tion proceeds through two steps with the formation of a phenylaryliodine (IV) as an intermediate.[6] For the

$$\text{Ar–I} + \text{Ph}\cdot \longrightarrow \underset{\text{IV}}{\text{Ar–}\dot{\text{I}}\text{–Ph}} \longrightarrow \text{Ar}\cdot + \text{Ph–I}$$

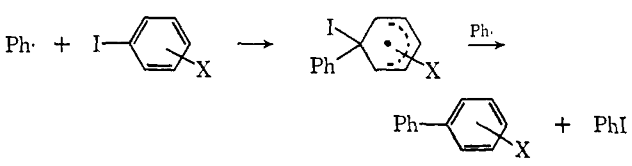
present discussion, a distinction between the two possible processes is unnecessary, the significant observation being the apparent accumulation in the transition state of excess charge on the carbon from which the iodine is being abstracted.

$$\overset{\delta^-}{\text{Ar}}\text{---}\overset{\delta^+}{\text{I}}\text{---Ph or }\overset{\delta^-}{\text{Ar}}\text{---}\overset{\delta^+}{\text{I}}\text{——Ph}$$

If it is assumed that the *meta* derivatives are well-behaved, it can be noted from Figure 1 that the *para*-substituted iodobenzenes appear somewhat less susceptible to iodine abstraction than expected. Although the data are by no means conclusive, this may reflect enhanced stability of the carbon–iodine bond of the substituted ring resulting from either substituent effects on the ground-state bond energies[7] or resonance stabilization of the presumed phenylaryliodine intermediate (*e.g.*, for *p*-iodonitrobenzene). However, this stabilization effect

is small and is almost completely overwhelmed by the more important polar contributions to bond cleavage.

It has been conclusively demonstrated that the phenyl radical indeed attacks the iodine atom rather than the carbon to which it is attached to form a phenyliodocyclohexadienyl radical analogous to the mechanism for homolytic arylation[8] and the free-radical interchange of halogens in aromatic compounds.[9] In view of phenylation studies on nitrobenzene which show enhanced reactivity of the *ortho* positions,[10] *o*-iodonitrobenzene would appear to be especially susceptible to attack by this process. In fact, less than 0.1% of *o*-nitrobiphenyl and approximately 80% iodobenzene were formed when *o*-iodonitrobenzene was allowed to react with PAT; the above mechanism demands formation of equal amounts of iodobenzene and *o*-nitrobiphenyl. This result also eliminates a direct SH2 displacement of iodine on carbon as a mechanistic possibility.[11]



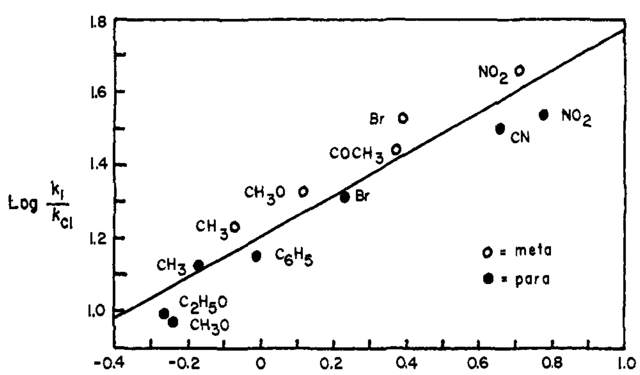


Figure 1. Plot of log $k_I k_{Cl}$ at 60° *vs*. Hammett σ constants (from the compilation by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958)). Each point represents the average of at least three independent experiments.

o-Iodonitrobenzene was found to be one of the more reactive compounds studied having $k_I/k_{Cl} = 186$.[12] An attempt to observe abstraction of bromine atom from *o*-bromonitrobenzene yielded less than 0.1% bromobenzene.

A series of *ortho*-substituted iodobenzenes were also studied, and an attempted Hammett correlation utilizing *ortho* σ constants specifically derived for such compounds[13] gave wide divergence. We believe that electrochemical reduction studies of such halogenated compounds are complicated by a rapid chemical reaction following electron transfer[14] and that the σ constants derived from such studies should not be applied to purely chemical processes.

Further work is in progress to learn more of the characteristics of the abstraction of halogen atoms from a variety of organic compounds.

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[6] H. E. Bachofner, F. M. Beringer, and L. Meites, *J. Am. Chem. Soc.*, **80**, 4269, 4274 (1958). We have attempted to determine the stability of the proposed phenylaryliodine intermediates (IV) presumably formed by electroreduction of several phenyliodonium salts. The cyclic voltammetry results were complicated by adsorption processes and no conclusive results were obtained. It was noted, however, that different results were observed when the electrode was changed from mercury to platinum. The absence of a reduction wave in the −0.2-V (sce) region utilizing platinum suggests that electrochemical studies of iodonium salts with a mercury electrode are probably complicated by chemical reactions of the substrate (or a reduced form of the substrate) with the electrode: O. A. Ptitsyna, S. I. Orlov, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1947 (1966); *Chem. Abstr.*, **66**, 75433 (1967).

[7] E. M. Kosower and I. Schwager, *J. Am. Chem. Soc.*, **86**, 5528 (1964); N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., 1958, p 83.

[8] It has been suggested that abstraction of iodine from iodobenzene by the trifluoromethyl radical proceeds through such a mechanism: R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, **62**, 128 (1966).

[9] B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *J. Am. Chem. Soc.*, **84**, 158 (1962); S. Levine and R. M. Noyes, *ibid.*, **80**, 2401 (1958).

[10] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, pp 57, 68.

[11] L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1753 (1967); *Chem. Commun.*, 754 (1968).

[12] This reactivity parallels the high reactivity of *o*-iodonitrobenzene in Ullmann coupling reactions: M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[13] W. W. Hussey and A. J. Diefenderfer, *J. Am. Chem. Soc.*, **89**, 5359 (1967).

[14] W. C. Danen, T. T. Kensler, J. G. Lawless, and M. D. Hawley, *J. Phys. Chem.*, in press.

[15] National Science Foundation Undergraduate Research Participant, Summer 1968.

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Received June 2, 1969

Ionic Dehydration of Aliphatic Alcohols in the Gas Phase

Sir:

The oxygen–proton–oxygen grouping is known to be important in the clustering of ions in the gas phase[1–3]

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[1] P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).

[2] P. Kebarle, R. N. Haynes, and J. G. Collins, *ibid.*, **89**, 5793 (1967).

[3] G. R. A. Johnson and G. Scholes, Ed., "The Chemistry of Ionization and Excitation," Taylor and Francis, New York, N. Y., 1967.

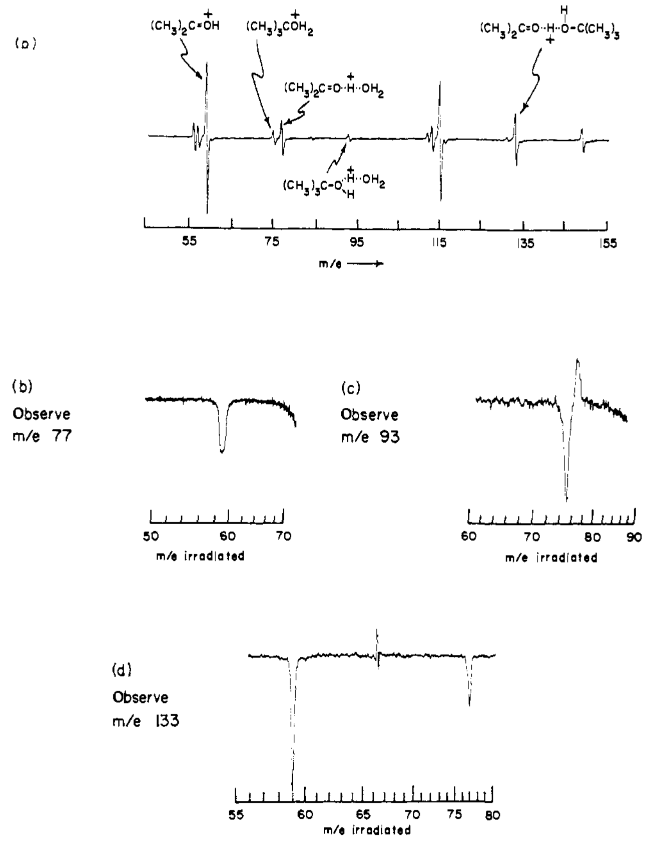


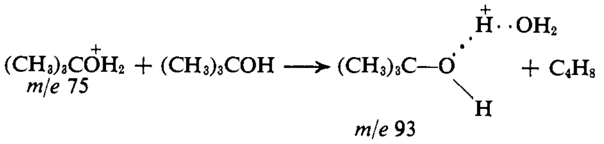
Figure 1. (a) Single-resonance spectrum of *t*-butyl alcohol at 2 × 10^{-6} Torr with 13.0-eV electron energy. Ionic species pertinent to the discussion in the text are identified. Pulsed double-resonance spectra of the products ions at (b) *m/e* 77, (c) *m/e* 93, and (d) *m/e* 133 are presented.

and has been observed and studied as well in certain crystalline solids,[4] notably the carboxylic acid salts.[5] In an examination of the ion chemistry of aliphatic alcohols[6] utilizing ion cyclotron resonance spectroscopy,[7] it has been found that the oxygen–proton–oxygen grouping is also of importance in the bimolecular ionic dehydration reaction (eq 1) where RH^+ is an oxygenated species possessing an acidic proton on oxygen, R′OH is an aliphatic alcohol, and R″ is the generated alkene product. *t*-Butyl alcohol serves as an example.

$$RH^+ + R'OH \longrightarrow R\cdots\overset{+}{H}\cdots OH_2 + R'' \qquad (1)$$

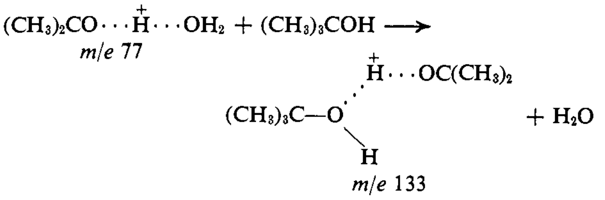
The base peak (comprising 82% of the total ionization) in the mass spectrum of *t*-butyl alcohol at 13.0 eV is the α-cleavage product corresponding to protonated acetone. This species undergoes a sequence of reactions with the parent neutral, giving rise to the majority of the product ion peaks evident in the single-resonance spectrum (Figure 1a). The pulsed double-resonance spectrum of the product ion at *m/e* 77 (Figure 1b) identifies[7] *m/e* 59 as the precursor ion, indicating the reaction which proceeds with a bimolecular rate constant $k = 3.7 \pm 0.5 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.[7,8] While other structures for the ionic product of reaction 2 can be postulated, the observation that the protonated parent undergoes a similar reaction (as confirmed by the double-resonance spectrum in Figure 1c)

$$\underset{m/e\ 59}{(CH_3)_2\overset{+}{C}OH} + (CH_3)_3COH \longrightarrow \underset{m/e\ 77}{(CH_3)_2CO\cdots\overset{+}{H}\cdots OH_2} + C_4H_8 \qquad (2)$$



$$\underset{m/e\ 75}{(CH_3)_3C\overset{+}{O}H_2} + (CH_3)_3COH \longrightarrow \underset{m/e\ 93}{(CH_3)_3C{-}O(H)\cdots\overset{+}{H}\cdots OH_2} + C_4H_8 \qquad (3)$$

suggests that the dehydration process is associated only with the presence of a labile proton on oxygen. In a subsequent collision the water molecule in the ionic product of reaction 2 is displaced by $(CH_3)_3COH$ (Figure 1d), attesting to a loosely bound complex.[9]



$$\underset{m/e\ 77}{(CH_3)_2CO\cdots\overset{+}{H}\cdots OH_2} + (CH_3)_3COH \longrightarrow \underset{m/e\ 133}{(CH_3)_3C{-}O(H)\cdots\overset{+}{H}\cdots OC(CH_3)_2} + H_2O \qquad (4)$$

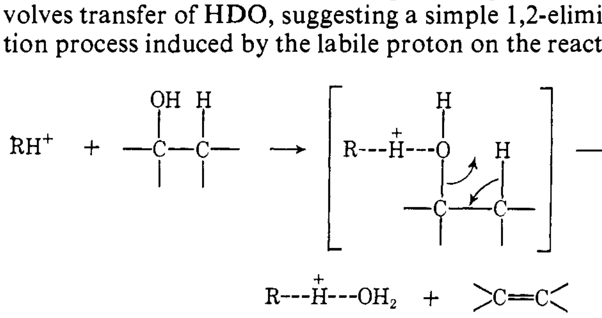
The energy of the "proton bond" in the above complexes can be estimated from the data of Kebarle and coworkers,[1,2] from whose work the enthalpy change for the two clustering reactions 5 and 6 can be approximated as −36 and −37 kcal/mole, respectively. Since the dehydration process 7 is endothermic by only 14 kcal/mole, reactions 2 and 3 are exothermic by as much as 20–30 kcal/mole.

$$H_3O^+ + H_2O \longrightarrow (H_2O)_2H^+ \qquad (5)$$

$$CH_3\overset{+}{O}H_2 + CH_3OH \longrightarrow (CH_3OH)_2H^+ \qquad (6)$$

$$(CH_3)_3COH \longrightarrow H_2O + C_4H_8 \qquad (7)$$

The dehydration reaction 1 has been observed as well in 2-propanol, 2-butanol, and cyclopentanol.[6] Curiously it is not observed in the case of ethanol.[10] With $(CD_3)_2CHOH$ the reaction analogous to process 3 involves transfer of HDO, suggesting a simple 1,2-elimination process induced by the labile proton on the reactant



(8)

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[4] A. F. Beecham, A. C. Hurley, M. F. Mackay, V. W. Master, and A. M. Mathieson, *J. Chem. Phys.*, **49**, 3312 (1968)

[5] G. Ferguson, J. G. Sime, J. V. Speakman, and R. Young, *Chem. Commun.*, 162 (1968).

[6] J. L. Beauchamp, to be published.

[7] For a recent description of the techniques employed, see M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

[8] The total ionization cross section of $(CH_3)_3COH$ for 75-eV electrons was estimated as 15 Å^2 to determine the pressure for the purpose of measuring reaction rates.

[9] As is evident in the double-resonance spectrum in Figure 1c, it is also possible to displace $(CH_3)_2CO$ from the ionic product of reaction 2. The sign of the double-resonance spectrum indicates that the rate of this process increases with increasing ion energy [J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968)].

[10] L. W. Sieck, J. H. Futrell, and F. P. Abramson, *ibid.*, **45**, 2859 (1966).

ion (eq 8). The dehydration of aliphatic alcohols in contact with acidic sites on catalysts, such as γ-aluminum oxide, may proceed through a similar intermediate.[11] Previously it has been suggested that such processes involve two active sites on the catalyst surface.[11] By way of contrast to the present observations, it is of interest to note in unimolecular ion chemistry that 1,2-elimination processes are not prevalent, it being postulated that the distances for abstraction from adjacent carbons are too great.[12] Further mechanistic details of this interesting reaction are under investigation.

[11] H. Knözinger, *Angew. Chem. Intern. Ed. Engl.*, **7**, 791 (1968), and references contained therein.

[12] See M. M. Green and R. J. Cook, *J. Am. Chem. Soc.*, **91**, 2129 (1969), and references contained therein.

[13] Alfred P. Sloan Fellow, 1968–1970. The author acknowledges the support of this research by the U. S. Atomic Energy Commission under Grant AT(04-3)767-8.

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Received July 7, 1969

Nuclear Magnetic Resonance Spectroscopy. Effects of Molecular Asymmetry on Carbon-13 Chemical Shifts[1]

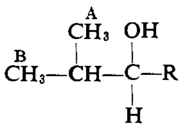
Sir:

A nearby center of molecular asymmetry often induces magnetic nonequivalence of the protons of an isopropyl group (or of a methylene group), and this phenomenon has been the subject of many investigations.[2] We report here the first observance of the effect of molecular asymmetry on the resonances of methyl carbons in isopropyl groups in compounds of the type $(CH_3)_2CH(CH_2)_nCHR_1R_2$.

For substantial nonequivalence of protons, it is usually considered necessary to have a preferred conformation(s) wherein the protons are in quite different magnetic environments. The occurrence or nonoccurrence of nonequivalence thus provides a rather sensitive probe for preferences. In many cases, the chemical-shift differences are small, and the method becomes impractical or even inapplicable.

The very substantial sensitivity of ^{13}C chemical shifts to conformational changes[3] and steric effects[4] and the relatively large magnitudes[3,4] of the resulting chemical-shift effects suggest that there should be considerable utility of ^{13}C nmr in studies of magnetic nonequivalence of the carbons associated with molecular asymmetry.[2] The utility is expected to be enhanced by proton decoupling which would allow easy observance of ^{13}C chemical shifts even where there are very complex proton-spin systems.

The ^{13}C chemical shifts (measured with proton decoupling as previously described)[3b] of the methyl carbons of isopropyl groups in isopropylalkylcarbinols of type **1** appear in Table I. The degree of nonequivalence of the methyl groups A and B increases very substantially in the change of R from methyl to ethyl to isopropyl to *t*-butyl in accord with an important nonbonded 1,5 CH_3–CH_3 interaction. When R is methyl, the difference $\nu_A - \nu_B$ is small and probably reflects the difference between a 1,4 CH_3–CH_3 interaction[4] and a 1,4 CH_3–OH interaction.[3] When R is ethyl, or a group more bulky than ethyl, the usual steric arguments[3,4] fail to explain the large shifts encountered, and it appears that a 1,5 CH_3–CH_3 interaction needs to be invoked which produces a *downfield* shift.



$$\overset{\text{B}}{\mathrm{CH_3}}-\overset{\overset{\text{A}}{\mathrm{CH_3}}}{\mathrm{CH}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{R}$$

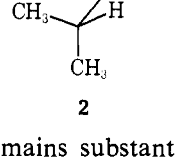
1

Table I. Magnetic Nonequivalence of the Methyl Carbons of Isopropylalkylcarbinols $(CH_3)_2CHCH(OH)R$

R	$\nu_A{}^a$	$\nu_B{}^a$	$\nu_A - \nu_B$
Methyl	174.5	174.3	0.2
Ethyl	175.1	173.6	1.5
n-Propyl	175.1	173.7	1.4
Isopropyl	175.3	172.6	2.7[b]
t-Butyl	175.7	168.8	6.9

[a] Shifts are in ppm relative to carbon disulfide. The designations A and B are more or less arbitrary (see text). [b] The observation of this shift indicates that the present arguments pertain equally well to disymmetric molecules.

The source of the large shift difference between the methyl carbons (A and B) of the isopropyl group with increasing R seems most reasonably to arise through increases in the population of, and steric effects operating in, conformers of type **2** in which the large alkyl groups are positioned most favorably between CH_3 and H, not between CH_3 and CH_3.[5,5a] That **2** is more favored than **3** with R = $(CH_3)_3C$ is perhaps unexpected in that **2** has two *gauche* CH_3–OH interactions while **3** has only one and a H–OH interaction. However, it will be seen that, if the CH_3–R interaction in **2** is large enough to cause considerable departure from the perfect staggered arrangement, then the interaction between the other CH_3 and the OH group is diminished. With **3**, departure from the staggered arrangement would increase the CH_3–OH interaction. One methyl resonance remains substantially unchanged as R is varied (see Table I), and this fact is in accord with **2** as the favored conformation and suggests that ν_A corresponds to the methyl between hydrogen and hydroxyl in **2**.



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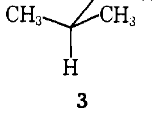

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[1] Supported in part by the Public Health Service, Research Grant 11072-05-06 from the Division of General Medical Sciences, and the National Science Foundation. We are pleased to acknowledge the help and suggestions of Dr. Frank J. Weigert in the course of this work.

[2] For references, see M. van Gorkom and G. E. Hall, *Quart. Rev.* (London), **22**, 14 (1968).

[3] (a) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967); (b) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *ibid.*, in press.

[4] D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315 (1967).

[5] Evidence for this comes from changes in the vicinal H,H couplings in **1** as R is increased in size. There is some change between R = H (J = 6.24 Hz) and R = $(CH_3)_2CH$ (J = 5.6 Hz), and a much larger change for R = $(CH_3)_3C$ (J = 2.4 Hz). The latter value is consistent with **2** as the exclusive conformation.

[5a] NOTE ADDED IN PROOF. Substantial proportions of conformations having *gauche* interactions involving *t*-butyl groups have been observed in other systems: D. C. Best, G. Underwood, and C. A. Kingsbury, *Chem. Commun.*, 627 (1969).