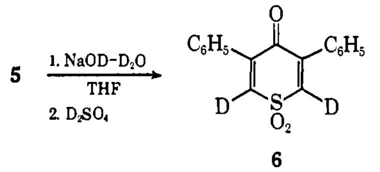
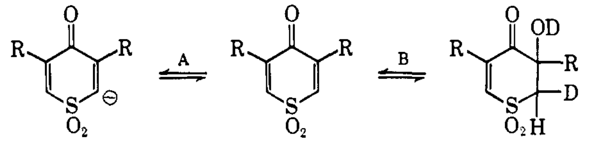
tetrahydrofuran with D_2SO_4 and rapid recovery of product gave a high yield of **6** in 81% isotopic purity (deuterium analysis). Finally, the ultraviolet absorption of **5** [λ_{max}^{EtOH} 240 (ϵ 4500) and 315 mμ (ϵ 2000)] is seen to be appreciably altered upon addition of 30% sodium hydroxide solution [λ_{max} 253 mμ (ϵ 1500) and considerable tailing into the visible region].



6

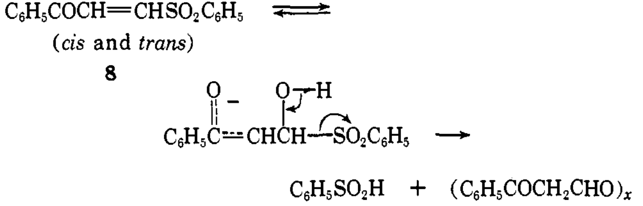
The substitution of deuterium at the 2 and 6 positions in **1** and **5** may proceed by way of intermediate vinyl carbanions (path A) or *via* reversible Michael addition (path B). Precedence for proton abstraction from an sp^2-hybridized α-sulfonyl carbon atom was recently obtained in a study of the base-catalyzed exchange of 2,3-dihydrothiophene 1,1-dioxide.[14] Differences in reactivity of **1** and **5**, however, are not entirely reconcilable with the carbanion mechanism. In agreement with the fact that a phenyl substituent (σ^* 0.6) is slightly more inductively electron withdrawing than hydrogen (σ^* 0.49), no system has yet been found, to our knowledge, wherein exchange rates have shown a decrease due to this effect.[15] The absence of protons at higher magnetic field in the nmr spectrum of **5** in alkaline media could reflect merely very rapid exchange under these conditions.



7

The relation of structure to reactivity, however, is explicable on the basis of the Michael addition path. The much slower exchange rate for **5** under neutral conditions would be anticipated from loss of conjugation in proceeding to **7** (R = C_6H_5) or its anion. Despite the fact that the above data suggest that detectable quantities of hydroxide adducts do not appear to be present, it is proposed that their formation in kinetically important quantities is the dominating factor in these isotopic exchanges.

Thus, it is the sulfonyl group which controls the direction of Michael addition in these cyclic keto sulfones. Interestingly, the acyclic keto sulfones **8** react with 5% aqueous potassium hydroxide to afford principally benzenesulfinic acid (>72% yield).[16] However, because the products in these examples could well be determined by the elimination step, these observations bear no necessary relation to the direction of Michael addition in the title compounds.


$$C_6H_5COCH{=}CHSO_2C_6H_5 \overset{OH^-}{\rightleftharpoons}$$

(*cis* and *trans*)

8

$$C_6H_5\overset{O^-}{\overset{|}{C}}{=}CH\overset{OH}{\overset{|}{C}}H{-}SO_2C_6H_5 \longrightarrow C_6H_5SO_2H + (C_6H_5COCH_2CHO)_x$$

Acknowledgment. This study was aided by a grant from the National Science Foundation (GP 5977) for which we are most grateful.

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[14] C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 3863 (1966).

[15] See, for example, A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **87**, 5388 (1965).

[16] E. P. Kohler and R. G. Larsen, *ibid.*, **57**, 1448 (1935).

[17] Fellow of the Alfred P. Sloan Foundation, 1965–1967.

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Free-Radical Iodination. A Novel Synthetic Method

Sir:

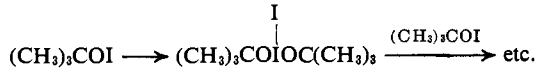
Methods of introducing iodine into unactivated organic substrates have been heretofore unknown. Since free-radical substitution reactions by molecular iodine are energetically unfavorable,[1] the replacement of hydrogen by iodine has been feasible only in electrophilic aromatic substitution and reactions leading to the substitution of hydrogens situated α to an activating carbonyl.

We wish to report here the preliminary results of a novel and synthetically useful free-radical method for the substitution of primary, secondary, and benzylic hydrogens by iodine.

Carbon tetrachloride or Freon 113 solutions of *t*-butyl hypochlorite (2 moles) at 0° react after a short induction period with a suspension of mercuric iodide (1 mole) to yield what can be formally considered to be *t*-butyl hypoiodite. The stochiometric relationship can be determined by observing the change in the nmr absorption of the *t*-butyl protons at various ratios of reactants (*t*-butyl hypochlorite τ 8.69, *t*-butyl hypoiodite τ 8.55) and by the isolation of a nearly quantitative yield (97%) of mercuric chloride which was filtered from the reaction mixture. Iodometric titration of the filtrate showed a nearly theoretical amount of active halogen.

$$2(CH_3)_3COCl + HgI_2 \longrightarrow 2(CH_3)_3COI + HgCl_2$$

The resulting purple solution shows ultraviolet (λ_{max} 241 mμ (ϵ ~930)) and infrared absorption very similar to that of *t*-butyl hypochlorite. The ultraviolet spectrum of the reaction mixture also shows absorption for small amounts (2 to 3%) of molecular iodine (λ_{max} 520 mμ (ϵ 840)). Upon standing overnight at 0° or upon immediate irradiation at 0° the solution was found to form a gelatinous precipitate, presumably of dimeric or polymeric trivalent iodine compounds.


$$(CH_3)_3COI \longrightarrow (CH_3)_3CO\overset{\overset{\textstyle I}{|}}{I}OC(CH_3)_3 \xrightarrow{(CH_3)_3COI} \text{etc.}$$

Both aged and freshly prepared carbon tetrachloride or Freon 113 solutions of the reagent upon irradiation (200-w incandescent light bulb) with hydrocarbon substrates give preparatively useful yields of iodinated hydrocarbons (see Table I).

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[1] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 376.

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%) *n*-Butyl iodide (5 ± 3%)	35 (39)
Cyclohexane	Cyclohexyl iodide	51 (60) (71[d])
Isobutane	Isobutyl iodide *t*-Butyl iodide	(<2) (<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°.

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.

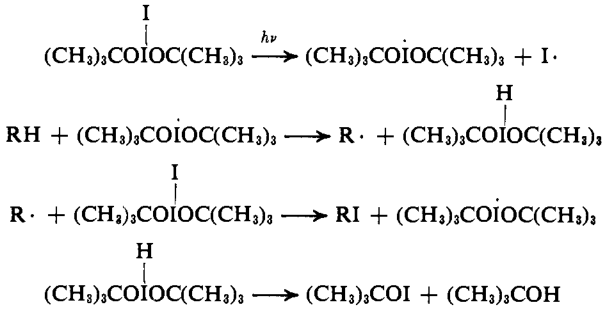
In order to optimize the yield of alkyl iodide and to determine the amount of *t*-butyl alcohol produced in the reaction, carbon tetrachloride solutions 0.133 *M* (based on the initial concentration of *t*-butyl hypochlorite) in the reagent and 2.47 *M* in cyclohexane were irradiated at 40° in sealed, 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]

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.



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

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

$$\mathrm{R}\cdot + \mathrm{(CH_2)_3CO}\overset{\mathrm{I}}{\overset{|}{\mathrm{I}}}\mathrm{OC(CH_3)_3} \longrightarrow \mathrm{RI} + \mathrm{(CH_3)_3CO\dot{I}OC(CH_3)_3}$$

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

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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(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.

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Received November 13, 1967

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).