

quantitative description on the reactivity of a σ -bond toward an electrophile. The related work is actively in progress and will be reported soon.

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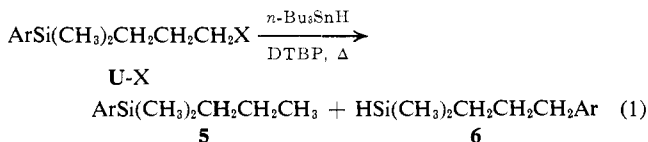
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Halogen Leaving Group Effect in the Reductive Rearrangement of γ -Silyl Halides with Tri-*n*-butyltin Hydride

Sir:

Although considerable information exists on the reduction of alkyl halides by organotin hydrides,¹ including the use of the reaction to study free radical rearrangements,² we have uncovered an unexpected and heretofore unreported aspect of the reaction. During a study of aryl group migration from silicon to carbon as reported³ for the chlorides in eq 1, it was found that



chlorides gave more rearranged product than did bromides. This halogen effect was more pronounced at higher reactant concentrations and appeared to level off with decreasing concentration. Some data are given in Table I.⁴

Table I. Effect of Halogen on Rearrangement^a

U-X, Ar	U-X $\xrightarrow[\text{DTBP, } \Delta]{n\text{-Bu}_3\text{SnH}}$ 5 + 6					
	Percentage rearranged product 6 ^b					
	10 ⁻¹ M _{init}		10 ⁻² M _{init}		10 ⁻³ M _{init}	
	Cl	Br	Cl	Br	Cl	Br
<i>p</i> -Anisyl, 1	12	<i>c</i>	26	<i>c</i>	41	<i>c</i>
<i>p</i> -Tolyl, 2	5.5	2.5	19	6.0	31	30
<i>p</i> -Fluorophenyl, 3	5.0	2.0	16	5.0	28	21
Phenyl, 4 ^d	4.5	tr	15	4.0	Not studied	

^a U-X:*n*-Bu₃SnH:DTBP = 30:10:3 in purified benzene at 140 ± 5° for 20 hr. Yields of 5 + 6 were 60–80%. ^b Determined by glpc. The values are percentage compositions rounded to the nearest 0.5%. The values are the average of several determinations with a precision of ±5%. ^c This bromide proved to be a sensitive substance. Only modest yields of 35–38% of unrearranged 5 were obtained, along with several unidentified compounds. ^d Data from ref 3.

The rearranged product from either halide of both 2

(1) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968), and references therein.

(2) J. W. Wilt, "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 8.

(3) J. W. Wilt and C. F. Dockus, *J. Amer. Chem. Soc.*, **92**, 5813 (1970).

(4) Most of our studies have centered on the γ -silyl halides U-X. However, the effect noted in the table occurs also with *p*-CH₃C₆H₄Si(CH₃)₂CH₂CH₂CH₂X, a δ -silyl halide. The extents of rearrangement here with 10⁻¹, 10⁻², and 10⁻³ M halide were, respectively, 7, 25, and 33% for X = Cl, and a trace, 3%, and 27% for X = Br.

and 3 still retained the para-oriented substituent, so the migration path is Ar₁-5 in nature, as earlier postulated.³

Normally, simple alkyl chlorides undergo reduction by tin hydrides about 10⁴ times more slowly than do bromides.⁵ Surprisingly, however, a 10⁻² M mixture of 1:1 3-Cl and 3-Br in benzene underwent competitive reduction with limited *n*-Bu₃SnH to give a reduced product containing 13% 6. Reduction of 5 × 10⁻³ M 3-Cl under the same conditions gave 25% 6, whereas the same treatment of 3-Br gave 9% 6. Clearly, these two halides have comparable reactivities toward reduction (within threefold). Suitable control experiments indicated that no thermal or Lewis acid catalyzed rearrangement of either the reactants or products occurred in any of these reductions.

These distant aryl migrations are not very favorable. Concentrations of *n*-Bu₃SnH larger than *ca.* 0.3 M gave no 6 in any case. Such rearrangements are therefore less facile than cyclizations or 1,2-aryl shifts⁶ (carbon to carbon⁹).

A sample reduction is described. The appropriate halide U-X^{11,12} was weighed into a volumetric flask, mixed with the proper volumes of stock solutions of redistilled tri-*n*-butyltin hydride and redistilled di-*tert*-butyl peroxide (DTBP), and diluted with purified, thiophene-free benzene to the mark. The final solution was made to contain U-X:*n*-Bu₃SnH:DTBP in the ratios 30:10:3, with the initial concentration of U-X either 10⁻¹, 10⁻², or 10⁻³ M. The reactant solution was then transferred to a 25-ml ampoule and put through three freeze-degas cycles on a vacuum line. The sealed ampoule was then heated in a wax bath at 140 ± 5° for 20 hr. The ampoule was cooled and opened and most of the benzene was removed by careful distillation. The remaining contents were then analyzed by glpc on a silicone gum rubber (SE 30) column. Products, yields, and composition data were all obtained by use of calibration mixtures of authentic samples.^{11,14}

To our knowledge, no other report exists of such a halogen effect in organotin hydride reductions. In fact,

(5) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968). For chlorides, chlorine abstraction is usually the slow step of the reduction. For bromides, hydrogen transfer from the tin hydride is normally rate determining.

(6) Cyclization of 5-hexen-1-yl radical⁷ has a calculated rate constant⁸ of *ca.* 10⁸ sec⁻¹ at 40°, and the 1,2-phenyl shift that rearranges the 2,2,2-triphenylethyl radical⁸ has a calculated rate constant⁸ of 5 × 10⁷ sec⁻¹ at 100°. Both of these processes have rate constants comparable to that for hydrogen transfer from tin hydrides⁵ (*ca.* 10⁴–10⁶ sec⁻¹ at 10⁻² M hydride). The present rearrangements are much slower. Very approximate calculations indicate a rate constant of *ca.* 10³ sec⁻¹ at 140°.

(7) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966).

(8) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

(9) Radical 1,2-aryl shifts from silicon to carbon remain unknown.¹⁰

(10) Reference 2, p 354.

(11) All new compounds gave C, H analyses within 0.3% of theory. The ir and nmr spectra were in agreement with the structures proposed.

(12) U-Cl compounds were prepared by coupling reactions between Cl₃SiCH₂CH₂CH₂Cl and the appropriate Grignard reagents. U-Br compounds were similarly prepared from Cl₃SiCH₂CH=CH₂. The allyl silanes so obtained were then converted to U-Br either by hydroboration-bromination¹³ or by hydroboration-oxidation to the corresponding alcohol, tosylation, and displacement with lithium bromide in acetone.

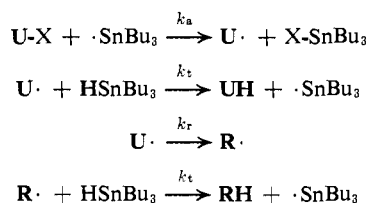
(13) H. C. Brown and C. F. Lane, *J. Amer. Chem. Soc.*, **92**, 6660 (1970).

(14) Compounds 5 were prepared by coupling reactions between (CH₃)₂SiCl₂ and the appropriate Grignard reagents. Compounds 6 were similarly prepared using 1 mol of the appropriate Grignard reagent followed by reduction of the chlorosilane intermediate with lithium aluminum hydride.

studies of rearrangement during such reductions using both chlorides and bromides are rare at best. In one, however, 5-chloro- and 5-bromonorbornenes gave an essentially identical mixture of norbornene and nortricyclene upon reduction with $n\text{-Bu}_3\text{SnH}$.¹⁵

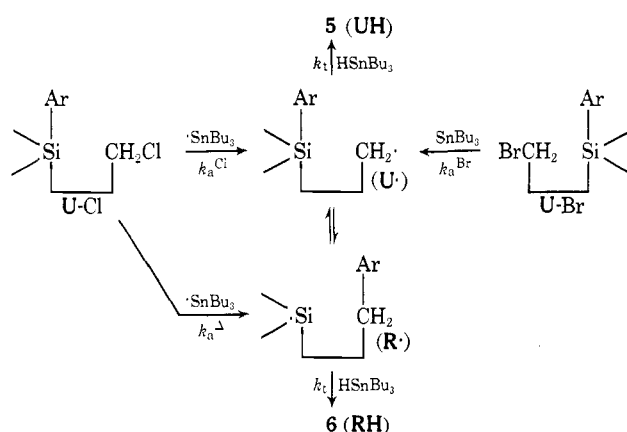
Mechanistically, the reactions of U-Cl and U-Br obviously differ in some regard. The accepted¹ chain process for such reactions is given in Scheme I, from

Scheme I



which it may be seen that the formation of rearranged product RH depends upon k_r , k_t , and the tin hydride concentration only. The extent of rearrangement of radical U· should be independent of its origin. Just how this sequence may be modified in the present case is not totally understood. Nonetheless, the fact that this halogen effect leveled off as the concentration of the reactants decreased, even as the extent of rearrangement expectedly³ increased, indicates that Scheme I may apply under very dilute conditions. That is, X plays no role and the extent of rearrangement is indeed governed by the ratio $k_r/k_t[\text{HSnBu}_3]$. There may be, in fact, an equilibrium¹⁶ established between U· and R· such that the extent of rearrangement under dilute conditions measures this equilibrium, assuming that the k_t values do not vary. At higher reactant concentrations some mechanistic feature must intrude, a feature that accommodates both an *increased extent of rearrangement* and an *increased reactivity* for U-Cl relative to U-Br. We suggest that a competitive process from U-Cl directly to R· can occur (k_a^Δ), utilizing anchimeric assistance by the propitiously positioned aryl group *via* an Ar₁-5 migration pathway, as shown in Scheme II. At any

Scheme II



concentration of reactants above that which would allow

(15) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966). In this paper, a citation is made that the relative reactivity of *endo*-5-chloronorbornene (their *endo*-4c) is 0.37 times that of cyclopentyl bromide. In another place, this reactivity ratio was assigned to *endo*-5-bromonorbornene (their *endo*-4b) *vs.* cyclopentyl bromide. Because bromides are usually so much more reactive than chlorides in such reductions, we believe that the first citation contains a misprint (4c should be 4b).

(16) For discussions on such reversible processes in group IV radicals, see H. Sakurai, ref 2, Vol. 2, pp 795-799; ref 2, pp 374-377.

equilibration of U· and R·, this scheme would correctly predict more RH from U-Cl than from U-Br. Moreover, the additional pathway available to U-Cl could allow its overall rate of reduction to approach that of U-Br.¹⁷

The effect of the para substituents thus far examined reflects a combination of processes: k_a^Δ , the U· and R· equilibrium, and the k_t 's. The fact that the rearrangement seems to be mildly increased by electron donors must be further tested with a wider variety of substituents. The present data allow no quantitative conclusions as to the various rates involved, but further studies are contemplated toward this end.

(17) This is a qualitative view. Further work must be done to establish more conclusively the existence and the extent of this participation pathway.

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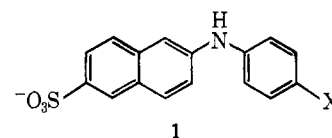
Fluorescence of

2-N-Arylamino-6-naphthalenesulfonates in Glycerol

Sir:

Fluorescence from 2-N-arylamino-6-naphthalenesulfonate (ANS) derivatives (**1**) occurs from either a naphthalene-centered ($S_{1,np} = (D - {}^1A)_{1,np}$) or a charge-transfer ($S_{1,ct} = (D^+ - A^-)_{1,ct}$) state.^{1,2} Conversion of the $S_{1,np}$ state to the $S_{1,ct}$ is effected by an intramolecular electron-transfer reaction which can occur only in a solvent of the appropriate polarity and fluidity. The latter requirement is related to the necessity for partial rotation of the 2-N-aryl group to a position in which overlap of the aryl π -orbitals with those of the naphthalene ring is sufficient to permit electron transfer.

The solvent glycerol is polar enough to stabilize the $S_{1,ct}$ state (Z value, 86.5; $E_T(30)$ value, 57.0³) and too viscous to allow rotation on the time scale of fluorescence. It was already known that viscous solvents (glycerol, 20% Ficoll, 60% sucrose) markedly enhanced the fluorescence of ANS derivatives over that expected in highly polar solvents⁵⁻⁷ and that anhydrous TNS (**1**,



X = CH₃) was strongly fluorescent, without any clear explanation for the phenomenon.⁸ We now report that the fluorescence maxima observed for ANS de-

(1) E. M. Kosower and K. Tanizawa, *Chem. Phys. Lett.*, **16**, 419 (1972).

(2) E. M. Kosower, H. Dodiuk, M. Ottolenghi, and N. Orbach, to be submitted for publication.

(3) Solvent polarity was measured with betaine-30 kindly supplied by Professor K. Dimroth (see ref 4) and the Z -value derived from the linear relationship between Z -value and $E_T(30)$ value shown in E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p. 303.

(4) C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968).

(5) W. O. McClure and G. M. Edelman, *Biochemistry*, **5**, 1908 (1966).

(6) C. J. Seliskar and L. Brand, *J. Amer. Chem. Soc.*, **93**, 5414 (1971).

(7) D. C. Turner and L. Brand, *Biochemistry*, **7**, 3381 (1968).

(8) A. Camerman and L. H. Jensen, *J. Amer. Chem. Soc.*, **92**, 4200 (1970).