607. *Aromatic Reactivity. Part VI.* Desilylations of α- and β-Trimethylsilylnaphthalene.*

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We have measured the rates of proto- and bromo-desilylation of α- and β-trimethylsilylnaphthalene and of mercuridesilylation of the latter. The results are compared with those for nitration and deuteration of naphthalene. In these electrophilic aromatic substitutions the α- is more reactive than the β-position, but particularly so in the desilylations because of steric acceleration.

We have examined the reactivity of α- and β-trimethylsilylnaphthalene in protodesilylation [1,2] and bromodesilylation [3] and of the β-isomer in mercuridesilylation (reactions which are electrophilic aromatic substitutions [1-4]). The results are given in the Table as the rate of reaction, *f*, relative to that of phenyltrimethylsilane. Partial rate factors are also given for the α- and the β-positions of naphthalene in nitration in acetic anhydride,[5] and in deuteration in the medium $CF_3\cdot CO_2H-H_2SO_4-CCl_4$.[6] Effects of *o*- and *p*-methyl groups are included for comparison.

Reaction	α-$C_{10}H_7$	β-$C_{10}H_7$	*o*-Me	*p*-Me	$\frac{\log f_p^{Me}}{\log f_\beta}$	$\frac{\log f_\alpha}{\log f_\beta}$	Notes
Protodesiln.	8·1	2·16	18	21	3·96	2·72	(*a*)
Bromodesiln.	196	12·5	82	49	1·54	2·09	(*b*)
Mercuridesiln.	—	2·9	—	17·5	2·69	—	
Nitration	550	54	42	58	1·02	1·58	(*c*)
Deuteration	178	24	350	350	1·84	1·63	(*d*)

(*a*) Data for tolyl compounds are from ref. 1. (*b*) Figures for the tolyl compounds are from ref. 3 and from unpublished work by D. E. Webster. (*c*) Figures for naphthalene are calculated from data in ref. 5, and figures for toluene are from Cohn, Hughes, and Ingold (*Nature*, 1952, **169**, 291). (*d*) Data for naphthalene are from ref. 6; data for toluene actually refer to de-deuteration in $CF_3\cdot CO_2H-H_2SO_4$ (Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309).

In all cases the α- is more reactive than the β-position. The β-position is less reactive than the *para*-position of the corresponding diphenyls in all three desilylations and in deuteration. (The partial rate factors for the *para*-position of diphenyl are 3·5 in protodesilylation,[1] 12·5 in bromodesilylation,[2] 3·3 in mercuridesilylation,[7] and 37 in deuteration [6].) This is in accord with calculations by the self-consistent-field method of the energy required to convert the hydrocarbon ArH into its conjugate acid ArH_2^+ [6] (which represents a reasonable approximation to the transition state in electrophilic aromatic substitutions) and with calculations of atom localization energies.[5] In nitration the β-position of naphthalene appears to be more reactive than the *para*-position of diphenyl, for which a partial rate factor of 11 has been calculated [8] from Dewar, Mole, and Warford's data.[5] However, the nitration figures, based on difficult competitive studies, may be inaccurate, and another study of the nitration of diphenyl under similar conditions gave a factor of 38 for the *para*-position.[9]

For each reaction, activation of the β-position, f_β, is compared with activation by a *p*-Me group f_p^{Me}, by means of the ratio $(\log f_p^{Me})/(\log f_\beta)$ (which is equivalent to examining

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* Part V, preceding paper.

[1] Eaborn, *J.*, 1956, 4858.

[2] Deans and Eaborn, *J.*, 1959, 2299.

[3] Eaborn and Webster, *J.*, 1957, 4449.

[4] Benkeser, Hoke, and Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5294.

[5] Dewar, Mole, and Warford, *J.*, 1956, 3576, 3581.

[6] Dallinga, Verrijn Stuart, Smit, and Mackor, *Z. Elektrochem.*, 1957, **61**, 1019.

[7] Deans, Eaborn, and Webster, preceding paper.

[8] de la Mare and Hassan, *J.*, 1957, 3004.

[9] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196.

substituent effects on the activation free energy of the reaction). The ratio varies considerably, and if, as seems to be the case,[10] the effect of a *p*-Me group can be reasonably represented by a single (electrophilic) substituent constant, σ^+,[11] then activation of the β-position of naphthalene cannot be so represented. Within the group of desilylations the ratio $(\log f_p^{\text{Me}})/(\log f_\beta)$ is lowest for bromodesilylation, probably because the neutral reagent, with its greater electron-demands, calls forth the electromeric effect of the activating ring more strongly than do the positive reagents in proto- and mercuri-desilylation.[8,12]

Activation of the α-position relative to the β-position, as measured by the ratio $(\log f_\alpha)/(\log f_\beta)$, is greater in desilylations than in the other reactions. This is because there is steric acceleration of desilylations at the α-position, interference between the α-Me_3Si group and the *peri*-hydrogen atom being relieved in a transition state in which the disposition of the bonds to the α-carbon atom approximates to tetrahedral. It is interesting to note that the abnormally low reactivity of 2-trimethylsilyldiphenyl in bromodesilylation [7] is not reflected in the reactivity of α-trimethylsilylnaphthalene in this reaction. For the diphenyl compound the effect was tentatively attributed to an unfavourable entropy effect on passing to the transition state,[7] and such effects do not arise with the naphthalene compound for which the rigidity of the molecule does not differ much in the ground state and the transition state.

EXPERIMENTAL

α-Trimethylsilylnaphthalene was prepared from trimethylchlorosilane, α-chloronaphthalene, and sodium in boiling toluene. Fractional distillation gave material of b. p. 162°/30 mm., n_D^{20} 1·5812.

The β-isomer, b. p. 164·5/37 mm., n_D^{20} 1·5736, was prepared analogously.

Protodesilylation was studied, as previously described,[1] in a mixture of 5 vol. of a methanolic solution of the organosilane (0·00052M for the naphthalene compounds and 0·014M for phenyltrimethylsilane) and 2 vol. of 9·16M-perchloric acid at 50·0°. Reactions were studied at wavelengths of 231 and 264 mμ for phenyltrimethylsilane, 297 and 299 mμ for the α-naphthyl compound, and 292 and 239 mμ for the β-isomer. Isosbestic points of 262·5 and 240·2 mμ (α-isomer) and 286 and 246 mμ (β-isomer) were used to check the stability of the system (see ref. 1). First-order rate constants of 0·0145, 0·0039, and 0·000180 min.$^{-1}$ were found for the α-isomer, β-isomer, and phenyltrimethylsilane, respectively.

The bromodesilylations were examined in acetic acid containing 1·5 wt.-% of water at 25·0° as previously described.[3]

Mercuridesilylations involved mercuric acetate in acetic acid containing 20 wt.-% of water at 25·0°. Details will be published later.

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[10] Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6992; Nelson, *J. Org. Chem.*, 1956, **21**, 145; Lauer, Matson, and Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6433.

[11] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[12] de la Mare and Harvey, *J.*, 1956, 36; 1957, 131.