

	R	R'	Hal
(a)	—(CH <sub>2</sub> ) <sub>4</sub> —		Br
(b)	CH <sub>3</sub>	CH <sub>3</sub>	Br
(c)	—(CH <sub>2</sub> ) <sub>5</sub> —		Br
(d)	—(CH <sub>2</sub> ) <sub>2</sub> —O—(CH <sub>2</sub> ) <sub>2</sub> —		Br
(e)	—(CH <sub>2</sub> ) <sub>4</sub> —		Cl
(f)	CH <sub>3</sub>	CH <sub>3</sub>	Cl

can be detected by NMR spectroscopy but may be isolated only with the less nucleophilic tetrafluoroborate as gegenion. By anion exchange with AgBF<sub>4</sub>, all the halides (2a) to (2f) are converted to the tetrafluoroborates, which, as expected, are more stable, and thus better suited for further investigations. The structure of the  $\sigma$ -complexes (2) has been unequivocally established both by chemical reactions and spectroscopically; some characteristic NMR and UV data are given in Table 1.

### $\sigma$ -Complexes in Halogenation of Aminobenzenes— Isolation and Secondary Reactions<sup>[1]</sup>

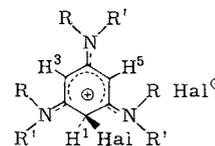
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$\sigma$ -Complex intermediates in electrophilic aromatic substitution have so far been established only for protonation and alkylation<sup>[2, 2a]</sup>. Due to exceptional mesomeric stabilization, they can be isolated in the case of protonation and alkylation of 1,3,5-tripyrrolidinobenzene<sup>[3a, b]</sup>.

The primary isotope effect found in bromination of 1,3,5-tri-*tert*-butylbenzene<sup>[4]</sup> and the observation that bromination of *N,N*-dialkylanilines is reversible even below 100°C<sup>[5]</sup> clearly indicate long-lived halo  $\sigma$ -complex intermediates in these cases. Steric factors are held responsible for the additional stabilization in the first instance, electronic influences in the second example. The intermediate identified NMR-spectroscopically for the bromination of 2-hydroxynaphthalene-6,8-disulfonic acid, however, is no  $\sigma$ -complex but rather the tautomeric quinonoid form<sup>[6]</sup>; corresponding quinonoid intermediates have been isolated from the bromination of sterically hindered phenols<sup>[7]</sup>.

If bromine is added to tris(dialkylamino)benzenes (1) in dry chloroform at -60°C, deep-red colored solutions are formed from which the dark-red  $\sigma$ -complexes may be precipitated by addition of ether. While (2a) and (2b) are stable for some time at ambient temperature, (2c) and (2d) rearrange to give the *N*-protonated aminobromobenzenes (3c) and (3d) respectively. When the aminobenzenes (1) are chlorinated with sulfuryl chloride or chlorine under like conditions, (2e) is obtained in crystalline form; (2f)

Table 1. <sup>1</sup>H-NMR and UV-spectroscopic data of halogen  $\sigma$ -complexes (2a) to (2f).



	<sup>1</sup> H-NMR data [a]		UV absorption bands (in CHCl <sub>3</sub> )		
	H <sup>1</sup>	H <sup>3,5</sup>	$\lambda_{max}$ [nm] ( $\epsilon$ )		
(2a)	6.12	4.8	250 (16200), 360 (14300), 490 (4600)		
(2b)	5.78	4.99	250 (12900), 355 (10500), 484 (3600)		
(2c)	5.92	5.28	256 (13900), 368 (9300), 488 (3000) [b]		
(2d)	6.44	5.61	250 (18800), 365 (14200), 488 (5500) [b]		
(2e)	6.13	4.79	250 (13200), 348 (13900), 466 (6100)		
(2f)	5.88	5.01			

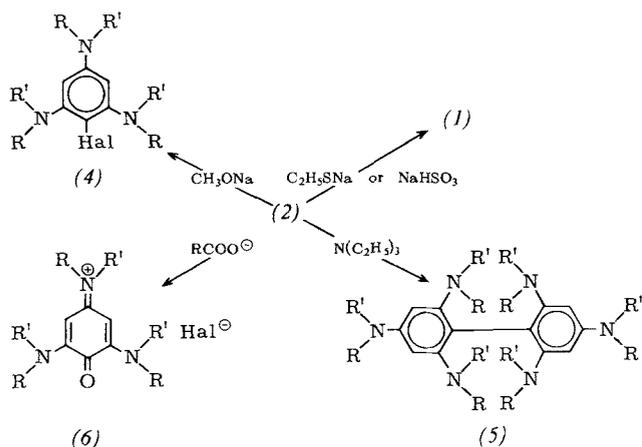
[a]  $\delta$  values (ppm) relative to TMS als internal standard. Solution: 0.5 M in CDCl<sub>3</sub>.

[b] UV spectrum of the tetrafluoroborate.

The  $\sigma$ -complexes formed as intermediates in normal arene halogenation suffer immediate deprotonation. Since we isolate the  $\sigma$ -complexes (2) in crystalline form, the secondary reactions can be directed along different routes. Deprotonation to give the halobenzenes (4) is the course taken with strong bases while highly nucleophilic or reducing agents cleave off a halogen cation thus re-forming (1). Tertiary amines produce the biphenyls (5) from (2a) and (2b), most likely *via* radical intermediates. These biphenyls are also formed when (1) is treated with iodine or iodine chloride under the reaction conditions described. From

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the reaction of (2) with carboxylate ions, quinone iminium salts (6) are isolated besides (1). We have ascertained that these compounds do not arise from interaction with atmo-



spheric oxygen. However, as to whether highly reactive cyclohexadienylium dications are precursors for the formation of (6) or whether the  $\sigma$ -complexes (2) are oxidized to (6) by carbonic acid hypohalites that are formed as intermediates, has yet to be investigated.

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[1] Electrophilic Substitution of Aromatic Compounds, Part 6.—Part 5: P. Fischer, W. Kurtz, and F. Effenberger, *Chem. Ber.*, in print.—For support of this work, we are indebted to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. We also thank W. Kinza, K. Hermann, and G. Pilidis for some of the experiments.

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[2a] Note added in proof: Olah *et al.* [*J. Amer. Chem. Soc.* 94, 3667 (1972)] now report the detection by NMR of  $\sigma$ -complexes for nitration and chlorination of persubstituted benzenes where follow-up reaction to give the substitution product is not possible.

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