Mechanism of Oxidative Dimerization of Aminobenzenes[1]

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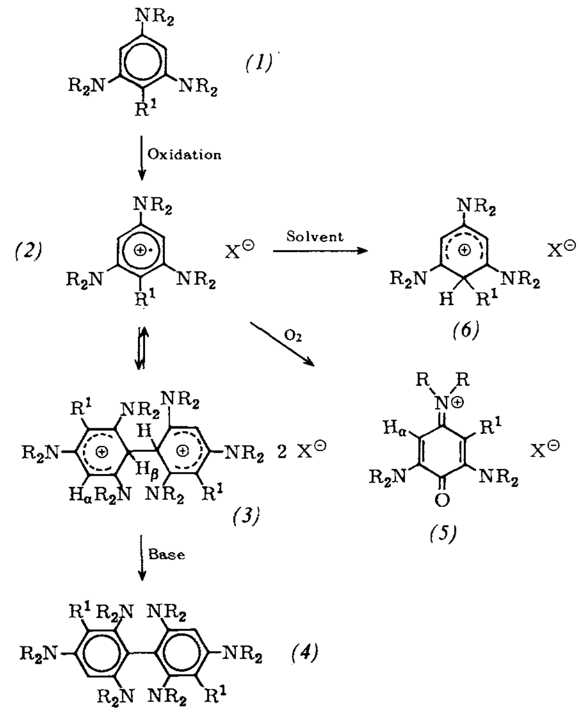
Compounds of type *(3)*, which hitherto have not been isolated[2], are postulated as intermediates in the oxidative dimerization of *N,N*-disubstituted anilines.

We have been able to prepare the red σ-complexes *(3)* in the crystalline state [UV absorption of *(3a)* in C_2H_5OH: $\lambda_{max} = 431$ nm, $\varepsilon = 12800$; $\lambda_{max} = 346$ nm, $\varepsilon = 41000$] by oxidation of symmetrical triaminobenzenes *(1)*[3]; on reaction with bases, these complexes afford the hexaaminobiphenyls *(4)*.



	–R–R–	R^1	X	*(3)* M.p. (°C)	*(3)* Yield (%)	*(5)* M.p. (°C)	*(5)* Yield (%)
(a)	$-(CH_2)_4-$	H	CBr_5	177–178	33	—	—
(b)	$-(CH_2)_4-$	H	ClO_4	254–256	91	200 to 201	93
(c)	$-(CH_2)_4-$	CH_3	ClO_4	158–159	82	—	—
(d)	$-(CH_2)_4-$	C_2H_5	ClO_4	123–127	96	—	—
(e)	$-(CH_2)_5-$	H	ClO_4	215–216	56	—	—
(f)	$-(CH_2)_2-O-(CH_2)_2-$	H	I_3	140–145	2.5	—	—

The oxidation was carried out at room temperature with silver salts in dimethylformamide and with tetrahalogenomethanes, cyanogen halides, or halogens in dichloromethane. The salts *(3)*, whose structure has been established by elemental analysis, molecular-weight determinations and ^1H-NMR spectra [*(3b)* in liquid SO_2: H_α = singlet at $\tau = 5.03$, H_β = singlet at $\tau = 5.67$] are obtained in good yields.

Noteworthy is the occurrence of a stable CBr_5 anion in the reaction of 1,3,5-tripyrrolidinobenzene with CBr_4 in dichloromethane. No CBr_4 is liberated from *(3a)* by extraction with ether for several days. Compound *(3a)* is formed smoothly from *(3b)* by treatment with alcoholic sodium perchlorate solution. The structure of $CBR_5^{\ominus}$ is at present being investigated.

On warming or on being allowed to stand in polar solvents the dimers *(3)* dissociate into the radical cations *(2)*, which abstract H from the solvent to form compounds *(6)*[4,5]. The tendency to dissociate is far greater in the case of the alkyl-substituted derivatives *(3c)* and *(3d)* than in the case of *(3b)*.

The radical cations *(2)*, which are obviously not very stable, cannot be detected by ESR spectroscopy[6]. Evidence of their intermediate formation is, for example, formation of a green salt in the oxidation of *(1)*, R—R = $(CH_2)_4$, $R^1 = H$, in the presence of atmospheric oxygen to which we ascribe the structure *(5)* on the basis of elemental analysis, molecular-weight determination, and spectroscopic data [UV absorption in CH_3OH: $\lambda_{max} = 627$ nm, $\varepsilon = 3300$, $\lambda_{max} = 431$ nm, $\varepsilon = 10680$; ^1H-NMR spectrum in $CDCl_3$: H_α = singlet at $\tau = 4.69$; IR absorption: $\nu(C{=}O) = 1700\ cm^{-1}$. Chemical proof of the structure of *(5)* has yet to be carried out.

Experimental:

a) *1,1'-Bi(2,4,6-tripyrrolidinocyclohexadienylium) pentabromocarbonate (3a)*

CBr_4 (19.9 g) is added to a solution of 1,3,5-tripyrrolidinobenzene (8.56 g) in dichloromethane (50 ml) cooled to −5 °C. The reaction mixture immediately turns deep red. The solvent is subsequently distilled off under vacuum, and the oily residue is dissolved in 30 ml of hot chloroform and filtered. After a short time 6.8 g (33 %) of brick-red crystals, m.p. 176—177 °C, precipitate, which can be recrystallized (m.p. 177—178 °C) from chloroform.

b) *1,1'-Bi(2,4,6-tripyrrolidinocyclohexadienylium) perchlorate (3b)*

Pulverized $AgNO_3$ (1.7 g) is added with stirring to a suspension of 1,3,5-tripyrrolidinobenzene (2.85 g) in dimethylformamide (15 ml) under pure nitrogen at −5 °C. The deep-red reaction mixture is stirred for 10 min, filtered, and the filtrate added dropwise to 100 ml of ether. An oil separates which crystallizes on rubbing. The crystalline paste is filtered by suction, and the recovered solids are dissolved in 100 ml methanol and treated with 20 ml of a saturated aqueous $NaClO_4$ solution. Compound *(3b)* precipitates as brick-red crystals (yield 3.5 g (91 %); m.p. 254—256 °C).

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