Dimerization and Oligomerization by Dehydrogenation as a General Synthetic Principle (1) Part III

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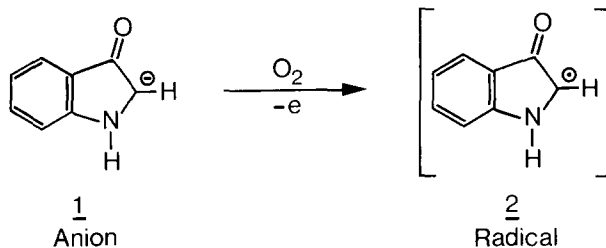
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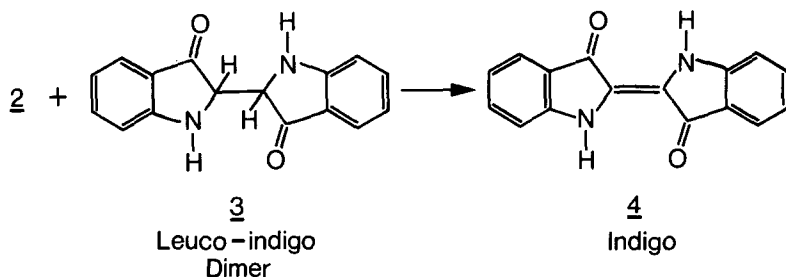
Dedicated to Professor Dr. Matthias Seefelder on the occasion of his 60th birthday

Summary

Capto-dative substituents determine the ease of selective hydrogen abstraction, but steric factors and the nature of the dehydrogenating agent influence the relative "radical scale" . This study underlines the value of preparative work in dehydrodimerizations. The method also allows the preparation of oligomers and polymers.

The well-known synthesis of indigo 4 via 3-hydroxy-indole 1, 2 and leucoindigo is a classic example for the dehydrodimerization of aromatic compounds (1a) .


$$\begin{array}{ccc} \underline{1} & & \underline{2} \\ \text{Anion} & & \text{Radical} \end{array}$$

$\underline{3}$
Leuco-indigo
Dimer

$\underline{4}$
Indigo

Korshak's work first revealed the possibility of building up systems with high molecular weights $\underline{6}$ via diisopropylbenzene - again by dehydrogenation with C - C bonding (2) .
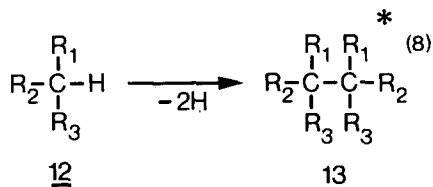

$\underline{5}$

$\underline{6}$
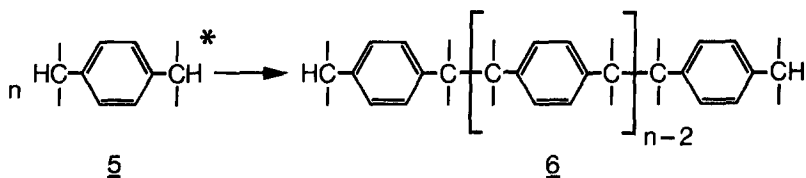
This reaction is not restricted to aromatic compounds containing isopropyl groups but can also be brought about by ,for example, aromatic compounds containing sec-butyl or cyclohexyl groups (3). Another interesting example of C - C bonding accompanied by quinone formation is the dimerization of octadecyl-3 (3,5-di-t-butyl-4-hydroxyphenyl) propionate $\underline{7}$ to $\underline{8}$ (4)

$\underline{7}$

$\underline{8}$
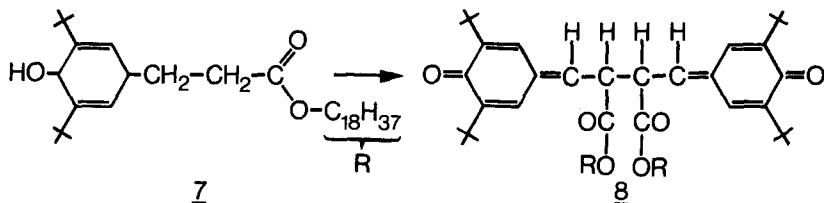
Fe^{+++}-catalyzed dehydrodimerization of phenols leads to the following dimers.

(5) (6) (7)

9 **10** **11**
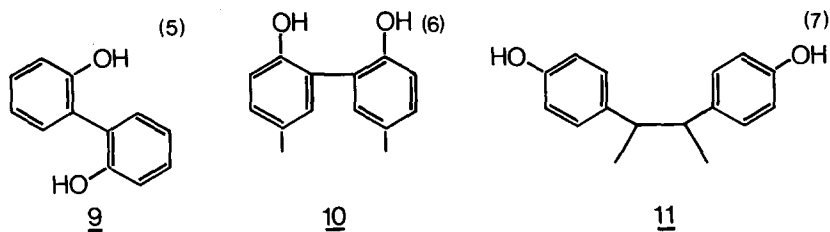
C - C bonds are preferentially brought about by metal
catalysts (MnO$_2$, Ag$_2$O & Cu$^+$/O$_2$) in systems of the $\underline{12}$
and $\underline{13}$ types.

$$R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{C}}-H \quad \xrightarrow{-2H} \quad R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{C}}-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{C}}-R_2 \qquad \overset{*}{} \quad (8)$$

$\underline{12}$ $\underline{13}$

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*If the p-substituted form of $\underline{5}$ is taken, $\underline{6}$ is a solid;
 and if the m-isomer is taken, $\underline{6}$ is a viscous liquid.

If the starting materials are bifunctional derivatives,
e.g., $\underline{14}$, this reaction allows high-molecular-weight
components of the $\underline{15}$ type to be obtained.

$\underline{14}$ $\underline{15}$
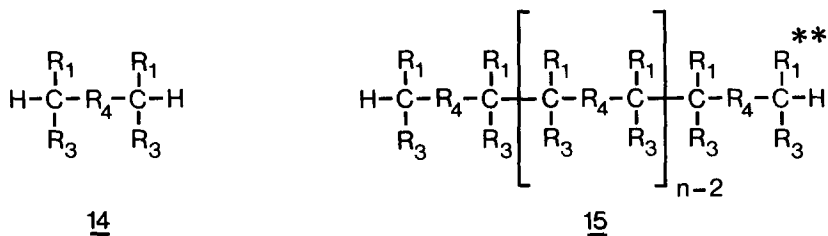
***R$_1$ = alkyl, aryl, -CO-C$_6$H$_5$, -CH$_2$-C$_6$H$_5$, CN
 R$_2$ = -COOR-, aryl,
 R$_3$ = H, COOR
 R$_4$

[+]On heating at about 200 $^{\circ}$C upwards; cleavage of the
C - C bond and the formation of diradicals

Particular attention is attracted by polyaromatic com-
pounds that can be obtained by oxidative coupling. The
first publication on this reaction was by P. Kovacic
et al (9). In the presence of $AlCl_3$, benzene is co-
ordinated and is converted with $CuCl_2$ into a poly-
phenylene.

16
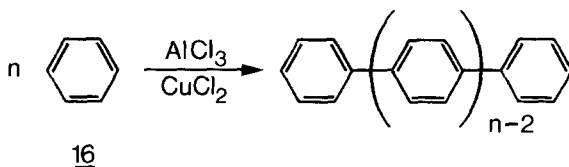
This type of reaction has been systematically studied
and has been adopted as a general principle for the
synthesis of polyaromatic compounds (10). A property
of these substances is that they are conductors of
electricity (11). Thus, by this means, not only benzene
but also other aromatic compounds, e.g., biphenyl,
terphenyl, naphthalene, anthracene, chrysene and tri-
phenylene, and also heterocyclic compounds, e.g.,
thiophene, pyrrole and quinodine, and even phthalo-
cyanines and ferrocene can enter into oxidative coup-
ling reactions.

Polyaromatic compounds deserve considerable interest,
because of their conductivity and because their conduc-
tivity can be drastically increased, e.g., from 10^{-6}
to 10^{+2} S/cm, by doping with Lewis acids (e.g., SbF_5
and $AlBr_3$) or with alkali metals (Na).

The degree of condensation n is determined by terminal
group analyses:
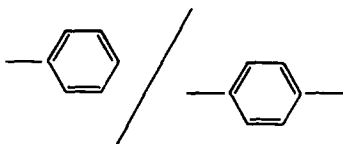
It can be adjusted by varying the coupling conditions,
i.e., the temperature, time and the amount of catalyst.
As n increases, the colour intensifies,

and the conductivity increases[+]. Examples are as follows.

a) n   10, pale product, conductivity 10^{-10} S/m, reaction temperature 30 °C

b) n   40, brown-black product, conductivity 10^{-3} S/m, reaction temperature 250 °C .

The polyaromatic compounds obtained are stable to heat (loss in weight on heating for one hour at 300 °C in air: less than 1 % wt); they are very brittle and can be processed by press sintering .

If biphenyl is taken instead of benzene and the reaction conditions are otherwise identical (b), the polymers obtained are much more stable to oxidation. Thus, if a polyphenylene with about 20 phenylene units (prepared from benzene[++]) is heated for one hour at 190 °C in oxygen, the oxygen content of the specimen will be 10.5 %. On the other hand, if a polyphenylene with about 20 phenylene units (prepared from biphenyl) is produced and oxidized under identical conditions, the oxygen content of the specimen will be less than 0.5 % . The greater stability to oxygen can be ascribed to a much more uniform p-p' structure in the sense of an ideal rod. If benzene is taken as the starting material for the oxidative coupling, branches occur in the o- and m- positions and yield carboxyl and carbonyl groups during oxidation.

The mechanism proposed for the oxidative polymerization of aromatic hydrocarbons is shown below (Eqns. 1 - 3). As has already been stated, other aromatic compounds may be taken instead of benzene; and other oxidizing agents, instead of $CuCl_2$, e.g., Pd^{2+}, Fe^{3+}, Pb^{4+}, etc.

In general, substituted aromatic compounds (toluene, ethylbenzene, etc.) yield soluble polymers with molecular masses of up to 5000 in this type of reaction. On the other hand, benzene, biphenyl, terphenyl, etc. yield insoluble products with molecular masses of about 3500, corresponding to about 45 phenylene units

16   16a   16b

16a + 16b → 17 + 16 → 18

18 − H⊕ → 19

19 − H $\xrightarrow[\text{AlCl}_3]{\text{CuCl}_2}$
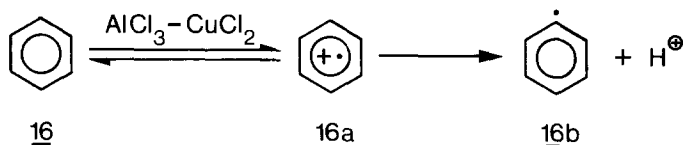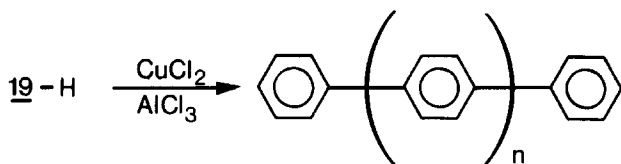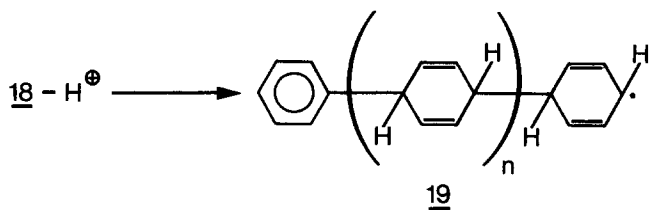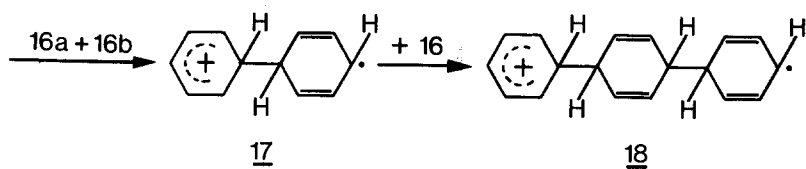
++ Reaction time one hour in each case, $AlCl_3$ or $CuCl_2$ each 25 % wt, expressed in terms of benzene amount[2] used

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1a cf. 1, Part I. This concerns an aromatic system condensed at the 5th and 6th rings according to the general scheme outlined in this work

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