Tetrahedron Letters No. 13, pp. 421-424, 1961. Pergamon Press Ltd. Printed
in Great Britain.

STRUCTURAL EFFECTS IN ELECTROPHILIC ALIPHATIC SUBSTITUTION REACTIONS OF ORGANOSILANES[1]

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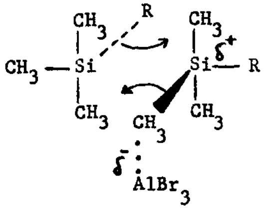
(Received 29 June 1961)

THE metal halide-catalyzed disproportionation of substituted tetraalkyl-

$$2\ RSi(CH_3)_3 \xrightarrow{Al_2Br_6} Si(CH_3)_4 + R_2Si(CH_3)_2$$

silanes is considered to involve electrophilic substitution on carbon and nucleophilic substitution on silicon.[2] The transition state is pictured as:



We have measured the initial rates of the forward step in the disproportionation of a number of alkyltrimethylsilanes in benzene solution at 40° by methods described previously.[2] Table 1 lists the relative rates of reaction observed for identical concentrations of reactants. In Table 1 the relative rates of a typical nucleophilic substitution ($R\text{-}I + I^{*-} \rightarrow R\text{-}I^{*} + I^{-}$) are also

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[1] Research sponsored by the National Science Foundation.

[2] G.A. Russell, J.Amer.Chem.Soc. 81, 4815, 4825, 4831 (1959).

given for comparison.[3]

TABLE 1

Relative Rates of Nucleophilic and Electrophilic Substitutions

R	Disproportionation of silanes at 40°*	Rate of iodide exchange**
allyl	71	42
ethyl	1.00	1.00
n-propyl	0.61	0.63
isopropyl	0.0048	0.038
n-butyl	0.15	0.42
isobutyl	0.025	0.059
cyclopentyl	0.059	0.046
cyclohexyl	0.0021	0.000007***

* 3.3 mmoles of silane, 1.8 mmoles of Al_2Br_6 in 5 ml of benzene (at 10°).

** Iodide exchange of RI in ethanol at 40°.

*** Extrapolated.

The similarity of structural effects in nucleophilic and electrophilic attack upon simple alkyl groups is obvious from Table 1. Fig. 1 demonstrates a more quantitative relationship. It seems unlikely that such a relationship could result from electrical effects since it might be expected that inductive effects would operate in opposite directions in S_N2 and S_Ei processes.[4]

Although transition states in S_N2 and S_Ei reactions have quite different geometry, with inversion of configuration in the S_N2 process and retention in S_Ei or S_E2,[5] it would appear that the data of Table 1 are best explained by

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[3] H.A.C. McKay, J.Amer.Chem.Soc. 65, 702 (1943); H.Seelig and D.E. Hull, Ibid. 64, 940 (1942); S.F. Van Straten, R.V.V. Nicholls and C.A. Winkler, Canad.J.Chem. 29, 372 (1951); S. May, P. Daudel, J. Schottey, M. Sarraf and A. Vobaure, C.R.Acad.Sci.,Paris 232, 727 (1951).

[4] E.D. Hughes and C.K. Ingold, J.Chem.Soc. 244 (1935).

[5] S. Winstein, T.G. Traylor and C.S. Garner, J.Amer.Chem.Soc. 77, 3741 (1955); F.R. Jensen and L.H. Gale, Ibid. 81, 1261 (1959); H.B. Charman, E.D. Hughes and C.K. Ingold, J.Chem.Soc. 2523, 2530 (1959).

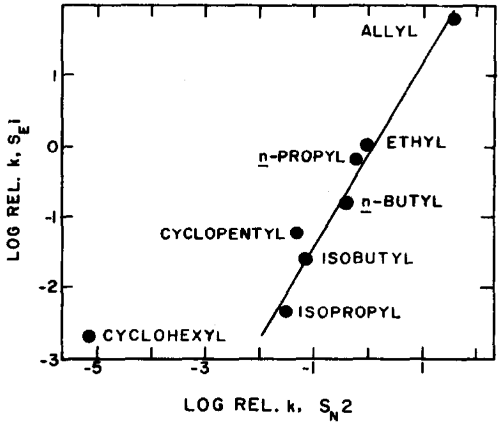

FIG. 1.

Free energy relationship between S_N2 and S_Ei reactions.

the conclusion that steric influences are the dominant effects in both reactions. The relationship displayed in Fig. 1 is as good as the average free energy relationship observed between different S_N2 processes. A similar conclusion is reached when the rates of cleavage of siliconalkyl bonds by strong acids are considered. The relative rates of cleavage of alkyltrimethylsilanes by hydrogen bromide-aluminum bromide in benzene at 40° are methyl$\gg$ethyl (1.00)> n-propyl (0.13), n-butyl (0.17) isopropyl (0.04).

The deviation of cyclohexyl, and to a lesser extent cyclopentyl, from the straight line relationship of Fig. 1 are understandable when the extreme differences in the geometry of the transition states for substitution are considered. In the cyclohexyl system substitution by S_Ei or S_E2 process can occur without the entering or leaving group occupying the hindered axial position whereas in S_N2 processes both the entering and leaving group must occupy sterically unfavorable positions. However, with these exceptions the transition states in the disproportionation of alkyltrimethylsilanes and exchange of iodide ion with alkyl iodides have nearly the same sensitivity to changes in size of the groups attached to the carbon atom undergoing attack. Electrical effects can also be important in S_Ei reactions as well as in S_N2 processes. For example, the relative rates of disproportionation of phenyl- or vinyl-trimethylsilane are approximately 30-50 times faster than ethyltrimethylsilane, a reactivity series quite different from that observed in S_N2 reactions. However, for simple alkyl groups the similarity of reactivities in S_N2 and S_Ei or S_E2 reactions indicates the unimportance of inductive effects in both processes.

Rate sequences similar to those of Table 1 have been observed in the cleavage of unsymmetrical dialkylmercury compounds by hydrogen chloride[6] and of alkylmercury iodides by hydronium ions.[7] In these cases the spread in reactivities is considerably less than in the disproportionation of tetraalkylsilanes and quite different rate sequences have been reported for cleavage reactions of symmetrical dialkylmercury compounds.[8] In the case of the alkyltrimethylsilanes any effect of a change in structure of the nonreacting alkyl group on the rate of reaction would be expected to be less important than a similar structural change in a cleavage reaction of a dialkylmercury compound.

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[6] M.S. Kharasch and A.L. Flenner, J.Amer.Chem.Soc. 54, 674 (1932); F.C. Whitmore and H. Bernstein, Ibid. 60, 2626 (1938).

[7] M.M. Kreevoy and R.L. Hansen, J.Amer.Chem.Soc. 83, 626 (1961).

[8] C.S. Marvel and H.O. Calvery, J.Amer.Chem.Soc. 45, 820 (1923); S. Winstein and T.G. Traylor, Ibid. 77, 3747 (1955); 78, 2597 (1956); R.E. Dessy, G.F. Reynolds and J.-Y. Kim, Ibid. 81, 2683 (1959); R.E. Dessy and Y.K. Lee, Ibid. 82, 689 (1960).