in a few milliliters of ether and a slight excess of ethereal diazoethane was added, converting the α,α-dimethylphenylacetic acid to its ethyl ester. The solvent was again removed under reduced pressure and the resultant mixture was again analyzed by glpc as above. The increase in the yield of ethyl α,α-dimethylphenylacetate represents the yield of the acid originally present in the reaction mixture.

α-Hydroxyisobutyrophenone. To 100 ml of a 1.8 *M* solution of potassium hydroxide in ethanol was added 2 g of α-bromoisobutyrophenone. The reaction mixture was stirred for 1 hr and was then added to 300 ml of water and was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave α-hydroxyisobutyrophenone as a viscous, colorless liquid with bp 63–68° (0.3 mm) (lit.[9] bp 101–106° (6 mm)). The ir and nmr spectra were consistent with the assigned structure.

α-Ethoxyisobutyrophenone. Treatment of α-bromoisobutyrophenone with sodium ethoxide in absolute ethanol did not produce α-ethoxyisobutyrophenone; it produced instead only 1-ethoxy-1,2-oxido-2-methyl-1-phenylpropene.[20]

The α-ethoxyisobutyrophenone was isolated by preparative glpc of a solvolysis reaction mixture. The nmr spectrum of **3** showed a triplet at δ 1.08 (3 H), singlet at 1.47 (6 H), quartet at 3.31 (2 H), and multiplets at 7.4 and 8.2 (5 H total).

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(20) C. L. Stevens and J. Tazuma, *J. Amer. Chem. Soc.*, **76**, 714 (1954).

Halogen Abstraction Studies. II. Free-Radical Abstraction of Iodine from Aliphatic Iodides. Evidence to Support Anchimeric Assistance by Neighboring Halogen in Homolytic Reactions[1]

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Abstract: The rate of abstraction of iodine from a series of aliphatic iodides relative to the rate of abstraction of bromine from bromotrichloromethane is reported. The influence of inductive effects on the rate of abstraction from various primary iodides is illustrated by a quite good correlation of relative reactivities with Taft polar substituent constants exhibiting a ρ value of +0.184. Both β-bromine and γ-iodine substituents cause a rate enhancement for abstraction of iodine over and above that anticipated from inductive effects alone while a β-chlorine substituent exhibits rather normal behavior. These results are discussed in terms of anchimeric assistance by the former two neighboring halogens in the homolytic abstraction process. A comparison of the present iodine abstraction results with hydrogen abstraction data by the phenyl radical is also presented.

We recently reported the facile abstraction of iodine from substituted iodobenzenes by the phenyl radical and noted that this process contrasts with hydrogen abstraction reactions in that a positive ρ value is observed in a Hammett correlation.[3] This indicates that there is a substantial difference in charge distribution for the two transition states with the halogen abstraction process producing anionic character on the carbon from which the iodine is being removed (eq 1),

$$\text{R–I} + \cdot\text{Rad} \longrightarrow [\text{R}^{\delta\cdot-}\text{---I---}{}^{\delta\cdot+}\text{Rad}]^{\ddagger} \longrightarrow \text{R}\cdot + \text{I–Rad} \quad (1)$$

while cationic character is produced in hydrogen abstraction reactions (eq 2). Although there is a paucity

$$\text{R–H} + \cdot\text{Rad} \longrightarrow [\text{R}^{\delta\cdot+}\text{---H---}{}^{\delta\cdot-}\text{Rad}]^{\ddagger} \longrightarrow \text{R}\cdot + \text{H–Rad} \quad (2)$$

of information available concerning electronic effects on halogen abstraction reactions, numerous hydrogen abstraction reactions have been reported, all of which occur more readily when electron-donating substituents are located on the substrate from which the hydrogen is being removed.[3,4]

We presently wish to report a study of the abstraction of iodine from a series of aliphatic compounds which, similar to the aromatic iodides,[3] produces a positive ρ value in a Taft correlation illustrating the generality of substituent effects on halogen abstraction reactions. The divergence from the correlation by the aliphatic iodides with β-bromo and γ-iodo substituents suggests that anchimeric assistance to abstraction of iodine by these neighboring groups is indeed authentic.[5]

Results

The phenyl radicals were generated by decomposition of phenylazotriphenylmethane (PAT) at 60.0 ± 0.1° and the k_I/k_Br results listed in Table I are presented as the relative reactivity of iodo compound per molecule of bromotrichloromethane calculated from eq 3. The

$$k_\text{I}/k_\text{Br} = \frac{[\text{C}_6\text{H}_5\text{I}][\text{CBrCl}_3]}{[\text{C}_6\text{H}_5\text{Br}][\text{RI}]} \quad (3)$$

values are virtually insensitive to the PAT concentration and the ratio of substrate to bromotrichloromethane; estimated reliability is ±5%. The combined yields of iodobenzene and bromobenzene typically averaged 80–90% based on PAT. Bromotrichloromethane is used as the reference solvent in the present study rather than carbon tetrachloride as for the aromatic iodides[3] be-

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF No. 1123-G1), and the Bureau of General Research, Kansas State University, for support of this work.

[2] National Science Foundation Undergraduate Research Participant, Summer 1969.

[3] W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

[4] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 170.

[5] D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 7398 (1969).

Table I. Relative Rates of Abstraction of Iodine from Aliphatic Iodides by Phenyl Radical at 60°

Compound	k_I/k_{Br}[a]	Compound	k_I/k_{Br}[a]
$(CH_3)_3CCH_2I$	0.24	CF_3CH_2I	0.92
$(CH_3)_2CHCH_2I$	0.27	$ICH_2CO_2C_2H_5$	1.34
$CH_3CH_2CH_2CH_2I$	0.31	ICH_2CO_2H	1.73
CH_3CH_2I	0.33		
$C_6H_5CH_2CH_2I$	0.37	c-$C_6H_{11}I$	0.49
$ICH_2CH_2CO_2H$	0.46	$CH_3CH_2CH(CH_3)I$	0.54
$ICH_2CH_2CH_2I$	0.47[b]	$(CH_3)_2CHI$	0.58
$ClCH_2CH_2I$	0.52		
$BrCH_2CH_2I$	0.86	CH_3I	0.17

[a] Rate of abstraction of iodine relative to the abstraction of bromine from bromotrichloromethane. [b] Corrected for a statistical factor of two.

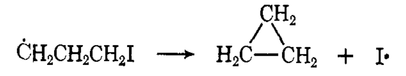
cause the intrinsic higher reactivity of the aliphatic iodides results in the formation of too little chlorobenzene to accurately measure, thus precluding reporting the relative rates as k_I/k_{Cl}.

Discussion

The present study of the abstraction of iodine from a series of aliphatic compounds allows a unique, detailed assessment of polar effects in such abstraction processes. Unlike hydrogen abstraction studies where a variety of different types of hydrogens in a molecule are available for abstraction and the composition of the solution can change as the reaction progresses,[5] use of the aliphatic iodides allows one to determine with certainty the reactivity of a specific site within a molecule. Furthermore, once the role of the inductive effect of substituents on the rate of reaction is established it is possible to ascertain the existence or absence of any additional stabilizing influence on the transition state such as conjugative delocalization or anchimeric assistance by a neighboring group.

The influence of inductive effects on the rate of abstraction from various primary iodides, RCH_2I, is illustrated in Figure 1, where it is seen a quite good correlation of relative reactivities with Taft polar substituent constants[6] is realized with $\rho = +0.184$ (correlation coefficient = 0.984). The agreement in sign of the ρ value with the results reported for the aromatic iodides[8] illustrates the generality of substituent effects on halogen abstraction reactions and further exemplifies the contrast of substituents on hydrogen *vs.* halogen abstraction, a result possibly attributable to differences in C–H and C–I bond polarities.[7]

It is apparent from Figure 1 that both a β-bromine and a γ-iodine substituent cause a rate enhancement for abstraction of iodine over and above that anticipated from inductive effects alone while a β-chlorine atom exhibits rather normal behavior. It was verified that essentially all the bromobenzene formed in the reaction of 1-bromo-2-iodoethane results from bromine abstraction from bromotrichloromethane. The phenyl radical does not competitively abstract bromine from 1-bromo-2-iodoethane; reaction of this compound with PAT in carbon tetrachloride produces less than 0.5% bromobenzene. It is conceivable, however, that the apparently enhanced rate of abstraction of iodine from 1,3-diiodopropane could be due to reaction of the phenyl radical with free iodine (or triphenylmethyl iodide) produced from the cyclopropane-forming reaction of the intermediate γ-iodopropyl radical.[8] Al-



$$\dot{C}H_2CH_2CH_2I \longrightarrow H_2C\overset{CH_2}{\diagup\diagdown}CH_2 + I\cdot \qquad (4)$$

though scavenging of the iodine produced by triphenylmethyl radical followed by reaction of the phenyl radical with triphenylmethyl iodide cannot be ruled out, there is no visible evidence for the presence of free iodine in the reacted solution.

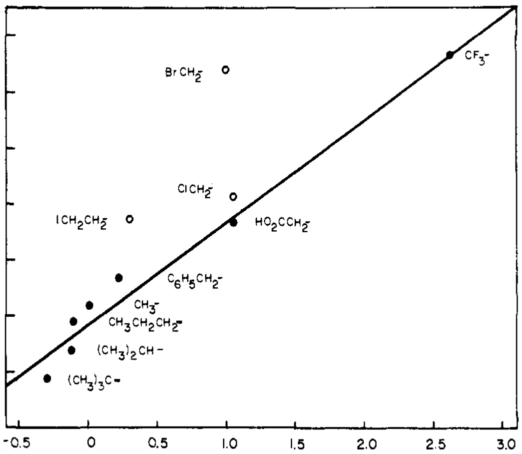
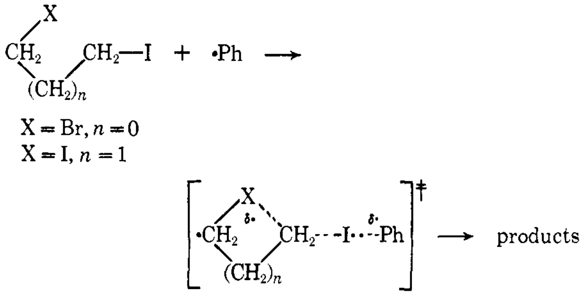


Figure 1. Plot of log k_I/k_{Br} for the primary iodides RCH_2I *vs.* Taft polar substituent constants for R. The σ^* value for ICH_2CH_2– was obtained by extrapolation of data in ref 6; the value for CF_3– is from M. Charton, *J. Org. Chem.*, **29**, 1222 (1964). The correlation coefficient reported in the text was calculated excluding values for the three compounds indicated by open circles.

A possible explanation for these results is that both β-bromine and γ-iodine substituents offer anchimeric assistance in the iodine abstraction step (eq 5).



(5)

This explanation is in accord with accumulated evidence supporting such participation in various hydrogen[9–13] and halogen[14–20] abstraction processes but differs from

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(6) R. W. Taft, Jr., *ibid.*, **74**, 2729 (1952); J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 222.

(7) I. J. Gardner and R. M. Noyes, *J. Amer. Chem. Soc.*, **83**, 2409 (1961).

(8) L. Kaplan, *Chem. Commun.*, 754 (1968).

(9) J. G. Traynham and W. G. Hines, *J. Amer. Chem. Soc.*, **90**, 5208 (1968).

(10) P. S. Juneja and E. M. Hodnett, *ibid.*, **89**, 5685 (1967).

(11) P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).

(12) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

(13) W. Thaler, *ibid.*, **85**, 2607 (1963).

(14) J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).

(15) D. M. Singleton and J. K. Kochi, *ibid.*, **89**, 6547 (1967).

(16) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

(17) W. C. Kray, Jr., and C. E. Castro, *J. Amer. Chem. Soc.*, **86**, 4603 (1964).

(18) J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968).

(19) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 582 (1969).

(20) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

the recent conclusions of Tanner, *et al.*[5] These authors have shown that the β position of 1-bromobutane is not significantly different in reactivity from that of 1-chlorobutane or other butanes substituted in the 1 position with electron-withdrawing substituents. The predominance of 1,2-dibromo product is observed only in the latter stages of the reaction and presumably results from an elimination–addition process occurring with the C-2 radical, a mode of reaction not available to the C-3 and C-4 radicals which react mainly with the accumulated HBr to regenerate 1-bromobutane. Although these results apparently rule out at least extensive anchimeric assistance by a neighboring bromine in the bromination of alkyl bromides, they do not account for the enhanced rate of halogen abstraction by chromous salts or trisubstituted tin radicals from appropriately substituted dihalo compounds.[14–20] Nor do they account for the recent observations of Cristol, *et al.*, in which the β-hydrogen in 5a-bromojanusene is activated by the adjacent *cis*-bromine substituent, a result attributed to a syn hyperconjugative electron delocalization.[21] Likewise, it is difficult to explain the retention of optical activity in the photobromination work of Skell, *et al.*,[12] without invoking some sort of bridged species. Moreover, electron spin resonance studies of alkyl radicals substituted in the β position with sulfur, silicon, germanium, and tin groups show a preferred conformational orientation in which the heteroatom eclipses the p orbital of the radical center.[22] Although these radicals are not truly symmetrically bridged structures, the incipient 1,3 bonding between the unfilled 3d orbitals of the heteroatom and the p orbital of the carbon radical center is ample to cause hindered internal rotation about the C_α–C_β bond which the authors suggest may be sufficient to control stereochemistry. Although the β-halogen free radicals were not investigated it seems reasonable to conclude that similar effects would be observed at least for a β-bromine substituent; it is worth noting that a bridged β-mercaptoalkyl radical has been postulated.[23]

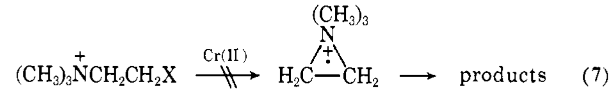
A concerted elimination of β-bromine during the abstraction of iodine from 1-bromo-2-iodoethane (eq 6)

$$\mathrm{Br{-}CH_2{-}CH_2{-}I} + \cdot\mathrm{Ph} \longrightarrow$$
$$[\mathrm{Br}^{\delta\cdot}\text{---}\mathrm{CH_2}{=\!=}\mathrm{CH_2}\text{---}\mathrm{I}\text{---}{}^{\delta\cdot}\mathrm{Ph}]^{\ddagger} \longrightarrow \mathrm{Br}\cdot + \mathrm{CH_2{=}CH_2} + \mathrm{PhI} \qquad (6)$$

does not appear to be able to account for the enhanced rate. Elimination of bromine from the 2-bromoethyl free radical is presumably an endothermic process by 5 kcal/mol with an activation energy consequently equal to or greater than that amount.[24] Although accurate values of the bond dissociation energies for the appropriate compounds are not available, it would appear that not more than *ca.* 2–3 kcal/mol would be available from the exothermic formation of the iodine–phenyl bond assuming one-half development of this bond in the transition state.[25]

While the enhancements of *ca.* 90 and 35% observed for the β-bromine and γ-iodine substituents, respectively, are substantial they are not truly dramatic. However, it must be noted that the phenyl radical is intrinsically quite reactive and not very selective. In these exothermic processes, the transition state occurs early along the reaction coordinate with relatively little radical character developed in the transition state and consequently little chance for the influences of neighboring substituents to exert themselves.

In view of the present results, there appears to be no need to invoke participation by a β-trimethylammonium group in the reduction of β-trimethylammonium ethyl halides by chromous salts.[16] The relatively rapid rate

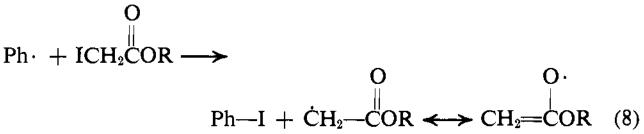


$$(\mathrm{CH_3})_3\overset{+}{\mathrm{N}}\mathrm{CH_2CH_2X} \xrightarrow[\;\;\not\;\;]{\mathrm{Cr(II)}} \mathrm{H_2C}\overset{\overset{(\mathrm{CH_3})_3}{\overset{+}{\mathrm{N}}}}{\text{—}}\mathrm{CH_2} \longrightarrow \text{products} \qquad (7)$$

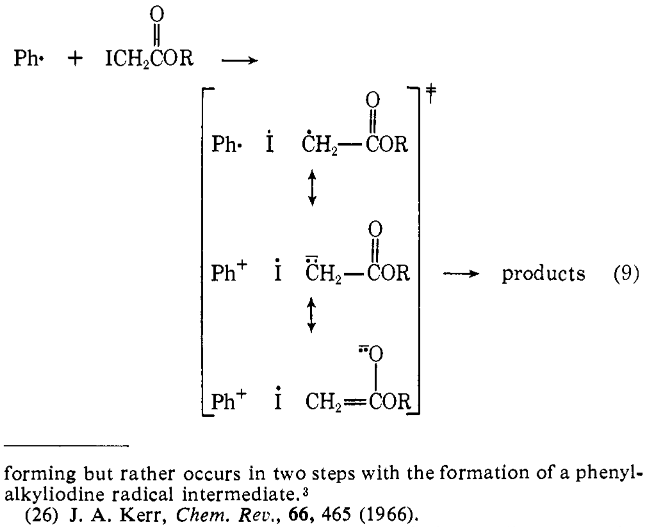
of reduction of these compounds is solely a consequence of the strongly electron-withdrawing nature of the substituent. Indeed, there is a fair correlation of the log of the relative rates of reduction of β-substituted alkyl halides by chromous salts with Taft substituent constants.[28]

Likewise, no participation by the β-phenyl group in 1-iodo-2-phenylethane is indicated by the present results in complete agreement with recent electron spin resonance studies showing no evidence for phenyl-bridged radical species.[29]

Both iodoacetic acid and ethyl iodoacetate are appreciably more reactive to iodine abstraction than anticipated from Taft polar substituent constants alone, indicating that resonance stabilization of the resulting radicals must be of significance (eq 8) or that the neighboring carbonyl group stabilizes the partial anionic charge developed on the 2-carbon in the transition state *via* resonance delocalization (eq 9). The former inter-



$$\mathrm{Ph}\cdot + \mathrm{ICH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} \longrightarrow$$
$$\mathrm{Ph{-}I} + \dot{\mathrm{C}}\mathrm{H_2{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} \longleftrightarrow \mathrm{CH_2{=}}\overset{\mathrm{O}\cdot}{\overset{|}{\mathrm{C}}}\mathrm{OR} \qquad (8)$$



$$\mathrm{Ph}\cdot + \mathrm{ICH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} \longrightarrow \left[\begin{array}{c} \mathrm{Ph}\cdot\;\;\dot{\mathrm{I}}\;\;\dot{\mathrm{C}}\mathrm{H_2{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} \\ \updownarrow \\ \mathrm{Ph}^{+}\;\;\dot{\mathrm{I}}\;\;\bar{\mathrm{C}}\mathrm{H_2{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} \\ \updownarrow \\ \mathrm{Ph}^{+}\;\;\dot{\mathrm{I}}\;\;\mathrm{CH_2{=}}\overset{{}^{-}\mathrm{O}}{\overset{|}{\mathrm{C}}}\mathrm{OR} \end{array}\right]^{\ddagger} \longrightarrow \text{products} \qquad (9)$$

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(21) S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *J. Org. Chem.*, **35**, 1722 (1970).

(22) P. J. Krusic and J. K. Kochi, unpublished results. We acknowledge the consideration of Dr. P. J. Krusic who supplied us with a preprint of this work.

(23) P. S. Skell, *Chem. Soc., Spec. Publ.*, **No. 19**, 131 (1965).

(24) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 241.

(25) This estimate is arrived at by taking half the difference in $D(R-I)$ for ethyl iodide and iodobenzene, 51 (or 53)[26] and 57 kcal/mol, respectively.[27] It is conceivable, however, that iodine abstraction does not involve a simultaneous R–I bond breaking and Ph–I bond forming but rather occurs in two steps with the formation of a phenylalkyliodine radical intermediate.[3]

(26) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

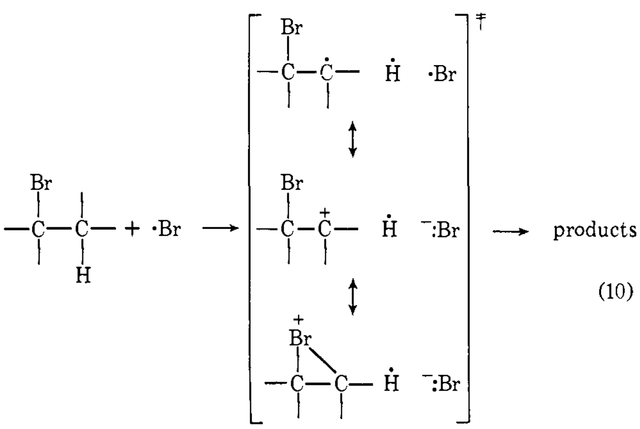
(27) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958, p 270.

(28) Reference 16, Table 5.

(29) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

pretation suffers from the fact that electron spin resonance studies have indicated that resonance delocalization of an unpaired electron in such α-carbonyl radicals is relatively unimportant.[30,31] This is also in agreement with the low reactivity to abstraction of α-hydrogens in aliphatic acids and esters, at least with electrophilic radicals, since the electron-withdrawing deactivating influence of the carboxy group overrides any stabilization due to delocalization. Both or either of these effects would exert a stabilizing influence in the present case and the observed deviations from the Taft correlation are not unexpected especially if it is recalled that the Taft substituent constants measure purely inductive effects and are not meant to apply to situations where direct delocalization of charge as depicted above is possible.

The latter interpretation also brings up an important consideration which has apparently been overlooked by authors concerned with anchimeric assistance in hydrogen abstraction studies. Insofar as neighboring group participation in many solvolysis reactions is well documented, oftentimes causing dramatic rate enhancement,[32] and since the carbon atom from which the hydrogen is being removed acquires cationic character in the transition state, it would seem that an adjacent bromine, sulfur, etc. substituent should likewise be effective in stabilizing the incipient positive charge in the homolytic reaction. In solvolyses, as in homolytic reactions, neighboring group participation is particularly effective when an anti orientation of leaving group and assisting substituent is possible, although a syn configuration may also produce some anchimeric assistance. Therefore, it is possible that a part of what has been attributed to anchimeric assistance in homolytic hydrogen abstraction reactions arises not from stabilization of a *radical site* by a neighboring bromine, sulfur, etc. group but rather stabilization of the *cationic character* developed in the transition state of a hydrogen abstraction process. The former mode of participation by, *e.g.*, a β-bromine, would presumably involve low lying unfilled d orbitals of the bromine while the latter would utilize a pair of electrons from a filled p orbital. One could conceivably test this hypothesis by a suitable choice of substituent groups.



(10)

Although the extent of participation, if any, in this manner by a neighboring group in hydrogen abstraction reactions is not presently known, a similar mode of stabilization in halogen abstraction processes does not seem likely because of the differences in charge distribution in the transition states of the two processes. The development of anionic character on the carbon from which the halogen is being removed precludes any significant participation of the type discussed above and assures that it is indeed the free radical which is being stabilized. The present results, therefore, appear to be best explained by invoking anchimeric assistance by a β-bromine and γ-iodine in the homolytic abstraction of an iodine atom.

This work also allows a comparison of halogen abstraction by the phenyl radical with the extensive hydrogen abstraction results of Bridger and Russell.[33] Thus, the 19% increase in relative reactivity of primary hydrogen atoms of methyl groups attached to quaternary carbon atoms (*e.g.*, neopentane and hexamethylethane) as compared to all other primary hydrogen atoms is paralleled by a 27% decrease in relative reactivity for iodine abstraction in going from ethyl iodide to neopentyl iodide. These results are precisely those expected from a consideration of polar effects on the rates of hydrogen and halogen abstraction. There is nothing unique about a methyl or iodomethyl group attached to a quaternary carbon; the inductive effect due to the accumulation of electron-donating substituents enhances the rate of hydrogen abstraction and retards iodine abstraction as anticipated. Moreover, there is a systematic decrease in reactivity of the primary iodide in the series ethyl iodide, *n*-butyl iodide, isobutyl iodide, neopentyl iodide; a similar decrease in reactivity of secondary iodides upon accumulation of alkyl groups can be noted from the data in Table I. Hence, the reactivity of an atom of a certain type (primary, secondary, etc.) is not invariant even in saturated hydrocarbon molecules. These results also indicate that alkyl groups even in saturated systems do have an inductive order of electron release increasing from methyl through *tert*-butyl.[34]

Experimental Section

Most of the compounds used in this study were commercially available and purified in all cases by either distillation or recrystallization until at least 99% pure as determined by gas–liquid phase chromatography (glpc). 1-Chloro-2-iodoethane was synthesized by the reaction of 2-iodoethanol and thionyl chloride; bp 61° (49 mm) [lit.[35] 140° (760 mm)]. 1-Bromo-2-iodoethane was conveniently synthesized in nearly quantitative yield by the reaction of iodine monobromide in glacial acetic acid[36] with ethylene according to the method of Simpson;[37] mp 28–29° (lit.[37] 28°). Neopentyl iodide was prepared from the commercially available neopentyl chloride by formation of the lithium compound followed by reaction with iodine in cyclohexane; bp 66–67° (100 mm) [lit.[38] 70° (100 mm)].

The relative rates reported in Table I were determined by weighing appropriate amounts of PAT, bromotrichloromethane, and iodo compound directly into Pyrex ampoules, degassing by the freeze–thaw method, and sealing the ampoules under vacuum. The PAT concentration was *ca.* 0.10 *M* in most experiments; the ratio of iodo compound to bromotrichloromethane varied depending

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[30] G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967).

[31] H. Fischer, *Z. Naturforsch. A*, **20**, 428 (1965).

[32] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 561.

[33] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

[34] P. v. R. Schleyer and C. W. Woodworth, *ibid.*, **90**, 6528 (1968).

[35] I. J. Lorenz and J. Auer, *Angew. Chem., Int. Ed. Engl.*, **4**, 241 (1965).

[36] W. Militzer, *J. Amer. Chem. Soc.*, **60**, 256 (1938).

[37] M. Simpson, *Ber.*, **7**, 130 (1874).

[38] F. C. Whitmore, E. L. Wittle, and B. R. Harriman, *J. Amer. Chem. Soc.*, **61**, 1585 (1939).

upon solubility and/or reactivity of the alkyl iodide but there was always maintained at least a tenfold excess of iodo compound to PAT. The sealed ampoules were wrapped in aluminum foil to exclude light and placed in an oil bath maintained at 60.0 ± 0.1° for 4 hr, after which time the ampoules were removed and opened, and an appropriate external standard for glpc analysis was added.

The yields of iodobenzene and bromobenzene were determined by glpc employing a Hewlett-Packard F&M Model 700-231 gas chromatograph equipped with thermal conductivity detectors. The analyses were conducted utilizing 6 ft × $^1/_4$ in. columns with liquid-phase packing of SE-30, Carbowax 20M, or FFAP on Chromosorb W, 60–80 mesh. Areas under the peaks were determined by tracing with a planimeter and a correction was applied to the areas obtained to account for the difference in detector sensitivity to iodobenzene and bromobenzene. The relative rates were calculated from eq 3 and reported in Table I.

Irradiation of Eucarvone in Polar Media

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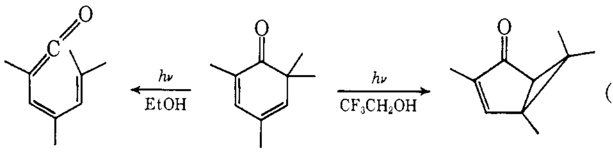
Abstract: The present study extends to a 2,4-cycloheptadienone a polar medium effect previously observed with 2,4-cyclohexadienones. The $\lambda_{\max}$ of eucarvone (**1**) is bathochromically shifted in highly polar media, from 303 nm in ethanol to 310 nm in trifluoroethanol (TFE) to 318 nm when adsorbed on silica gel suspended in cyclohexane (SGC). Irradiation through Pyrex of **1** on SGC is rapid compared with similar irradiation in cyclohexane solution. In addition to previously observed photoproducts of **1**, two new compounds were observed: 3,7,7-trimethylbicyclo[4.1.0]hept-2-en-4-one (**5**) and 1,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (**6**). Two photoisomers of **1**, the Büchi isomer 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one (**2a**, major product) and compound **5** (minor product, up to 20% of the photolysis mixture), are produced initially. These photoisomerize further, as confirmed by separate irradiations. Compound **5** undergoes a photochemical vinylcyclopropane–cyclopentene rearrangement to **6** and dehydrocamphor (**4**), whereas **2a** undergoes the familiar 1,3-acyl migration (to 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one (**2b**)) very slowly in highly polar media. Similar results were obtained by irradiating **1** in TFE solution. The formation of **4–6** in TFE was not quenched by piperylene or 1,3-cyclohexadiene. Silica gel and TFE do not seem to be functioning simply as proton donors, since only traces of 1,5,5-trimethyl-2-norbornen-7-one (**3**), an acid-catalyzed photoproduct of **1**, were obtained in these irradiations; furthermore, only **2a** and **3** were produced when **1** was irradiated in dioxane containing sulfuric acid; compounds **4–6** were not formed. The particular excited states of **1** which give rise to **2a** and **5** remain to be firmly identified, but they are predominantly singlet states.

Highly polar media alter the spectra and normal photoisomerization path of 2,4-cyclohexadienones.[1] Most conjugated cyclohexadienones show weak $n-\pi^*$ absorption at about 350 nm and a much more intense $\pi-\pi^*$ band at about 290–310 nm; when irradiated in ether, hexane, methanol, or other common solvents they produce ketenes,[2,3] probably from the $n-\pi^*$ singlet state.[3] Dissolution of the dienones in trifluoroethanol or adsorption on silica gel causes a large (10–40 nm, depending on substituents) bathochromic shift of the $\pi-\pi^*$ band. The band also broadens considerably, and because of its greater intensity it usually completely obscures the $n-\pi^*$ absorption band. When the dienones are irradiated under these conditions, they isomerize directly to bicyclo[3.1.0]hexenones rather than to ketenes; an example is shown in eq 1.



(1)

At least two explanations for this phenomenon are plausible. Since the $\pi-\pi^*$ state is more polar than the ground state, whereas the reverse is true for the $n-\pi^*$ state, polar solvents lower the energy of the former and raise that of the latter.[4] Exceedingly polar solvents such as CF_3CH_2OH or the silica gel surface may reverse the relative energies of the two states. Whereas ring opening to a ketene occurs from the $n-\pi^*$ state,[3] isomerization to the bicyclo[3.1.0]hexenone may be a $\pi-\pi^*$ singlet reaction of the dienone. If the $n-\pi^*$ and $\pi-\pi^*$ states of a molecule are not too far apart in energy (say 50 nm), such reversals by highly polar media may be general, and useful in altering the customary photochemistry of such molecules.

Alternatively, trifluoroethanol or silica gel may be functioning as proton donors, and one may be witnessing a $\pi-\pi^*$ photoisomerization of the protonated dienone (a hydroxybenzenonium ion). Low-temperature irradiations of such ions are now well established,[5] and would lead to intermediates which, by cyclopropylcarbinyl-type rearrangement,[6] would give the observed products (eq 2).

The present work, which involves the irradiation of eucarvone (**1**) adsorbed on silica gel or in trifluoro-

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