Table I. Comparison of δ-Secondary Deuterium Isotope Effects for Limiting Solvolysis in Saturated and Unsaturated Systems

Compound	Solvent	$k \times 10^4$, sec^{-1}	k_H/k_D	Ref
$(CR_3)_3CCH_2C(CH_3)_2Cl$, R = H	80% EtOH	2.106 ± 0.002	0.983	*a*
R = D		2.143 ± 0.002		
trans-$CR_3CH{=}CHCHClCH_3$, R = H	95% EtOH	2.172 ± 0.001	1.132	*b*
R = D		1.919 ± 0.001		
$CR_3C{\equiv}C{-}C(CH_3)_2Cl$	95% EtOH		1.095	*c*

[a] This work. [b] Unpublished results from this laboratory. [c] Reference 2b.

stant in the activation process. The conformational dependence of such β-isotope effects and their transmission through unsaturated linkages are results most readily accommodated by the hyperconjugation explanation.[2] Nonetheless, it has been argued that these effects may be entirely steric in origin.[3]

In order to assess experimentally the magnitude of secondary *steric* isotope effects in solvolytic reactions, it is necessary to investigate a system in which: (a) hyperconjugation involving the isotopically substituted bond is prohibited and (b) release of nonbonded interactions in the vicinity of the seat of isotopic substitution plays a role in the activation process. Karabatsos and coworkers have recently reported the results of such a study on the solvolysis of 8-methyl- and 8-deuteriomethyl-1-chloromethylnapthalene.[4] The very small normal isotope effect on the rate of this solvolysis and extended calculations using the Bartell equations[5] led these authors to conclude that release of steric strain produces less than 10% of the observed β-secondary isotope effect in the solvolysis of simple tertiary alkyl chlorides.

We here report the results of a similar study of a completely saturated system, dimethylneopentylcarbinyl chloride (**1**). Chloride **1** and its δ-nonadeuterated

$$(CR_3)_3CCH_2C(CH_3)_2Cl$$

1a, R = H
b, R = D

analog were prepared by standard methods[6] and their rates of solvolysis were determined by a precise conductometric method.[7] The results are presented in Table I along with δ-secondary isotope effects on the rates of solvolysis of two unsaturated systems. Aqueous alcoholysis of **1a** proceeds about 20 times as fast as that of *t*-butyl chloride, presumably because of steric assistance to ionization.[8] In spite of this substantial kinetic steric effect, the δ-secondary deuterium isotope effect in this system is slightly *inverse*.[9] On the other hand, the δ effect is *normal* in the solvolysis of the allylic and acetylenic chlorides where hyperconjugation with the electron-deficient solvolytic center is stereoelectronically possible. Steric assistance to ionization must be more important in the solvolysis of **1** than it is in the case of simple tertiary alkyl chlorides and secondary arenesulfonate esters. We conclude that nonbonded interactions *of the magnitude involved in usual solvolytic systems* have a negligible effect on β-C–H force constants and that a hyperconjugation model best explains β-secondary isotope effects on solvolytic reactions.

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[3] H. C. Brown, M. E. Azzaro, J. G. Koelling, and G. J. McDonald, *ibid.*, **88**, 2520 (1966).

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[6] Deuterium content at the labeled position was estimated by mass spectrometry and nmr measurements to be greater than 97%.

[7] The kinetic method is that described by B. L. Murr and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **84**, 4672 (1962). We are indebted to Professor Shiner and to Dr. W. E. Buddenbaum for a copy of the computer program used to analyze the raw kinetic data. The precision of the method is better than ±0.1%.

[8] H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

[9] The direction of this effect is the same as that observed by Streitwieser[10] in the effect of ring deuteration on the solvolysis of benzhydryl halides and that observed by Kresge[11] in the effect of ring deuteration on the ionization of triphenylcarbinol and is probably inductive in origin.

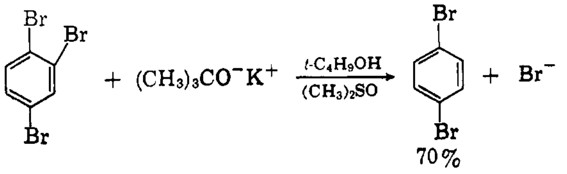
[10] A. Streitwieser and H. S. Klein, *J. Am. Chem. Soc.*, **85**, 2759 (1963).

[11] A. J. Kresge and R. J. Preto, *ibid.*, **89**, 5510 (1967).

Base-Induced Dehalogenation of Aryl Halides in *t*-Butyl Alcohol–Dimethyl Sulfoxide and Similar Solvent Mixtures

Sir:

Moyer[1] discovered that 1,2,4-tribromobenzene, on exposure to excess potassium *t*-butoxide (*t*-BuO$^-$K$^+$) in 50% *t*-butyl alcohol–50% dimethyl sulfoxide (DMSO) at 53°, suffered reductive loss of the 2-bromine. *p*-Dibromobenzene was formed in 70% yield, and the bromine removed appeared as bromide ion. We have studied this unusual reaction and obtained evidence indicating its mechanism.



A number of chloro, bromo, and/or iodo derivatives of benzene are partially and selectively dehalogenated by this reagent. In general, protodehalogenation occurs only at sites *ortho* to other halogen atoms and is most facile for halogens flanked on both sides by *ortho* halogens. Other things being equal, deiodination occurs more readily than debromination, while dechlorination has not been observed. Electron-attracting substituents facilitate the reaction. Representative yields are 99% *m*-dibromobenzene from 1,2,3-tribromo-

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[1] C. E. Moyer, Jr., Dissertation, Brown University, 1964; *Dissertation Abstr.*, **25**, 4412 (1965).

benzene and 72% chlorobenzene from 1-chloro-2-iodobenzene.

Relative reactivities of several oligohalobenzenes were estimated from competition experiments at room temperature on the assumption of a second-order rate law; such mild conditions were necessary in order that some of each reactant be unconsumed at the end of the experiment. Reactivities relative to unity for 1-bromo-2,6-dichlorobenzene were as follows (the halogen removed is in *italics*): *4-bromo*-3,5-dichlorotoluene, 0.2; *1-bromo*-2,6-dichlorobenzene, (1.0); *1-iodo*-2,4-dibromobenzene, 1.4; 1,*2*,3-tribromobenzene, 4.6; *1-bromo*-2,4,6-trichlorobenzene, 33; *1*,4-dibromo-2,6-dichlorobenzene, 34; 1,*2*,3,5-tetrabromobenzene, 80; and *1-iodo*-2,4,6-trichlorobenzene, 900. All these compounds were so much more reactive than 1,2,4-tribromobenzene that no estimate of the relative reactivity of the latter could be made from competition experiments.

Dehalogenation is also effected by t-BuO$^-$K$^+$ in 50:50 mixtures of t-BuOH with certain other dipolar, "aprotic" solvents, but there is a wide variation in reactivity depending on the cosolvent employed. In a series of experiments, 1 equiv of 1-bromo-2,6-dichlorobenzene was exposed to ~0.75 equiv of t-BuO$^-$K$^+$ in constant total solvent volume for 22 hr at room temperature. Bromide ion yields, based on aryl bromide, with the several cosolvents were: DMSO, 74%; N-methylpyrrolidone, 22%; N,N-dimethylacetamide, 10%; sulfolane, 4%; dimethylformamide, 0.1%; and hexamethylphosphoramide, 0.08%. Dehalogenation fails to occur in t-BuOH alone (without cosolvent). With diphenyl sulfoxide cosolvent, 1,2,4-tribromobenzene was unaffected by excess t-BuO$^-$K$^+$ in 6.8 hr at 100°.

Because of concurrent studies on deiodination reactions involving aryl radical intermediates,[2,3] we sought to detect radicals in the dehalogenation of 1-bromo- and 1-iodo-2,6-dichlorobenzenes and 1,2,4-tribromobenzene in benzene-rich systems, such as t-BuO$^-$K$^+$ in 25% t-BuOH–25% DMSO–50% benzene. Dehalogenation occurred as usual, but no biphenyl derivatives were formed. On the other hand, the diazonium fluoroborate from 2,6-dichloroaniline gave, under the same conditions, a substantial amount of 2,6-dichlorobiphenyl.

Although these results discouraged consideration of a radical mechanism, the possibility that the aryl halides somehow accepted an electron, expelled a halide ion, and thereby formed an aryl radical, as in the radical-induced deiodination of aryl iodides in alkaline methanol,[3] was nevertheless examined. In 2 *M* methanolic sodium methoxide with 1-phenyl-2-benzenesulfonhydrazide, 1-chloro-2-bromo-4-iodobenzene lost only iodine, forming *o*-bromochlorobenzene, but with t-BuO$^-$K$^+$ in 50% t-BuOH–50% DMSO the same halide afforded mainly bromide ion (55%) and *p*-chloroiodobenzene (37%), though 39% iodide ion and 22% *o*-bromochlorobenzene were also formed. Thus the reactivity pattern observed in the t-BuOH–DMSO system is not that characteristic of the electron-transfer mode of dehalogenation.

The following mechanism is compatible with these observations.

$$t\text{-BuO}^- + \text{CH}_3\text{SOCH}_3 \rightleftarrows t\text{-BuOH} + \text{CH}_3\text{SOCH}_2\text{:}^- \qquad (1)$$

$$\text{CH}_3\text{SOCH}_2\text{:}^- + \text{ArX} \longrightarrow \text{Ar:}^- + \text{CH}_3\text{SOCH}_2\text{X} \qquad (2)$$

$$\text{Ar:}^- + t\text{-BuOH} \longrightarrow \text{ArH} + t\text{-BuO}^- \qquad (3)$$

$$\text{base} + \text{CH}_3\text{SOCH}_2\text{X} \longrightarrow \text{X}^- + \ ? \qquad (4)$$

Step 1 is amply precedented.[4] Step 2 is a nucleophilic displacement *on halogen*, forming an aryl anion and a halomethyl methyl sulfoxide. Nucleophilic displacements on halogen are implicated in the base-catalyzed isomerization and disproportionation of oligohalobenzenes[5] and in the scrambling of 1,2,4-triiodobenzene.[6] Step 3 is straightforward. Little is known about the chemistry of halomethyl sulfoxides, but step 4 seems likely to occur. Both SN2 and α-elimination reactions are conceivable, but no organic products from the proposed step 4 have been detected.

The proposed mechanism accounts for the beneficial effect of *o*-halogen substituents (they stabilize phenyl anions[7]), the dehalogenation susceptibility order I > Br > Cl, the absence of radical intermediates, and the dependence of reactivity on cosolvent identity. The reactive cosolvents are "semiprotic" in the sense that they can yield protons to strong bases to form carbanions which may react analogously to the dimsyl anion in step 2, but truly aprotic solvents such as diphenyl sulfoxide, dimethylformamide, and hexamethylphosphoramide are ineffective (We have some evidence that the very slow reactions in the latter two solvents are of a different character.)

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Diamagnetic Susceptibility Exaltation as a Criterion of Aromaticity

Sir:

We wish to report the development of an experimental criterion of aromatic character based on the diamagnetic susceptibility exaltation of a compound, a criterion which responds uniquely to the presence of appreciable *cyclic* π-electron delocalization in molecules.

The molar susceptibility, χ_M, of a compound in a fluid system is the average of three orthogonal components: $\chi_M = {}^1/_3(\chi_x + \chi_y + \chi_z)$.[1,2] For benzenoid aromatics it is known[1] that $\chi_x \approx \chi_y < \chi_z$ (if z is taken normal to the molecular plane); benzenoid aromatics thus exhibit enhanced diamagnetic anisotropy, *i.e.*, $\Delta\chi \gg 0$, where $\Delta\chi = \chi_z - {}^1/_2(\chi_x + \chi_y)$. The great magnitude of the anisotropy has been attributed[3,4] to

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