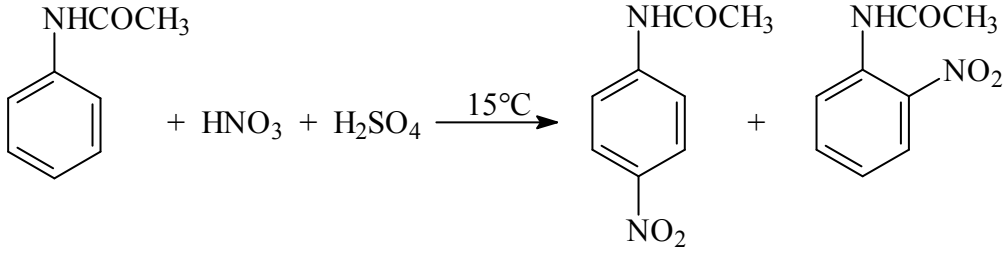
(Кост-Сагитуллин)
R - электроноакцепторная группа

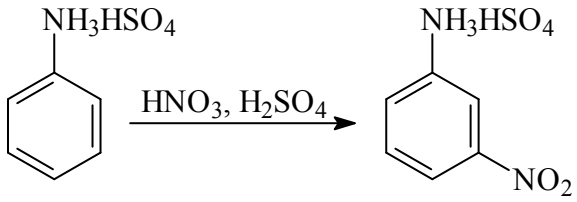
37.2. Реакции

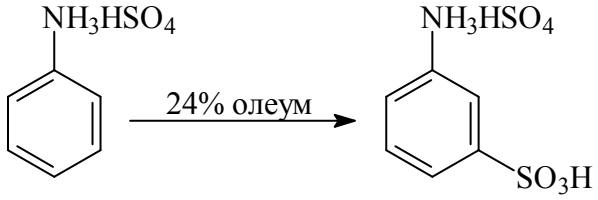
37.2.1. Реакции электрофильного замещения

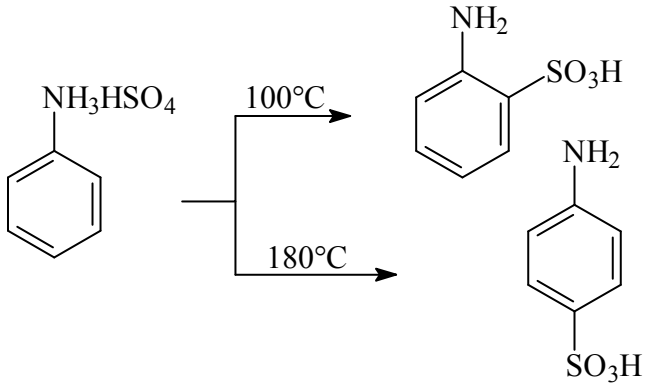
1. 

2. 

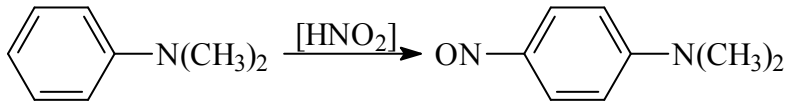
3. 

4. 

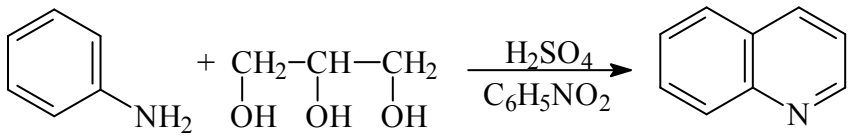
5. 

6. 

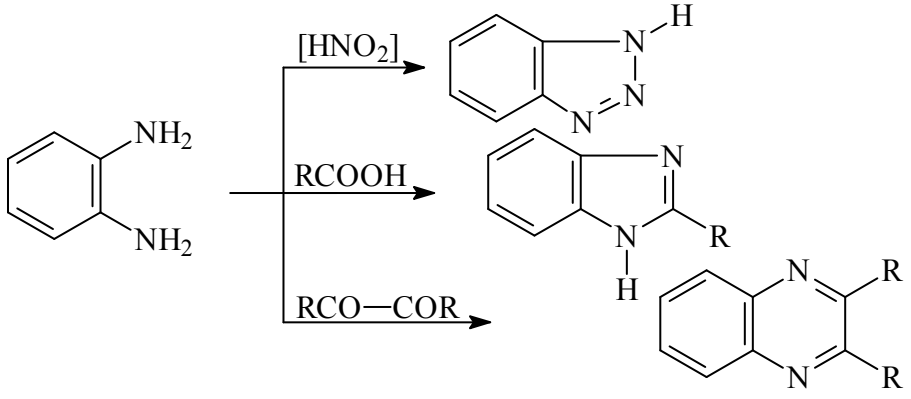
сульфаниловая кислота

7. 

37.2.2. Реакции гетероциклизации

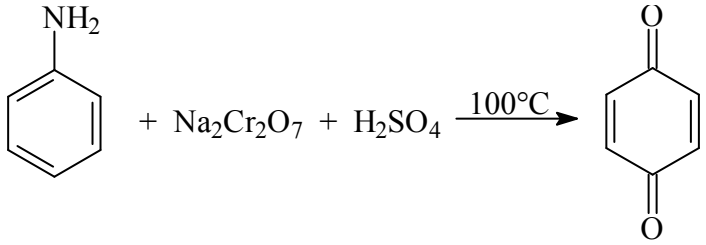
1. 

хинолин (Скрауп)

2. 

37.2.3. Другие реакции

1. $ArNH_2 + H_2O_2 \longrightarrow ArNO_2$

2.  $+ Na_2Cr_2O_7 + H_2SO_4 \xrightarrow{100°C}$

3. $ArNH_2 + ArNO \longrightarrow Ar–N=N–Ar$

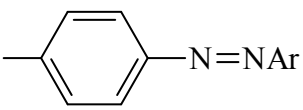
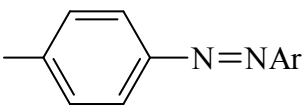
4. $ArNH_2 + C_6H_5CHO \xrightarrow[t°]{KOH} ArN=CHC_6H_5$ (Шифф)

38. Соли арендиазония

38.1. Синтезы

1. $ArNH_2 + NaNO_2 + HX \longrightarrow ArN_2X + NaX + H_2O$ (Грисс)
2. $ArNO + NO \longrightarrow ArN_2NO_3$
3. $ArNO + H_2NOH \longrightarrow ArN=N–OH \xrightarrow{HX} ArN_2X$

38.2. Реакции без выделения азота

4. $ArN_2X + NaCN \longrightarrow ArN=N–CN$
5. $ArN_2X + NaHSO_3 \longrightarrow ArN=N–SO_3H$
6. $ArN_2X + RONa \longrightarrow ArN=N–OR$
7. $ArN_2X + NaOH \longrightarrow ArN=N–OH \xrightarrow{NaOH} ArN=N–ONa$
8. $ArN=N–ONa + CH_3I \longrightarrow ArN(CH_3)–N=O$
9. $ArN=N–OAg + CH_3I \longrightarrow ArN=N–OCH_3$
10. $ArN_2X + R^2NH \longrightarrow ArN=N–NR^2$
11. $ArN_2Cl + SnCl_2 + H_2O \xrightarrow{HCl} ArNH–NH_3Cl$
12. $ArN_2X + Na_2SO_3 \xrightarrow{H^+} ArNH–NH_2$ (Фишер)
13. $ArN_2Cl + AgBF_4 \longrightarrow ArN_2BF_4$
14. $ArN_2Cl + HgCl_2 \longrightarrow ArN_2Cl \cdot HgCl_2$
15. $ArN_2X + ArNH_2 \xrightarrow{pH = 7} ArN=N–NH–Ar$
16. $ArN_2X + ArNHOH \longrightarrow ArN=N–N(OH)–Ar$
17. $ArN_2X + C_6H_5NH_2 \xrightarrow{pH = 5}$ 
18. $ArN_2X + C_6H_5OH \xrightarrow{pH = 9}$ 

38.3. Реакции с выделения азота

1. $ArN_2Cl \xrightarrow[0\text{-}5°C]{Cu_2X_2,\ HX,\ H_2O} ArX$ X = Cl, Br, NO_2, CN, SCN, SH, SO_3H, N_3 (Зандмейер)

2. $ArN_2Cl \xrightarrow[\approx 50°C]{Cu,\ HX,\ H_2O} ArX$ X = Cl, Br, NO_2, CN (Гаттерман)

3. $ArN_2Cl \cdot HgCl_2 + Cu \longrightarrow ArHgCl + N_2 + CuCl$ (Несмеянов)

4. $ArN_2X + NaI \longrightarrow ArI$

5. $ArN_2BF_4 \xrightarrow{t°} ArF + N_2 + BF_3$

6. $ArN_2X + H_2O \xrightarrow{H^+} ArOH$

7. $ArN_2X + KSH + H_2O \longrightarrow ArSH$

8. $ArN_2BF_4 \xrightarrow[H_2O]{NaNO_2/Cu} ArNO_2$

9. $ArN_2Cl + CH_2{=}CH_2 \xrightarrow{CuCl} ArCH_2{-}CH_2Cl$ (Меервейн)

10. $ArN_2Cl + CH_2{=}CH{-}CN \xrightarrow{CuCl} ArCH_2CHCl{-}CN$

11. $ArN_2Cl + H_3PO_2 \longrightarrow ArH + HCl + H_3PO_3 + N_2$

12. $ArN_2Cl + CH_3CH_2OH \longrightarrow ArH + HCl + CH_3CHO + ArOC_2H_5 + N_2$

13. $ArN_2Cl + HCHO + H_2O \longrightarrow ArH + HCOOH + HCl + N_2$

14. $ArN_2X + NaOH \xrightarrow[t°]{Cu^+} Ar{-}Ar$

15. $ArN_2Cl + C_6H_6 \xrightarrow{NaOH} Ar{-}C_6H_5$ (Гомберг)

39. Диазоалканы

1. $H_2N{-}NH_2 + CHCl_3 + 3NaOH \longrightarrow CH_2N_2 + 3NaCl + 3H_2O$

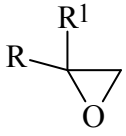
2. $CH_3NHCONH_2 \xrightarrow{[HNO_2]} \xrightarrow{NaOH} CH_2N_2 + Na_2CO_3 + NH_3 + H_2O$

3. $CH_3NHCOOR \xrightarrow{[HNO_2]} \xrightarrow{NaOH} CH_2N_2 + Na_2CO_3 + C_2H_5OH + H_2O$

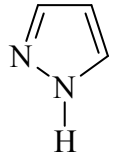
4. $R_2C{=}N{-}NH_2 + HgO \longrightarrow R_2CN_2 + Hg + H_2O$

5. $CH_2N_2 + H_2O \xrightarrow{H^+} CH_3OH + N_2$

6. $CH_2N_2 + RCOOH \longrightarrow RCOOCH_3 + N_2$

7. $CH_2N_2 + RCOR^1 \longrightarrow$  $\longrightarrow RCOCH_2R^1$

8. $CH_2N_2 + RCOCl + (C_2H_5)_3N \longrightarrow RCOCH_2N_2 + [(C_2H_5)_3NH]Cl$

9. $CH_2N_2 + HC{\equiv}CH \longrightarrow$  пиразол

40. Органические соединения фосфора

40.1. Синтезы

1. $PCl_3 + 3CH_3MgBr \longrightarrow (CH_3)_3P + 3MgBrCl$
2. $POCl_3 + 3C_2H_5MgCl \longrightarrow (C_2H_5)_3P{=}O + 3MgCl$
3. $PCl_3 + RX \xrightarrow{AlCl_3} [RPCl_3]X$
4. $C_6H_6 + PCl_3 \xrightarrow{AlCl_3} C_6H_5PCl_2 \cdot AlCl_3 + HCl$
5. $3ROH + I_2 + 2P \longrightarrow R_3PI_2 + P(OH)_3$
6. $Cl_3P{=}O + RLi \longrightarrow RP(O)Cl_2$

40.2. Реакции

1. $[(CH_3)_3PCH_2C_6H_6]X \xrightarrow{OH^-} (CH_3)_3P{=}O + C_6H_5CH_3$
2. $PH_3 + RCH{=}CH_2 \xrightarrow{h\nu} RCH_2CH_2PH_2 + (RCH_2CH_2)_2PH$
3. $PH_3 + CH_2{=}CH{-}CN \xrightarrow{OH^-} H_2PCH_2CH_2{-}CN$
4. $(RO)_3P + R^1Br \longrightarrow (RO)_2P(O)R^1 + RBr$ (Арбузов)
5. $(RO)_2P{-}ONa + R^1X \longrightarrow (RO)_2P(O){-}R^1$ (Михаэлис-Беккер)
6. $R_3P + R^1Cl \longrightarrow [R_3PR^1]Cl$
7. $[R_3P{-}CH_2R]Cl + CH_3Li \longrightarrow R_3P{=}CH_2$ метиленфосфораны
8. $(C_6H_5)_3P{=}CH_2 + R_2CO \longrightarrow (C_6H_5)_3P{=}O + CH_2{=}CR_2$ (Виттиг)
9. $(C_2H_5)_2P(O){-}CH_2R + R_2CO \xrightarrow{NaNH_2} \xrightarrow{H_2O} R_2C{=}CHR + (C_2H_5)_2P(O){-}OK$ (Хорнер)

41. Органические соединения серы

41.1. Сульфоновые кислоты

1. $RH + SO_2 + O_2 \xrightarrow{h\nu} RSO_3H$
2. $RSH + H_2O_2 + CH_3COOH \longrightarrow RSO_3H$
3. $RCH_2Cl + Na_2SO_3 + H_2O \longrightarrow RCH_2SO_3Na$
4. $CH_3CH{=}CH_2 + NaHSO_3 \xrightarrow{[O]} CH_3CH_2CH_2SO_3Na$
5. $ArH + SO_3 + H_2SO_4 \longrightarrow ArSO_3H$
6. $ArH + ClSO_3H \longrightarrow ArSO_3H$
7. $ArSO_3H + PCl_5 \longrightarrow ArSO_2Cl$
8. $ArSO_2Cl + ROH \longrightarrow ArSO_2OR$
9. $ArSO_2Cl + NH_3 \longrightarrow ArSO_2NH_2$
10. $ArSO_2Cl + ArH \xrightarrow{AlCl_3} ArSO_2Ar + HCl$

11. $ArSO_3H + H_2O \xrightarrow{H^+} ArH$

12. $C_6H_5SO_3H \xrightarrow{\text{олеум}} \underset{95\%}{3\text{–}HO_3S\text{–}C_6H_4\text{–}SO_3H} + \underset{5\%}{4\text{–}HO_3S\text{–}C_6H_4\text{–}SO_3H}$

13. $ArSO_3Na + NaOH \xrightarrow{t^\circ} ArONa + Na_2SO_3 + H_2O$

14. $ArSO_3Na + NaCN \xrightarrow{t^\circ} ArCN$

15. $ArSO_2OR + NaX \longrightarrow RX + ArSO_3Na$

16. $ArSO_2\text{–}OCH_2CH_3 \xrightarrow{RONa} CH_2{=}CH_2 + ROH + ArSO_3Na$

17. $Ts\text{–}OR + PhSNa \longrightarrow Ph\text{–}S\text{–}R + Ts\text{–}ONa$

41.2. Тиолы

1. $RX + NaSH \longrightarrow RSH$

2. $RX + H_2N\text{–}C(S)\text{–}NH_2 \longrightarrow H_2N\text{–}C(SR){=}NH \cdot HX \xrightarrow{KOH} \xrightarrow{H_3O^+} RSH$

3. $PhSO_2Cl \xrightarrow{[H]} PhSH$ тиофенол

4. $RS\text{–}SR + LiAlH_4 \longrightarrow \xrightarrow{H_3O^+} RSH$

5. $ArSC(S)\text{–}OC_2H_5 \xrightarrow{KOH} \xrightarrow{H_3O^+} ArSH$

6. $RMgX + S \longrightarrow \xrightarrow{H_3O^+} RSH$

7. $ROH + H_2S \xrightarrow[400^\circ C]{kat.} RSH + H_2O$

8. $RSH + R^1X \xrightarrow{OH^-} RSR^1$

9. $RSH + CH_2{=}CH\text{–}R \xrightarrow{h\nu \text{ или } R\bullet} RSCH_2CH_2R$

10. $RSH + HC{\equiv}CR \xrightarrow{OH^-} RSCH{=}CHR$ (*цис*-изомер)

11. $RSH \xrightarrow{[O]} RSOH \xrightarrow{[O]} RSO_2H \xrightarrow{[O]} RSO_3H$

12. $RSH + Cl_2 \longrightarrow RSCl$

13. $ClCH_2CH_2SH \xrightarrow{RO^-}$ 

14. $ArSH + CH_3SOCH_3 \xrightarrow{t^\circ} ArSCH_2SCH_3 + H_2O$

41.3. Сульфиды

1. $Na_2S + HC{\equiv}CH + H_2O \xrightarrow[ДМСО]{KOH} CH_2{=}CH\text{–}S\text{–}CH{=}CH_2$

2. $RC(S)\text{–}SR^1 + CH_2N_2 \longrightarrow R^1SC(R){=}CH_2$

3. $Et–S–S–Et + (EtO)_3P \longrightarrow Et–S–Et$

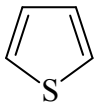
4. $RSCl + CH_2=CH–R \longrightarrow RS–CH_2CH(Cl)–R$

5. $CH_2=CH_2 + SCl_2 \longrightarrow ClCH_2CH_2–S–CH_2CH_2Cl$

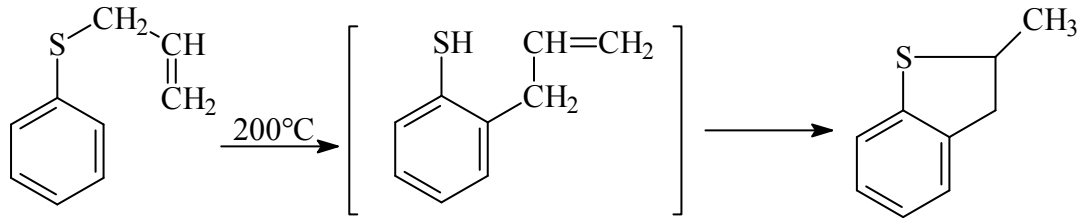
6. $RSR + R^1X \longrightarrow [RS(R^1)R]X$

7. $RSR + H_2O_2 + CH_3COOH \longrightarrow RS(O)R + RS(O_2)R$

8. $ArC(O)–CH_2S(O)–CH_3 \longrightarrow ArC(O)–CH(OH)–SCH_3$ (Пуммерер)

9. $CH_2=CH–S–CH=CH_2 \xrightarrow{t°}$ 

10. $RSCH_2CH=CH_2 \xrightarrow[ДМСО]{KOH} RSCH=CHCH_3$

11. 

12. $R_3C–S–R + H_2 \xrightarrow{Ni} R_3CH$

42. Кремнийорганические соединения

1. $CH_3Cl + Si \xrightarrow[300°C]{Cu} SiCl_4 + CH_3SiHCl_2 + CH_3SiCl_3 + (CH_3)_2SiCl_2$

2. $SiCl_4 + 4RLi \longrightarrow R_4Si + 4LiCl$

3. $SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$

4. $Si(OC_2H_5)_4 + 4RMgBr \longrightarrow R_4Si + 4Mg(C_2H_5O)Br$

5. $HSiCl_3 + RCH=CH_2 \xrightarrow{kat.} RCH_2CH_2SiCl_2$

6. $R_3SiH + PhLi \longrightarrow R_3Si–Ph$

7. $R_3SiH + HI \longrightarrow R_3Si–I + H_2$

8. $R_3SiH + (CH_3)_2C=CH_2 + HX \longrightarrow (CH_3)_3CH + R_3SiX$

9. $R_3SiH + C_2H_5OH \xrightarrow[Pt]{C_2H_5ONa} R_3SiOC_2H_5 + H_2$

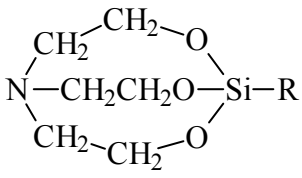
10. $(CH_3)_2Si(Cl)–CH_2Cl + C_2H_5MgCl \longrightarrow (CH_3)_2Si(C_2H_5)–CH_2Cl$

11. $R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 \longrightarrow –R_2SiOSiR_2–OSiR_2–$

12. $R_3SiCl \xrightarrow{NaBH_4} R_3SiH$

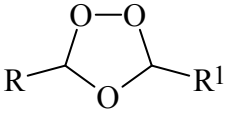
13. $(CH_3)_3SiCH_2CH_2Cl + NaOH \longrightarrow (CH_3)_3SiOH + CH_2=CH_2 + NaCl$

14. $R_3SiCl + R^1OH \xrightarrow{Et_3N} R_3SiOR^1$

15. $(HOCH_2CH_2)_3N + RSiCl_3 \longrightarrow$ 

43. Алифатические монокарбоновые кислоты

43.1. Синтезы

1. $RCCl_3 + H_2O \xrightarrow{H^+ \text{ или } OH^-} RCOOH + HCl$
2. $RCN + H_2O \xrightarrow{H^+ \text{ или } OH^-} RCOOH + NH_3$
3. $RCOOX + H_2O \xrightarrow{H^+ \text{ или } OH^-} RCOOH$ X = Hal, OR, NH_2, NHR
4. $RCH{=}C{=}O + H_2O \xrightarrow{H^+ \text{ или } OH^-} RCOOH$
5. $R_2C{=}NOH \xrightarrow{H^+} RC(O){-}NHR \xrightarrow{H_3O^+} RCOOH$
6. $RX + CO + H_2O \xrightarrow{HCo(CO)_4} RCOOH$ X = OH, Hal, OR, OOCR
7. $RONa + CO \xrightarrow{P,\ t^\circ} RCOONa \xrightarrow{H_3O^+} RCOOH$
8. $NaOH + CO \xrightarrow{P,\ t^\circ} HCOONa$
9. $RCH{=}CH_2 + CO + H_2O \xrightarrow[P,\ t^\circ]{Ni(CO)_4} RCH_2CH_2COOH$
10. $XCH_2COR + NaOH \longrightarrow RCH_2COONa + NaX + H_2O$ (Фаворский)
11. $RCOCHN_2 \xrightarrow{H_2O,\ Ag_2O} RCH_2COOH + N_2$ (Арндт-Эйстерт)
12. $RMgBr + CO_2 \longrightarrow RCOOMgBr \xrightarrow{H_3O^+} RCOOH$
13. $CH_3CH_2CH_2CH_3 + O_2 \xrightarrow{h\nu} CH_3COOH$
14. $RCH{=}CHR^1 \xrightarrow[t^\circ]{KMnO_4,\ KOH} RCOOK + R^1COOK$
15. $RC{\equiv}CR^1 \xrightarrow[t^\circ]{KMnO_4,\ KOH} RCOOK + R^1COOK$
16. $RCH_2OH \xrightarrow{HNO_3 \text{ или } KMnO_4/KOH} RCOOH$
17. $RCHO + O_2 \xrightarrow[\text{или } Ag_2O]{h\nu} RCOOH$
18.  $\xrightarrow[CH_3COOH]{H_2O_2} RCOOH + R^1COOH$

43.2. Реакции

1. $RCOOH + NaOH \longrightarrow RCOONa + H_2O$

2. $RCOOH + MgO \longrightarrow (RCOO)_2Mg + H_2O$

3. $RCOOH + Zn \longrightarrow (RCOO)_2Zn + H_2$

4. $RCOOH + NaH \longrightarrow RCOONa + H_2$

5. $RCOOH + NH_3 \longrightarrow [RCOO]NH_4 \xrightarrow{t^\circ} RCONH_2$

6. $RCOOH + CH_3MgX \longrightarrow RCOOMgX + CH_4$

7. $RCOOH + R^1C{\equiv}CNa \longrightarrow RCOONa + R^1C{\equiv}CH$

8. $3RCOOH + BR_3 \longrightarrow (RCOO)_3B + 3RH$

9. $RCOOH + NaBH_4 \longrightarrow RCH_2OH$

10. $RCOOH + R^1OH \xrightarrow{H^+} RCOOR^1$

11. $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

12. $RCOOH + P_2O_5 \longrightarrow (RCO)_2O + HPO_3$

13. $CH_3CH_2COOH + Cl_2 \xrightarrow{h\nu} ClCH_2CH_2COOH + CH_3CH(Cl)–COOH$

14. $CH_3CH_2COOH + Cl_2 \xrightarrow{P} CH_3CH(Cl)–COOH$

15. $RCH_2COOH + Br_2 + PBr_3 \longrightarrow RCH(Br)–COBr$

16. $CH_3COOH \xrightarrow[\text{электролиз}]{HF} CF_3COF$

17. $HCOOH + H_2SO_4 \longrightarrow H_2O + CO$

18. $HCOOH + Ag_2O \longrightarrow Ag + CO_2 + H_2O$

19. $RCOONa + R^1X \longrightarrow RCOOR^1$

20. $RCOONa + NaOH \xrightarrow{300^\circ C} RH + Na_2CO_3$

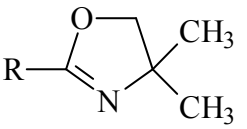
21. $CCl_3COOH \xrightarrow{t^\circ} CHCl_3 + CO_2$

22. $(CH_3COO)_2Ca \xrightarrow{t^\circ} (CH_3)_2CO + CaCO_3$

23. $RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$

24. $RCOOH + HgO + Br_2 \longrightarrow RBr + HgBr_2 + CO_2 + H_2O$

25. $HCOONH_4 + R_2CO \xrightarrow{t^\circ} R_2CH–NH_2 + CO_2 + H_2O$ (Лейкарт)

26. $RCOOH + (CH_3)_2C(NH_2)–CH_2OH \longrightarrow$  защита карбоксильной группы

44. Ароматические монокарбоновые кислоты

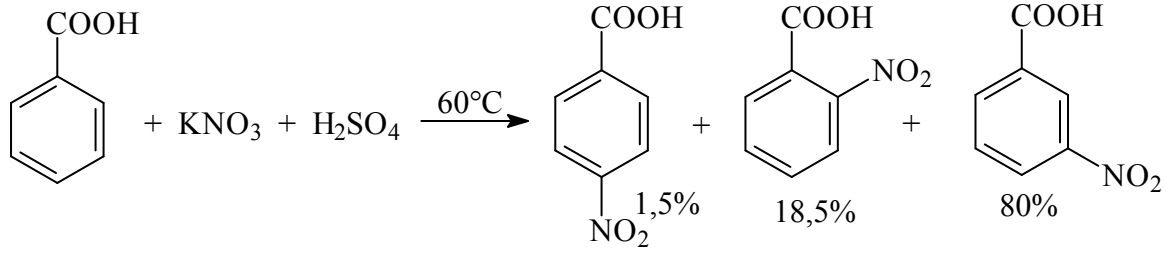
1. $C_6H_5CH_3 \xrightarrow{[O]} C_6H_5COOH$

2. $ArCHO + O_2 \xrightarrow{h\nu} ArCOOH$

3. $ArCOCH_3 \xrightarrow{NaOCl} ArCOOH + HCOOH$

4. $C_6H_5–C(O)–C_6H_5 + NaOH \xrightarrow{t°} C_6H_5COONa + C_6H_6$

5. $C_6H_5Li + CO_2 \longrightarrow C_6H_5COOLi \xrightarrow{H_3O^+} C_6H_5COOH$

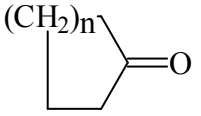
6. 

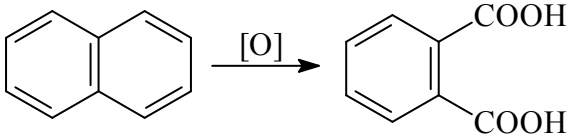
7. $ArCOOH \xrightarrow[Cu]{t°} ArH + CO_2$

45. Дикарбоновые кислоты

1. $NC–CN + H_2O \xrightarrow{H^+} HOOC–COOH$

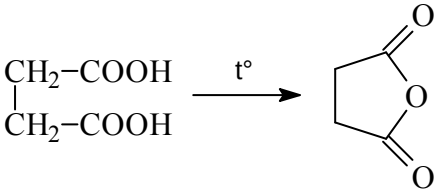
2. $HCOONa \xrightarrow{t°} NaOOC–COONa + H_2$

3.  $\xrightarrow{HNO_3}$ $HOOC—CH_2—(CH_2)_n—CH_2—COOH$ n = 1, 2, 3

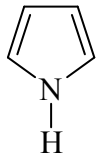
4. 

фталевая кислота

5. $4\text{-}CH_3–C_6H_4–CH_3 + O_2 \xrightarrow[P,\ t°]{Co(OCOCH_3)_2} 4\text{-}HOOC–C_6H_4–COOH$ терефталевая к-та

6. 

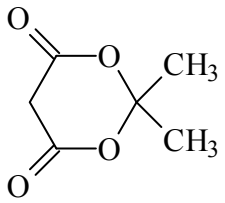
янтарный ангидрид

7. $HOOC–(CHOH)_4–COOH + 2HN_4OH \xrightarrow{t°}$  пиррол

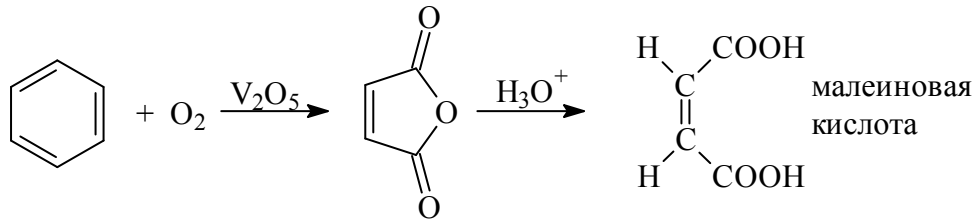
8. $HOOC–CH_2–COOH \xrightarrow{t°} CH_3COOH + CO_2$

9. $HOOC–COOH \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$

10. $HOOC–CH_2–COOH + RCHO \xrightarrow{RO^-} RCH{=}C(COOH)_2$

11. $HOOCCH_2COOH + (CH_3)_2CO \xrightarrow[H_2SO_4]{(CH_3CO)_2O}$  кислота Мельдрума

46. Непредельные кислоты

1.  малеиновая кислота

2. $CH_2=CH–CN + H_2O \xrightarrow{H^+} CH_2=CH–COOH$ акриловая кислота

3. $HC\equiv CH + CO + H_2O \xrightarrow{Ni(CO)_4} CH_2=CH–COOH$

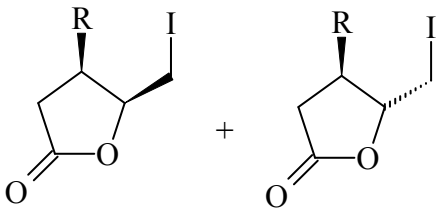
4. $RCHO + (C_6H_5)_3P=CH–COOCH_3 \longrightarrow RCH=CH–COOCH_3 + (C_6H_5)_3P=O$

5. $RCH=CH(CH_2)_nCH_2OH \xrightarrow{[O]} RCH=CH(CH_2)_nCOOH$

6. $RCHXCH_2COOH \xrightarrow{OH^-} RCH=CHCOOH$

7. $RCHX–CHX–COOH \xrightarrow{OH^-} RC\equiv C–COOH$

8. $HOOC–C\equiv C–COOH \xrightarrow{t^\circ} HC\equiv C–COOH$ пропаргиловая кислота

9. $H_2C=CH–CH_2–CH_2–COOH + I_2 \xrightarrow{NaHCO_3 + H_2O}$  (галогенлактонизация)

47. Галогенангидриды кислот

1. $RCHO + Cl_2 \longrightarrow RCOCl + HCl$
2. $RCOOH + SOCl_2 \longrightarrow RCOCl + HCl + SO_2$
3. $CH_3COOH + COCl_2 \longrightarrow CH_3COCl + HCl + CO_2$
4. $C_6H_5CCl_3 + H_2O \longrightarrow C_6H_6COCl + 2HCl$
5. $RCOCl + R^1OH \longrightarrow RCOOR^1$
6. $RCOCl + RCOOH \longrightarrow (RCO)_2O$
7. $RCOCl + NH_2R \longrightarrow RCONHR$ R = H, OH, NH_2, RNH
8. $ArCOCl + ArNH_2 \xrightarrow{NaOH} ArCONH–Ar$ (Шоттен-Бауман)

9. $RCOCl + NaN_3 \longrightarrow RCON_3$

10. $RCOCl + Na_2O_2 \longrightarrow RCO–O–O–CO–R$

11. $RCOCl + H_2 \xrightarrow{Pd} RCHO + HCl$ (Розенмунд)

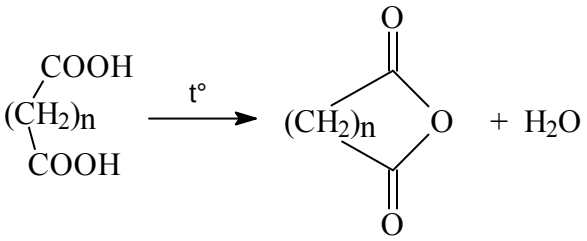
48. Ангидриды кислот

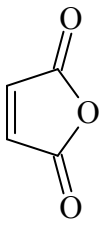
1. $RCOOH + P_2O_5 \xrightarrow{t°} (RCO)_2O$

2. $RCOOH + (CF_3CO)_2O \xrightarrow{t°} (RCO)_2O + CF_3COOH$

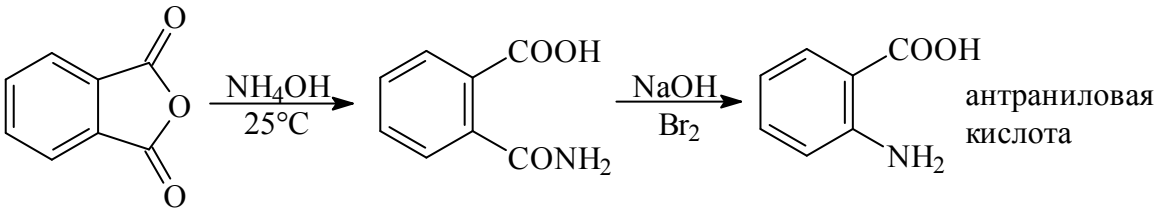
3. $RCOCl + RCOONa \longrightarrow (RCO)_2O$

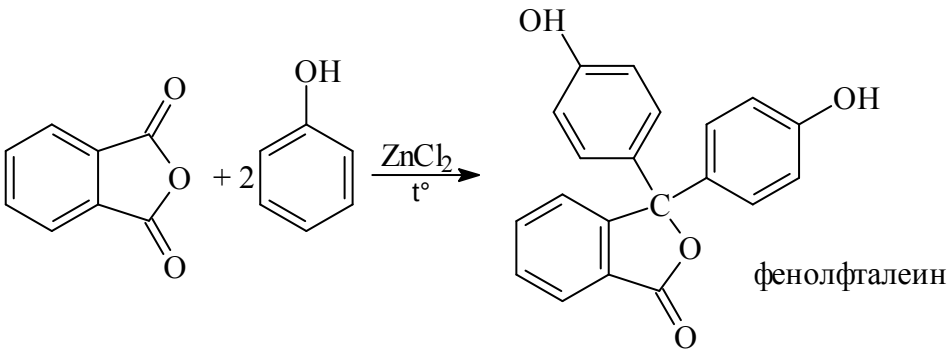
4. $CH_3COOH + CH_2=C=O \longrightarrow (CH_3CO)_2O$

5. 

6. $C_4H_8 + O_2 \xrightarrow{V_2O_5}$ 

7. $ArCHO + (CH_3CO)_2O \xrightarrow{RO^-} \xrightarrow{H_3O^+} ArCH=CHCOOH$ (Перкин)

8. 

9. 

10. $(RCO)_2O + H_2N–Y \longrightarrow RCO–NH–Y$ Y = H, OH, NH_2, NH_3

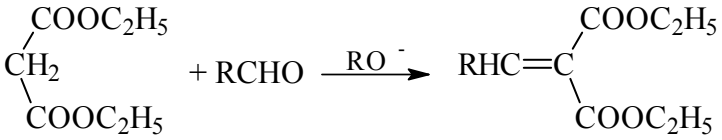
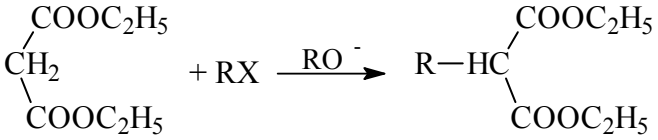
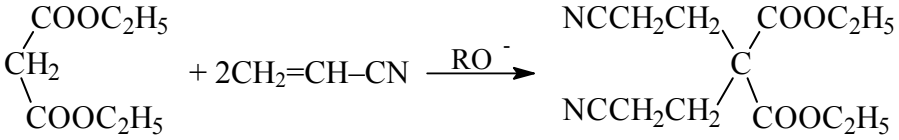
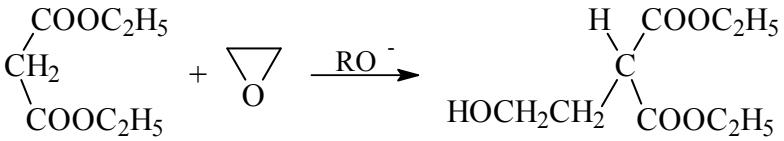
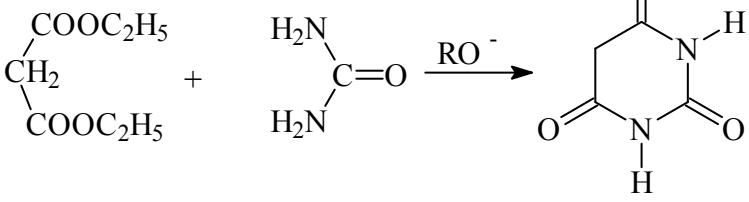
11. $(RCO)_2O + R^1OH \longrightarrow RCOOR^1 + RCOOH$ R^1 = H, R, RCO

49. Сложные эфиры

49.1. Синтезы

1. $RCOX + R^1OH \longrightarrow RCOOR^1 + HX$ X = OH, Hal, RCOO
2. $R_2CO + R^1CO{-}OOH \longrightarrow RCOOR + R^1COOH$ (Байер-Виллигер)
3. $2CH_2{=}CH_2 + O_2 \xrightarrow[P,\ t^\circ]{LiCl + CH_3COOLi} CH_3COO{-}CH{=}CH_2 + H_2O$
4. $RCH_2COOC_2H_2 \xrightarrow{RO^-} RCH_2COCHRCOOC_2H_5$ (Кляйзен)

49.2. Реакции

1. $RCOOC_2H_5 \xrightarrow{LiAlH_4} \xrightarrow{H_3O^+} RCH_2OH + C_2H_5OH$
2. $RCOOC_2H_5 \xrightarrow{Na + C_2H_5OH} \xrightarrow{H_3O^+} RCH_2OH + C_2H_5OH$ (Буво)
3. $RCOOC_2H_5 \xrightarrow{Na} \xrightarrow{H_2O} RC(O){-}CH(R){-}OH$ ацилоиновая конденсация
4. $RCH_2CH_2COCH_3 \xrightarrow{500^\circ C} RCH{=}CH_2 + CH_3COOH$
5. $RCOOR^1 + H_2O \xrightarrow{H^+} RCOOH + R^1OH$
6. $RCOOR^1 + NaOH \xrightarrow{H_2O} RCOONa + R^1OH$
7. $RCOOR^1 + R^2OH \underset{}{\overset{H^+ \text{ или } RO^-}{\rightleftharpoons}} RCOR^2 + R^1OH$
8. $RCOOR^1 + H_2N{-}Z \longrightarrow RCONH{-}Z$ Z = H, OH, NH_2, Ph–NH
9. 
10. 
11.  Михаэль
12. 
13. 
14. $RO{-}C(O){-}C(O){-}OR + CH_3COOR \xrightarrow[2.\ H_3O^+]{1.\ C_2H_5O^-} ROC(O){-}C(O){-}CH_2COOR$

15. $BrZnCH_2COOR + (CH_3)_2CO \longrightarrow \xrightarrow{H_3O^+} (CH_3)_2C(OH)\text{-}CH_2COOR$ (Реформатский)

50. Нитрилы

50.1. Синтезы

1. $RCONH_2 + POCl_3 \longrightarrow R–CN + HPO_2Cl_2 + HCl$
2. $RCOOH + NH_3 \xrightarrow[>300^\circ C]{Al_2O_3} R–CN + 2H_2O$
3. $RCH{=}NOH \xrightarrow{H^+} R–CN + H_2O$
4. $RX + NaCN \longrightarrow R–CN + NaX$ X = Hal, OSO_2R^1
5. $ClCH_2CN + NaCN \longrightarrow CN–CH_2–CN$ малонодинитрил
6. $ArX + CuCN \xrightarrow[t^\circ]{ДМФА} Ar–CN + CuX$
7. $ArN_2X + CuCN \longrightarrow Ar–CN$
8. $ArSO_3Na + NaCN \xrightarrow{t^\circ} Ar–CN$
9. $CH_2{=}CH–CH_3 \xrightarrow{O_2,\ NH_3} CH_2{=}CH–CN$ акрилонитрил
10. $HC{\equiv}CH + HCN \longrightarrow CH_2{=}CH–CN$

50.2. Реакции

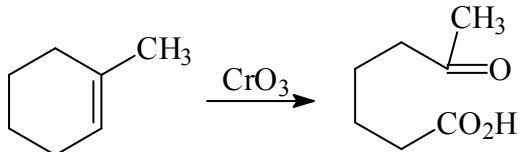
1. $R–CN + H_2O \xrightarrow{H^+ \text{ или } OH^-} RCONH_2$
2. $R–CN + R^1OH + HX \longrightarrow R{-}C(=NH_2X)(-OR^1)$
3. $R–CN + H_2 \xrightarrow{Ni} R–CH_2–NH_2$
4. $R–CN \xrightarrow{LiAlH_4} \xrightarrow{H_2O} RCHO$
5. $CH_2{=}CH–CN + ROH \xrightarrow{RO^-} RO–CH_2–CH_2–CN$ (цианэтилирование)
6. $CH_2{=}CH–CN + RNH_2 \longrightarrow R–NH–CH_2–CH_2–CN$

51. Изонитрилы

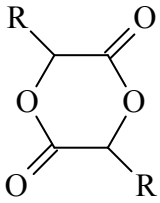
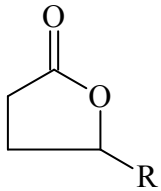
1. $RX + AgCN \longrightarrow R–NC + R–CN$
2. $RNH_2 + CHCl_3 + NaOH \longrightarrow R–NC$
3. $R–NC \xrightarrow{[O]} R–N{=}C{=}O$
4. $R–NC + S \longrightarrow R–N{=}C{=}S$
5. $R–NC + H_2 \xrightarrow{Ni} R–NH–CH_3$
6. $R–NC + H_2O \xrightarrow{H^+} R–NH–CHO$

52. Гидроксикислоты

52.1. Синтезы

1. $HOCH_2CH_2OH \xrightarrow{[O]} HOCH_2COOH$ гликолевая кислота
2. $CH_3CHCl–COOH + H_2O \longrightarrow CH_3CH(OH)–COOH$ молочная кислота
3. $CH_3CH(OH)–CN + H_2O \xrightarrow{H^+} CH_3CH(OH)–COOH$
4. $HOOC–CH=CH–COOH + KMnO_4 + H_2O \longrightarrow HOOC–CH(OH)–CH(OH)–COOH$
5. $C_6H_5ONa + CO_2 \xrightarrow{P,\ t°} 2\text{-}HO–C_6H_4–COONa$
6. $C_6H_5–CO–CO–C_6H_5 + NaOH \longrightarrow (C_6H_5)_2C(OH)–COONa$ бензиловая п-ка
7. $(CH_3)_2CO + BrCH_2COOC_2H_5 \xrightarrow{Zn} \xrightarrow{H_3O^+} (CH_3)_2C(OH)–CH_2COOH$ (Реформатский)
8. 

52.2. Реакции

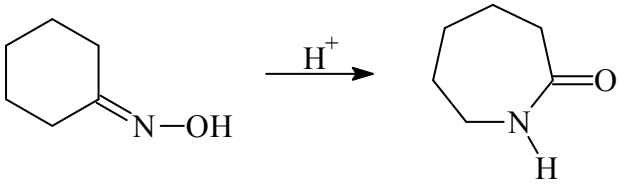
1. $2RCH(OH)–COOH \xrightarrow{H^+}$  лактид
2. $RCH(OH)–CH_2CH_2–COOH \xrightarrow{t°}$  лактон
3. $RCHOH–CHOH–COO^- \xrightarrow[t°]{H_2O_2,\ Fe(III)} RCHOH–CHO$ (Руфф-Фентон)

53. Аминокислоты

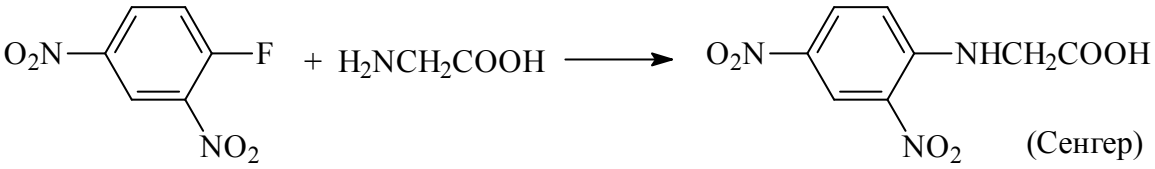
53.1. Синтезы

1. $RCHO + NH_4Cl + NaCN \longrightarrow RCH(NH_2)–CN \xrightarrow{H_3O^+} RCH(NH_2)–COOH$
2. $NH_3 + ClCH_2COOH \longrightarrow H_2N–CH_2–COOH$

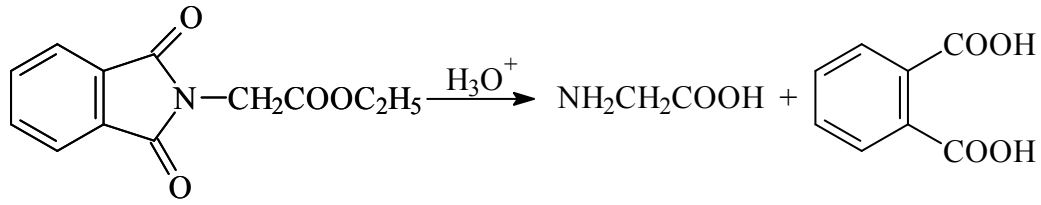
3. $CH_2{=}CH{-}COOH + NH_3 \longrightarrow H_2NCH_2CH_2{-}COOH$

4. 

$H_2N(CH_2)_5COOH$ (Бекман)

5. 

(Сенгер)

6. 

7. $RCHO + R^1CH(COOH)_2 + NH_3 \xrightarrow{t^\circ} RCH(NH_2){-}CR^1(COOH)_2$ (Родионов)

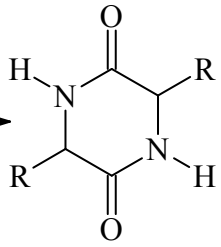
53.2. Реакции

1. $2RCH(NH_2)(CH_2)_nCOOH \xrightarrow{t^\circ} RCH(NH_2){-}(CH_2)_n{-}CONHCHR{-}(CH_2)_n{-}COOH + H_2O$

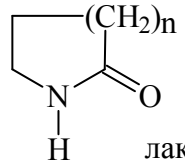
2. $RCH(NH_2)CH_2COOH \xrightarrow{t^\circ} RCH{=}CH{-}COOH + NH_3$

3. $H_2NCH(R){-}COOH \xrightarrow{>200^\circ C} H_2NCH_2R + CO_2$

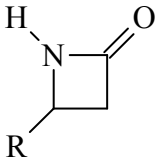
4. $RCH(NH_2){-}COOH \xrightarrow{[HNO_2]} RCH(OH){-}COOH + N_2 + H_2O$

5. $2RCH(NH_2){-}COOH \xrightarrow{t^\circ}$ 

дикетопиперазин

6. $H_2NCH_2(CH_2)_nCOOH \xrightarrow{t°}$  n = 1, 2, 3

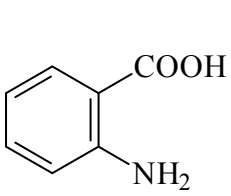
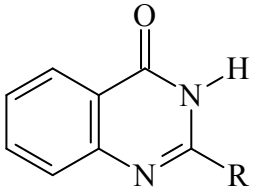
лактам

7. $RCH(NH_2)–CH_2–COOH \xrightarrow{R^1N=C=NR^1}$ 

8. $RCH(NH_2)–COOH \xrightarrow{[O]} RCHO + NH_3 + CO_2$

9. $NH_2–CHR–COOH + C_6H_5–CH_2–O–COCl \longrightarrow C_6H_5–CH_2–O–CO–NH–CHR–COOH$

10. $NH_2–CHR–COOH + (CH_3)_3C–O–CO–N_3 \xrightarrow{MgO} (CH_3)_3C–O–CO–NH–CHR–COOH$

11.  + $RCONH_2 \xrightarrow{120\text{-}130°C}$  (Ниментовский)

54. Оксокислоты

54.1. Синтезы

1. $HO–CH_2–CH_2–OH \xrightarrow{[O]} HOC–COOH$ глиоксиловая кислота

2. $HOOC–COOH \xrightarrow{[H]} HOC–COOH$

3. $Cl_2CHCOOH + H_2O \longrightarrow HOC–COOH$

4. $CH_3COCH_2COOC_2H_5 \xrightarrow{H_3O^+} CH_3COCH_2COOH$ ацетоуксусная кислота

5. $HOOC–CH(OH)–CH(OH)–COOH \xrightarrow{t°} CH_3CO–COOH + CO_2 + H_2O$

6. $RCO–CN \xrightarrow{H_3O^+} RCO–COOH$

54.2. Реакции

1. $CH_3COCH_2COOH \xrightarrow{t°} (CH_3)_2CO + CO_2$

2. $CH_3COCH_2COOH + ROH \xrightarrow{H^+} CH_3COCH_2COOR$

3. $HOOC–CO–CH_2–COOH \xrightarrow{t°} CH_3–CO–COOH + CO_2$

4. $CH_3–CO–COOH \xrightarrow{Ag_2O} CH_3COOH + CO_2$

5. $OHC–COOH \xrightarrow[t°]{H_2O} HOCH_2–COOH + HOOC–COOH$

6. $RCO–COOH \xrightarrow[150° C]{H_2SO_4(разб.)} RCHO + CO_2$

7. $RCO–COOH \xrightarrow[60° C]{H_2SO_4(конц.)} RCOOH + CO$

54.3. Ацетоуксусный эфир

1. $CH_3COOC_2H_5 \xrightarrow{RO^-} CH_3COCH_2COOC_2H_5$

2. $CH_3COCH_2COOC_2H_5 + H_2O \xrightarrow{NaOH\ разб.} (CH_3)_2CO + NaHCO_3 + C_2H_5OH$

3. $CH_3COCH_2COOC_2H_5 \xrightarrow{NaOH\ конц} 2CH_3COONa + C_2H_5OH$

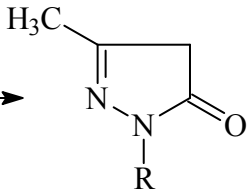
4. $CH_3COCH_2COOC_2H_5 + RNH_2 \longrightarrow CH_3C(NHR)=CH–COOC_2H_5$

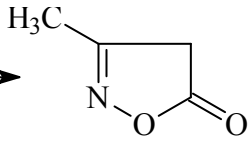
5. $CH_3COCH_2COOC_2H_5 + PCl_5 \longrightarrow CH_3C(Cl)=CH–COOC_2H_5$

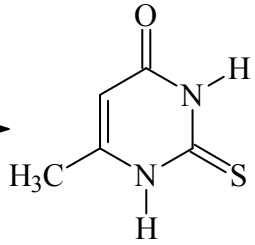
6. $CH_3COCH_2COOC_2H_5 \xrightarrow[CH_3COOH]{NaNO_2} CH_3-CO-\underset{\underset{NOH}{\|}}{C}-COOC_2H_5$

7. $CH_3COCH_2COOC_2H_5 + CH_3COCl \xrightarrow{Py} CH_3-\underset{\underset{OCOCH_3}{|}}{C}=CH-COOC_2H_5$

8. $CH_3COCH_2COOC_2H_5 + RX \xrightarrow{RO^-} CH_3COCHR–COOC_2H_5 +$
$CH_3C(OR)=CHCOOC_2H_5$

9. $CH_3COCH_2COOC_2H_5 + H_2N–NHR \longrightarrow$  $+ C_2H_5OH$

10. $CH_3COCH_2COOC_2H_5 + H_2NOH \longrightarrow$  $+ C_2H_5OH$

11. $CH_3COCH_2COOC_2H_5 + (NH_2)_2C=S \xrightarrow{RO^-}$ 

55. Производные угольной кислоты

55.1. Фосген

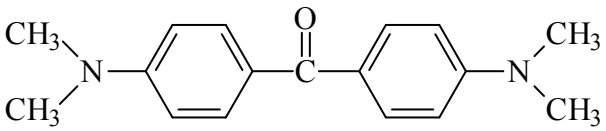
1. $COCl_2 + ROH \longrightarrow RO–CO–Cl \xrightarrow{ROH} RO–CO–OR$

2. $COCl_2 + RNH_2 \longrightarrow [RNH–CO–Cl] \longrightarrow R–N=C=O$

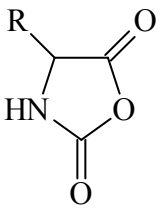
3. $COCl_2 + R_2NH \longrightarrow R_2N–CO–Cl$

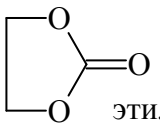
4. $COCl_2 + RLi \longrightarrow R–CO–R$

5. $COCl_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCl$

6. $COCl_2 + C_6H_5N(CH_3)_2 \longrightarrow$ 

кетон Михлера

7. $COCl_2 + RCH(NH_2)–COOH \longrightarrow$  (Фуке)

8. $COCl_2 + HOCH_2CH_2OH \longrightarrow$  этиленкарбонат

55.2. Мочевина и тиомочевина

55.2.1. Синтезы

1. $NH_4OCN \xrightarrow{t^\circ} (NH_2)_2CO$

2. $NH_4SCN \xrightarrow{t^\circ} (NH_2)_2CS$

3. $CaNCN \xrightarrow{HX} H_2N{-}CN \xrightarrow{H_3O^+} (NH_2)_2CO$

4. $2NH_3 + CO_2 \xrightarrow{P,\ t^\circ} (NH_2)_2CO$

5. $RNH{-}CN + H_2O \xrightarrow{H^+} RNH{-}CO{-}NH_2$

6. $COCl_2 + NH_3 \longrightarrow (NH_2)_2CO + NH_4Cl$

7. $RNH_2 + CS_2 \xrightarrow{NH_3} RNH{-}CS{-}NH_2$

55.2.2. Реакции

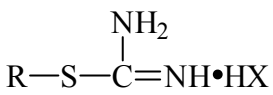
1. $(NH_2)_2CO + 2[HNO_2] \longrightarrow 2N_2 + CO_2 + 3H_2O$

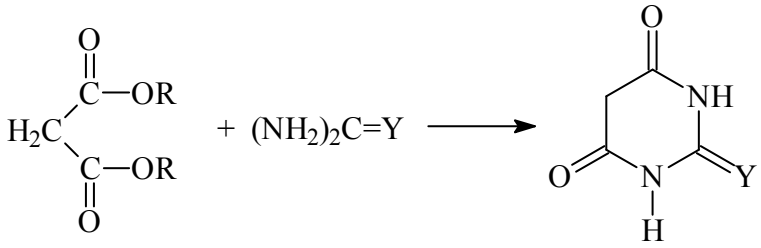
2. $2(NH_2)_2CO \xrightarrow{t^\circ} NH_3 + H_2N{-}CO{-}NH{-}CO{-}NH_2$ биурет

3. $(NH_2)_2CO + RCOCl \longrightarrow RCO{-}NH{-}CO{-}NH_2 + HCl$

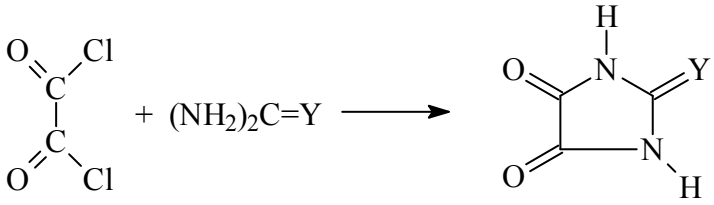
4. $(NH_2)_2CO + RX \longrightarrow R{-}NH{-}CO{-}NH_2 + HX$

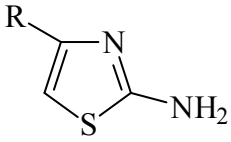
5. $RNH{-}CS{-}NHR + HgO \longrightarrow R{-}N{=}C{=}N{-}R + HgS + H_2O$

6. $(NH_2)_2CS + RX \longrightarrow$  (изотиурониевые соли)

7.  Y = O, S

барбитуровые кислоты

8.  Y = O, S

9. $(NH_2)_2C=S + ClCH_2COR \xrightarrow{H^+}$  (Ганч)

55.3. Изоцианаты

55.3.1. Синтезы

1. $AgOCN + CH_3I \longrightarrow CH_3–N=C=O$

2. $KOCN + RX \longrightarrow R–N=C=O + R–O–CN$

3. $R–NC \xrightarrow{[O]} R–N=C=O$

4. $RCONH_2 \xrightarrow[Br_2]{NaOH} R–N=C=O$

5. $RCON_3 \xrightarrow{t^\circ} R–N=C=O$

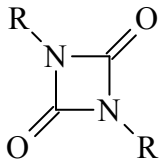
55.3.2. Реакции

1. $R–N=C=O + H_2O \xrightarrow{H^+} R–NH_2 + CO_2$

2. $R–N=C=O + R^1OH \longrightarrow R–NH–CO–O–R^1$ уретаны

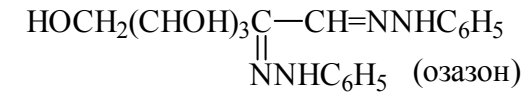
3. $R–N=C=O + R^1NH_2 \longrightarrow R–NH–CO–NH–R^1$

4. $2R–N=C=O + R_3P=O \longrightarrow R–N=C=N–R$ карбодиимиды

5. $2R–N=C=O \rightleftharpoons$ 

56. Углеводы. D-Глюкоза.

1. $HOCH_2\text{-}(CHOH)_4\text{-}CHO + H_2N\text{-}Y \xrightarrow{H^+} HOCH_2\text{-}(CHOH)_4\text{-}CH{=}NY$ Y = OH, C_6H_5NH

2. $HOCH_2(CHOH)_4CHO + 3C_6H_5NHNH_2 \xrightarrow{H^+}$  (озазон)

3. $HOCH_2–(CHOH)_4–CHO + HCN \xrightarrow{H^+} HOCH_2–(CHOH)_5–CN$

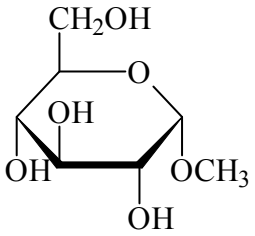
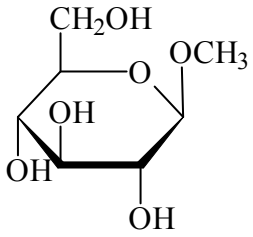
4. $HOCH_2–(CHOH)_4–CHO + Br_2 + H_2O \longrightarrow HOCH_2–(CHOH)_4–COOH$ глюконовая к-та

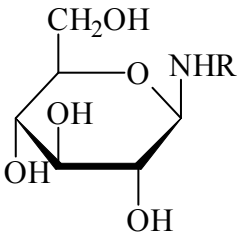
5. $HOCH_2–(CHOH)_4–CHO + HNO_3 \longrightarrow HOOC–(CHOH)_4–COOH$ гликаровая к-та

6. $HOCH_2–(CHOH)_4–CHO \xrightarrow{NaIO_4} HCHO + 5HCOOH$

7. $HOCH_2–(CHOH)_4–CHO + H_2 \xrightarrow{Ni} HOCH_2–(CHOH)_4–CH_2OH$ сорбит

8. $HOCH_2–(CHOH)_4–CHO \xrightarrow{(CH_3CO)_2O} C_6H_7O(OCOCH_3)_5$

9. $HOCH_2–(CHOH)_4–CHO \xrightarrow[HCl]{CH_3OH}$  + 

10. $HOCH_2–(CHOH)_4–CHO \xrightarrow[t°]{RNH_2}$ 

11. $HOCH_2–(CHOH)_4–CHO \xrightarrow[H^+]{RSH} HOCH_2–(CHOH)_4–CH(SR)_2$

ЛИТЕРАТУРА

1. Терней А. Современная органическая химия. - М.: Мир, 1981.-Т.1.-678с;Т.2.-651с.
2. Моррисон Р., Бойд Р. Органическая химия. - М.: Мир, 1974.-1132с.
3. Нейланд О. Я. Органическая химия. - М.: Высш. шк., 1990.-751с.
4. Шабаров Ю. С. Органическая химия. - М.: Химия, 1994.-Ч.1,2.-847с.
5. Робертс Дж., Касерио М. Основы органической химии. -М.: Мир, 1978.-Т.1.-842с;Т.2.-888с.
6. Несмеянов А. Н., Несмеянов Н. А. Начала органической химии. -М.: Химия, 1969.-Кн.1.-661с;Кн.2.-824с.
7. Гауптман З., Грефе Ю. Г., Ремане Х. Органическая химия. - М.: Химия, 1979.-463с.
8. Марч Дж. Органическая химия. - М.: Мир. 1988.-Т.1.-381с;Т.2.-504с;Т.3.-459с; Т.4.-468с.
9. Кери Ф., Сандберг Р. Углубленный курс органической химии. -М.: Химия, 1981.-Кн.1.-519с;Кн.2.-455с.
10. Матье Ж., Панико Р. Курс теоретических основ органической химии. -М.: Мир,1975.-556с.
11. Мищенко Г. Л., Вацуро К. В. Синтетические методы органической химии. -М.: Химия, 1982. -440с.
12. Вацуро К. В., Мищенко Г. Л. Именные реакции в органической химии. -М.: Химия, 1976. -528с.
13. Яновская Л. А., Юфит С. С. Органический синтез в двухфазных системах. -М.: Химия, 1982. -184с.

Автор с благодарностью примет замечания и просит их выслать по адресу:
454021, Челябинск, ул. Бр. Кашириных 129, ЧелГУ, химфак, Киму Д. Г.
E-mail: kim@csu.ru

УСЛОВНЫЕ СОКРАЩЕНИЯ И ОБОЗНАЧЕНИЯ

Адоген 464	триалкил(C_8-C_{10})метиламмонийхлорид
Аликват 336	метилтриоктиламмонийхлорид
БТМАХ	бензилтриметиламмонийхлорид
ТБАБ	тетрабутиламмонийбромод
ТБАХ	тетрабутиламмонийхлорид
ТБГДФБ	трибутилгексадецилфосфонийбромид
ТЭБАХ	триэтилбензиламмонийхлорид
ДМФА	диметилформамид
ДМСО	диметилсульфоксид
ГМФТА	гексаметилфосфотриамид
ТЭА	триэтиламин
Py	пиридин
Ac_2O	уксусный ангидрид
Ac	ацетил
Ar	арил
Alk	алкил
t-Bu	*трет*-бутил, $(CH_3)_3C–$
Bn	бензил, $C_6H_5CH_2–$
Bz	бензоил, $C_6H_5CO–$
Ph	фенил
Ts	тозил, 4-$CH_3–C_6H_4–SO_2–$
E	электрофил
Nu	нуклеофил
B:	основание Льюиса
	знак резонанса
	смещение электронной пары
t°, Δ	при нагревании
P	при повышенном давлении
kat.	катализатор
МФК	межфазный катализ
п-ка	перегруппировка

ОГЛАВЛЕНИЕ