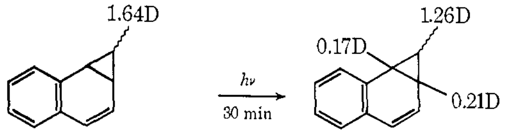
it was observed to have undergone deuterium scrambling into the two remaining cyclopropyl positions (eq 4). This result can be rationalized by invoking two

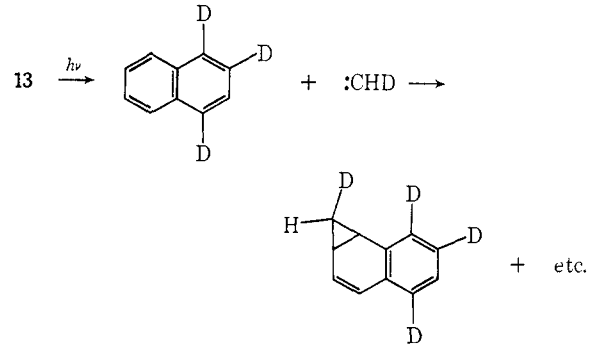


(4)

9

Berson–Willcott Bones rearrangement isomers, **10** and **11** (Scheme I). In support of the intermediacy of **12**, and therefore of **11**, is the presence of **7** in irradiations of **1** run to partial completion. Furthermore, the 3,4-benzotropilidene-d_2 produced from irradiation (5–10 min)[8] of **9** was shown by nmr spectroscopy (mixture with **9**) to be identical with authentic **12**,[3a] since its nmr spectrum showed two vinyl doublets, one being somewhat broadened. These results, therefore, provide the first direct evidence of a photochemical rearrangement of this type occurring in both directions.[14]

An additional mechanistic interpretation of the above observations deserves consideration. Methylene extrusion–readdition could explain the observed labeling patterns. By employing 1,4,6,7-tetradeuteriobenzonorcaradiene (**13**)[3b,15] such a sequence was eliminated since methylene extrusion–readdition would be expected to lead to products with aromatic deuterium (eq 5). Oxidation (alkaline permanganate) of the reaction mixture from irradiation of **13** followed by esterification



(5)

with diazomethane produced dimethyl phthalate which contained, within experimental error (*ca.* 1%), no deuterium, as determined by low-voltage mass spectroscopy.

The photochemistry of **1** can therefore be summarized as shown in Scheme II.[16]

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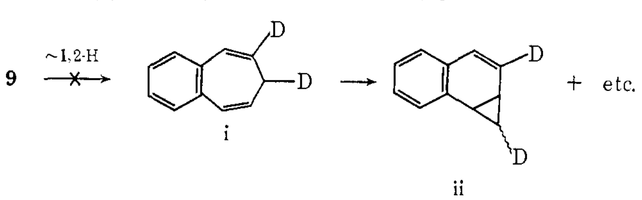
[14] That a hydrogen-shift mechanism is not operative and that **11** and **12** are intermediates in the photorearrangement of **9** can be deduced from additional evidence. If the 3,4-benzotropilidene produced in the reaction came about by a hydrogen-shift mechanism i would be produced. This would in turn lead to a benzonorcaradiene with vinyl deuterium (ii);[3a] this is, however, not observed (eq 4).



[15] The photorearrangement results with 1,4,6,7-tetradeuteriobenzonorcaradiene are consistent with those of **9**.

[16] In a given irradiation of **9**, comparison of the amount of deuterium scrambling to the amount of naphthalene formed indicates that rearrangement occurs more rapidly than methylene extrusion.

Nuclear Magnetic Resonance Studies of Ion Association

Sir:

In recent years the fundamental theories of ion association have undergone continued revision and discussion.[1] Manifestations of solute–solvent interactions as evidenced by the dependence of the ion-pair contact distance on solvent[2] and dielectric constant,[3] and the often observed deviation[1] from linearity of plots of the logarithm of the association constant *vs.* reciprocal dielectric constant have drawn increasing attention to the inadequacy of present theories.[4] With the hope of bringing new information to bear on the problem, we have initiated a study of the association of methyltributylammonium tetraphenylboride (MB) in nonaqueous solvents by nuclear magnetic resonance techniques.

The α-methyl resonance of methyltributylammonium picrate appears 192 Hz downfield from TMS in a 0.05 *M* chloroform solution, and in the limit of infinite dilution approaches a resonance frequency 197 Hz downfield from TMS. In contrast, the α-methyl resonance of a 0.05 *M* chloroform solution of MB appears only 80 Hz downfield from TMS. This unusually large upfield shift (greater than 100 Hz) can only be due to the formation of associated species in which the α-methyl of the cation is in close proximity to the phenyl rings[5] of the anion. It is likely that at these concentrations in a low dielectric solvent such as chloroform highly associated species are present.[6] However, proper choice of higher dielectric solvents and concentration ranges should facilitate the isolation and study of an ion, ion pair equilibrium (*vide infra*).

Rapid exchange between free ions and the associated species results in only one α-methyl resonance, this being a weighted average of the contribution of free and paired ions to the observed resonance frequency, ν_{obsd}.

$$\nu_{\text{obsd}} = \gamma\nu_{\text{free}} + (1 - \gamma)\nu_{\text{paired}} \qquad (1)$$

γ is the fraction of free ions, and ν_{paired} and ν_{free} are the resonance frequencies of paired and free ions, respectively. As the picrate anion has only a slight effect on the α-methyl resonance of the cation, ν_{free} can accurately be determined by extrapolation of the α-methyl resonance of methyltributylammonium picrate to infinite dilution.

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(1) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968), and references therein.

(2) (a) R. M. Fuoss and E. Hirsch, *J. Amer. Chem. Soc.*, **82**, 1013 (1960); (b) D. S. Berns and R. M. Fuoss, *ibid.*, **82**, 5585 (1960).

(3) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

(4) (a) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958); (b) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

(5) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, p 140.

(6) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, New York, N. Y., 1959, p 249.

A shift *vs.* concentration analysis[7] was used to obtain an ion association constant, K, and limiting shift, Δ, where $K = (1 - \gamma)/C\gamma^2$, C is the stoichiometric salt concentration, and $\Delta = \nu_{\text{paired}} - \nu_{\text{free}}$. Concentration ranges studied were generally from about 0.004 to 0.1 *M*. Samples were run on a Varian A-60-A spectrometer and chemical shifts relative to internal TMS (~1% v/v) were determined by standard side-band techniques. A computer of average transients was used when needed.

Although in the solvents studied the salt concentrations exceed the limits of applicability of Debye-Hückel theory,[8] we attempted to introduce extended Debye-Hückel activity coefficients to the analysis. This yielded extremely large values for Δ (greater than 400 Hz) which are physically unreasonable, and subsequently the data were analyzed without applying corrections due to ionic atmosphere effects. A simple ion-pair mechansim[7] describes the data well, no experimental point being more than 0.25 Hz from its calculated value.

Table I. Association of Methyltributylammonium Tetraphenylboride in Various Nonaqueous Solvents

Solvent	Dielectric constant[a,b]	K_{nmr}, l./mole[a]	$-\Delta$, limiting shift, Hz	$K_{\text{conductivity}}$ l./mole[c]
Acetonitrile	34.3	1.25 ± 0.3	75 ± 10	6.0,[d] 2.2,[e] 0.0[f]
Nitromethane	34.2	1.55 ± 0.3	80 ± 10	0.0[f]
Nitrobenzene	32.2	4.9 ± 0.9	79 ± 10	4.7[g]
Benzonitrile	24.0	20.0 ± 3.0	33 ± 2	
Acetone	19.3	25.0 ± 3.0	32 ± 1	91.0[e]

[a] At 40 ± 2°. [b] Estimated using data provided in A. A. Maryott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular No. 514, U. S. Government Printing Office, Washington, D. C., issued Aug 1951. [c] At 25°. [d] Reference 2b. [e] J. F. Coetzee and D. K. McGuire, *J. Phys. Chem.*, **67**, 1810 (1963). [f] J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, **87**, 2529 (1965). [g] Reference 2a.

Table I displays the results for five solvents and conductivity results for the analogous tetrabutylammonium salt, when available. The association constant increases and the limiting shift decreases as the dielectric is lowered. The trend for the nmr association constant is qualitatively in agreement with simple theory,[4] although there is marked curvature in a log K *vs.* $1/D$ plot. The trend in the limiting shift provides new information. ν_{free} and ν_{paired} depend explicitly on the magnetic environment of the solvent. We assume Δ is only a function of the average distance between the α-methyl group of the cation and the phenyl rings[5] of the anion in an ion pair for a given solvent because of the large magnetic anisotropy of the phenyl rings of the anion. Note that Δ is approximately the same in the three nearly isodielectric solvents, nitromethane, acetonitrile, and nitrobenzene. This fact and the magnitude of the shift suggest that a considerable fraction of the ion pairs are of the contact variety in the above-mentioned solvents. The much smaller limiting shifts in benzonitrile and acetone indicate that the ion pair on the average is not as "tight" as it is in the higher dielectric solvents. It must be emphasized that continuum theory[4] predicts that the interionic distance will be independent of both solvent and dielectric constant. Our findings are consistent with recent conductivity experiments which have revealed the general tendency of the contact distance in an ion pair to increase at lower dielectric constant, an effect possibly attributable to solute-solvent interaction.[3] Other effects possibly due to specific solvation are the increase of the effective Stokes radius of ions at lower dielectric constant[9] and the nonlinearity of plots of log K *vs.* $1/D$.[10] We believe our results represent independent experimental observation of specific solute-solvent interactions.[11]

The temperature dependence of the chemical shifts is of extreme interest. Present theories[4] of ion association predict less association at lower temperatures and it is generally assumed[4b] that the interionic distance will be temperature independent as well. Thus one expects the α-methyl resonance to be shifted *downfield* at lower temperature. In all our studies the α-methyl resonance appeared further *upfield* at lower temperature (relative to the value of ν_{free} at that temperature), indicating either greater association or the formation of "tighter" ion pairs.[12]

Inasmuch as the alkylammonium tetraphenylborides have served as model salts in the investigation of the "sphere in continuum" model[14] of ion association, we believe the observed trend in limiting shifts and the temperature dependence effects provide further evidence questioning the validity of this model of association. The nmr method provides an independent means for obtaining both association constants *and* information pertaining to interionic separations. The usefulness of this technique and the questions raised here concerning the current theories[4] of ion association have prompted us to undertake a more complete study of the problem.

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[7] For methods of calculation see, for example (a) I. D. Kuntz and M. D. Johnston, *J. Amer. Chem. Soc.*, **89**, 6008 (1967); (b) R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).

[8] Reference 6, p 106.

(9) D. F. Evans and P. Gardam, *J. Phys. Chem.*, **73**, 158 (1969).

(10) H. K. Bodenseh and J. B. Ramsey, *ibid.*, **67**, 140 (1963).

(11) Alternatively, Bjerrum's model [N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, 7, No. 9 (1926)] which predicts formation of more distant ion pairs at lower dielectric may be more applicable than the currently accepted Fuoss-Denison-Ramsey[4] model which allows for the formation of contact ion pairs only: G. Atkinson and S. Petrucci, *J. Phys. Chem.*, **70**, 3122 (1966).

(12) It is interesting to note that Larsen[13] observed the same temperature dependence in his nmr studies of the association of the tetramethylammonium ion with the hexacyanoferrate(III) ion in water.

(13) D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, **4**, 1281 (1965).

(14) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1871 (1963).

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Hydroplatination of an Acyclic Diolefin

Sir:

The reaction of diene-platinum(II) halide complexes with alkoxides,[1] amines,[2] and carbanions[3] proceeds by nucleophilic attack on one of the diene double bonds to afford σ-bonded organoplatinum complexes (**1**, Y = nucleophile). We wish to report an unusual reaction

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(1) J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, **88**, 5135 (1966), and references therein.

(2) G. Paiaro, A. DeRenzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967).

(3) H. Takahashi and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 2387 (1968).