Table I. The Reaction of "t-C_4H_9OI" with Hydrocarbons at 47°[a]

Hydrocarbon	Product[b]	Yield,[c] %
Neopentane	Neopentyl iodide	28 (34)
n-Butane	2-Iodobutane (95 ± 3%)	35 (39)
	n-Butyl iodide (5 ± 3%)	
Cyclohexane	Cyclohexyl iodide	51 (60) (71[d])
Isobutane	Isobutyl iodide	(<2)
	t-Butyl iodide	(<2)
Toluene	Benzyl iodide	34 (38)

[a] Preparative reactions were run in Freon 113 solutions 1.0–1.2 M in t-butyl hypoiodite and 3.8–4.2 M in hydrocarbon. [b] The products were characterized by comparison of their ir and nmr spectra and glpc retention times with those of authentic samples. [c] The values reported were based on the initial concentration of t-butyl hypochlorite used and represent yields of pure product isolated from the reaction by distillation. Values in parentheses were determined by glpc analysis using Freon 112 as an internal standard. [d] Yield obtained using carbon tetrachloride solution 0.133 M in t-butyl hypoiodite and 2.47 M in cyclohexane at 40°.

In order to optimize the yield of alkyl iodide and to determine the amount of t-butyl alcohol produced in the reaction, carbon tetrachloride solutions 0.133 M (based on the initial concentration of t-butyl hypochlorite) in the reagent and 2.47 M in cyclohexane were irradiated at 40° in sealed, degassed Pyrex ampoules, using Freon 112 as an internal standard. Analysis of the reaction mixture by glpc showed a 71% yield of cyclohexyl iodide and a 62% yield of t-butyl alcohol.

The iodination failed with compounds containing tertiary hydrogens; neither isobutane nor 2,3-dimethylbutane gave detectable amounts of the tertiary iodide. Titration of the reactant mixture showed that 42% of the theoretical amount of iodine was present as molecular iodine. When the reaction with isobutane was run with initially added t-butyl iodide, more of the alkyl iodide was found to react than the hydrocarbon substrate. The high reactivity of the tertiary halide clearly explains the absence of tertiary iodide which must be consumed on formation faster than the unreacted substrate (see Table II). Further investigation of this reaction is in progress.

In an attempt to determine the chain-carrying species in the iodination reaction the selectivity for primary to secondary hydrogen abstraction was investigated. For substrate n-butane the selectivity was found to be primary:secondary (per H), 1:29, while the primary:secondary selectivity reported for t-butoxy radicals (t-butyl hypochlorite) is 1:8.[2] The primary:secondary selectivity obtained by iodination may be suspect and must be taken as a lower limit for the selectivity since the alkyl iodides themselves react with the reagent in the order tertiary > secondary > primary (see Table II). Higher yields could be obtained in the preparative reactions using larger ratios of hydrocarbon to halogenation reagent since the competitive reaction of the haloalkane with the reagent becomes less important at higher hydrocarbon concentrations.

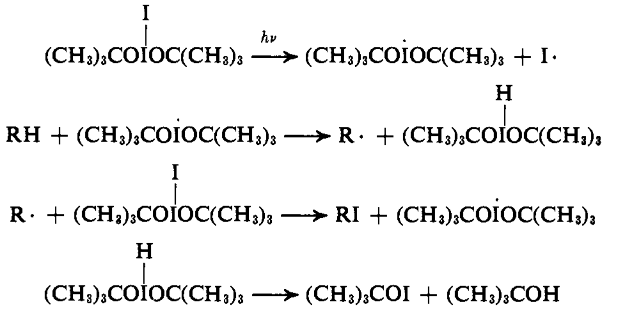
Because of the relative lack of stability of alkyl iodides, the relative rates for the competitive reactivity of several hydrocarbon substrates have been examined. The relative reactivity of cyclohexane over 2,3-dimethylbutane serves as an example of the obtained results. The iodinating reagent shows relative rates of hydrocarbon consumption of 2.5:1 while the less selective t-butoxy radical has a reported value[2] of 1.9:1. Both the selectivity and the relative reactivity experiments seem to indicate a hydrogen-abstracting species which is more selective than the t-butoxy radical, and its selectivity is reminiscent of that observed in the abstraction reactions of PhICl (primary:secondary reactivity of 1:21).[3]

Table II. Relative Reactivities of Alkyl Iodides and Cyclohexane toward t-Butyl Hypoiodite at 40°[a]

Substrate	Relative reactivity per molecule
Cyclohexane	1.00
t-Butyl iodide	5.6
2-Iodobutane	0.76
Isobutyl iodide	0.61

[a] The competitive reactions were run in Freon 113 solutions 0.133 M in t-butyl hypoiodite and 0.270 M in substrate using Freon 112 as an internal standard.

On the basis of the selectivity and relative reactivity data the following radical chain process is proposed for the photoinitiated iodination, where the iodonyl radical is the abstracting species.



$$(CH_3)_3CO\overset{I}{I}OC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CO\dot{I}OC(CH_3)_3 + I\cdot$$

$$RH + (CH_3)_3CO\dot{I}OC(CH_3)_3 \longrightarrow R\cdot + (CH_3)_3CO\overset{H}{I}OC(CH_3)_3$$

$$R\cdot + (CH_3)_3CO\overset{I}{I}OC(CH_3)_3 \longrightarrow RI + (CH_3)_3CO\dot{I}OC(CH_3)_3$$

$$(CH_3)_3CO\overset{H}{I}OC(CH_3)_3 \longrightarrow (CH_3)_3COI + (CH_3)_3COH$$

A detailed investigation of the mechanism of formation of the reagent and its iodination reactions as well as an expansion of its synthetic utility will be reported shortly in a full paper.

Acknowledgment. We are indebted to the National Research Council of Canada and the University of Alberta for their generous support of this work.

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Received November 13, 1967

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(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(3) D. D. Tanner and P. B. Van Bostelen, *J. Org. Chem.*, **32**, 1517 (1967).

(4) University of Alberta Postdoctoral Fellow, 1966–1968.

Remote Secondary Deuterium Isotope Effects

Sir:

Although it is generally agreed that secondary deuterium isotope effects are vibrational in origin,[1] the interaction mechanism responsible for the force constant changes during activation (or reaction) remains a subject of controversy. In the case of β-secondary isotope effects on the rates of solvolytic reactions, the controversy hinges on the relative importance of hyperconjugation and the release of nonbonded interactions in producing the mainfest reduction of a β-C–H force con-

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(1) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1965).

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.

Acknowledgment. The authors wish to thank the donors of the Petroleum Research Fund (Grant 380G), administered by the American Chemical Society, for partial support of this research. Computations were performed at the Ohio University Computing Center.

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[2] (a) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963); (b) V. J. Shiner, Jr., and G. S. Kriz, Jr., *ibid.*, **86**, 2643 (1964).

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

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[5] L. S. Bartell, *ibid.*, **83**, 3567 (1961).

[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.

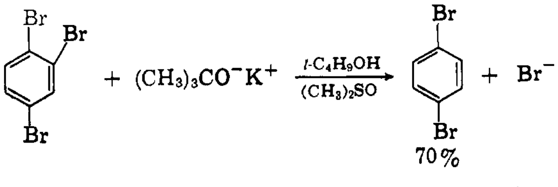
[10] A. Streitwieser and H. S. Klein, *J. Am. Chem. Soc.*, **85**, 2759 (1963).

[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).