Table II. Observed Rate Constants for the Imidazole-Catalyzed Hydrolysis of *p*-Nitrophenyl Acetate in Water Pools Dissolved in Octane at 25.0°

[Imidazole][a]	[I][b]	$[H_2O]$[c]	R[d]	10^3k_{obsd}, sec^{-1}
0.805	0.105	2.76	26	6.68[e]
0.805	0.105	2.76	26	6.70
0.805	0.104	2.76	26	6.82
0.805	0.0523	1.38	26	3.76
0.805	0.0262	0.689	26	2.08
0.805	0.0131	0.344	26	1.15
0.805	0.105	1.10	10	2.34
0.402	0.099	3.86	39	4.50
0.402	0.105	2.76	26	3.20
0.402	0.0523	1.38	26	1.79
0.402	0.105	1.10	10	1.13
0.201	0.099	3.86	39	2.22
0.200	0.105	2.76	26	1.66
0.200	0.104	2.73	26	1.72
0.200	0.0523	1.38	26	0.950
0.100	0.105	2.76	26	0.783
0.100	0.0523	1.38	26	0.489

[a] Total concentration of imidazole in the water pools. [b] Concentration of di-2-ethylhexyl sodium sulfosuccinate in the octane-water solution. [c] pH 8.00. [d] $R = [H_2O]/[I]$. [e] The corresponding bimolecular rate constant (9.1×10^{-3} M^{-1} sec^{-1}) is approximately 53 times slower than that for the same reaction in bulk water.

taneously by dilution with pure octane. The rate constants were found to decrease proportionally with the dilution factor. The simplest explanation is that the concentration of the micelles—but not their size—decreases with decreasing [I] as long as a constant $[H_2O]/[I]$ ratio is maintained. Such behavior was assumed in calculating molecular weights from light scattering data.

Only a small solvent isotope effect was observed when deuterium oxide was substituted for water ($k_{H_2O}/k_{D_2O} = 1.10$). We infer that imidazole within the micelles, as in bulk water,[13] performs as a nucleophile rather than as a general base toward *p*-nitrophenyl acetate.

One final experiment deserves mention. Two octane-I-water solutions were prepared, one containing imidazole and the other containing an ionic substrate, *p*-nitrophenyl *p'*-guanidinobenzoate hydrochloride (*p*-NPGB), in the water pools. These solutions were equilibrated at 25.0°, mixed, and observed spectrophotometrically at 400 nm. The *p*-NPGB was found to hydrolyze at a significant rate, although 57 times slower than *p*-nitrophenyl acetate at equal concentrations of imidazole, water, and I.[14] Clearly, imidazole in one set of micelles is able to "communicate" with *p*-NPGB in the second set. Either the water pools merge and separate rapidly (despite their surfactant shells), or else the reactants travel among the micelles with surprising ease.

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(13) T. C. Bruice and S. J. Benkovic, *J. Amer. Chem. Soc.*, **86**, 418 (1964).

(14) *p*-NPGB reacts 12 times slower with imidazole in bulk water than does *p*-nitrophenyl acetate.

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Electron Spin Resonance Studies of Ion Pairs in Solutions of Cation Radicals

Sir:

The technique of electron spin resonance (esr) spectroscopy has had great success in recent years in providing detailed information on the ion pairs existing in solutions of anion radicals in various solvents and with several different counterions.[1,2] The effects observed include hyperfine splittings from the counterion, *g* shifts from the free ion value, perturbation of proton hyperfine splittings, and the study of several types of equilibria. Somewhat surprisingly, no observations of ion-pair effects in solutions of cation radicals have been reported and it is the purpose of this communication to present esr evidence for the existence of ion pairs in these solutions.

The usual methods of preparation of cation radicals include oxidation by compounds such as H_2SO_4, $AlCl_3$, $SbCl_5$, BF_3, etc., in solvent of high dielectric constant. Certainly these conditions are not favorable for the observation of effects due to the formation of ion pairs. The counterions in these systems are not simple species, and the solvents have high solvating powers thus preventing close approach of the ion pairs. Oxidation with bromine or iodine is sometimes successful with easily oxidized compounds and under these conditions one might expect the counteranion to be simply Br^- or I^-. Combining these oxidants with solvents of lower dielectric constant would seem most likely to produce effects due to ion-pair formation.

In view of the above considerations, the 1,2,4,5-tetramethoxybenzene (TMB) cation radical was selected as a model system in which to search for the effects of ion pairing. $TMB\cdot^+$ has previously been generated by electrochemical oxidation[3] and by chemical oxidation in H_2SO_4 and $AlCl_3$-CH_3NO_2,[4] and its esr spectrum is characteristically simple ($a^H_{OCH_3} = 2.20$ G, $a^H_{CH} = 0.85$ G) consisting of groups of 1:2:1 triplets. The oxidation potential of TMB is 0.82 V[3] which indicates that oxidation by bromine should also be successful. This proved to be the case and allowed us to investigate $TMB\cdot^+$ in a variety of solvents. In each case the radical was produced by reaction in an evacuated system using dried and degassed solvents. For bromine oxidations care was taken to use the minimum amount of bromine required to produce an esr signal.[5] The radical was identified in each solvent by its proton splittings which remained essentially constant in all solvents. The most interesting results were those of the *g* factors which are shown in Table I. The large positive *g* shifts observed for the bromine-chloroform and bromine-methylene chloride systems are attributed to the formation of ion pairs in these solvents. Solvent effects alone have much less effect on the *g* value as seen from the results using aluminum chloride as the oxidizing agent (see Table I).

Assuming that ion pairs are formed in $CHCl_3$ and CH_2Cl_2, one might ask why hyperfine splittings from the

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(1) M. C. R. Symons, *J. Phys. Chem.*, 71, 139 (1967).

(2) T. Takeshita and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6421 (1971), and references cited therein.

(3) A. Zweig, W. G. Hodgson, and W. H. Jura, *ibid.*, **86**, 4124 (1964).

(4) W. F. Forbes and P. D. Sullivan, *J. Chem. Phys.*, **48**, 1411 (1968).

(5) In this way effects due to the presence of molecular bromine are thought to be minimal.

Table I. *g* Values and Line Widths for the TMB Cation Radical

Oxidation system[a]	*g* value[b,c]	*g* shift × 10^5 [d]	Line width, G
Br_2-CH_3NO_2	2.00401	5	0.07
Br_2-CH_3CN	2.00399	3	0.09
Br_2-CH_2Cl_2	2.00440	44	0.27
Br_2-$CHCl_3$	2.00472	76	0.34
$AlCl_3$-CH_3NO_2	2.00396	0	0.04
$AlCl_3$-CH_2Cl_2	2.00406	10	0.06
$AlCl_3$-$CHCl_3$	2.00403	7	0.08

[a] All measurements are for a temperature of −20°. [b] *g* values were measured in dual sample cavity relative to the perylene radical anion whose *g* value is taken to be 2.00267. [c] All measured values are ±0.00001. [d] *g* shift relative to the *g* value of the $AlCl_3$-CH_3NO_2 system.

counteranions are not observed.[6] This is most easily rationalized in terms of the mechanisms leading to the hyperfine splitting, for halide anions electron transfer would place unpaired spin density in the p orbital which must in turn spin polarize the s electrons before hyperfine splitting is observed. For alkali metal cations direct electron transfer into the s orbital is, however, possible. One might expect that hyperfine splittings are much more likely for alkali metal cations than for halide anions.

The sign and magnitude of the observed *g* shifts can be compared with shifts observed for the alkali metal naphthalenide systems.[7] The largest *g* shift observed is for cesium–naphthalene which has a shift of -17×10^{-5}. Simple considerations of *g* tensors allow us to explain the positive *g* shift of halide ion pairs as opposed to the negative *g* shift of alkali metal ion pairs.[8] The much larger magnitude of the *g* shift of $Br^{-}TMB\cdot^{+}$ is undoubtedly due to the larger spin–orbit coupling constant of bromine as compared to cesium (*i.e.*, 2400 and 369 cm^{-1}, respectively).

Additional experiments have indicated that the observed *g* shifts are temperature dependent. For $TMB\cdot^{+}$ in Br_2-$CHCl_3$ the *g* shift changes from 80×10^{-5} at +20° to 73×10^{-5} at −60°. This is probably due to an increase in solvation as the temperature is decreased.

Another compound which is readily oxidized by bromine is 1,4-diethoxy-2,5-diethylthiobenzene. This compound is found to give *g* shifts similar to TMB. For example, in Br_2-CH_3NO_2, $g = 2.00696$; in Br_2-$CHCl_3$, $g = 2.00767$, a shift of $+71 \times 10^{-5}$.

From the above results it is concluded that for the first time direct esr evidence has been obtained for the formation of ion pairs in solutions of simple organic cation radicals. These results open up the possibility of further study of ion pairs of cation radicals which, in view of the many interesting results found for ion pairs of anion radicals, is certainly an area worthy of further investigation.

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[6] Additional splittings have been observed in dilute solutions of $TMB\cdot^{-}$ in Br_2-CH_2Cl_2. The origin of these splittings is presently in doubt and they may be due to secondary radicals.

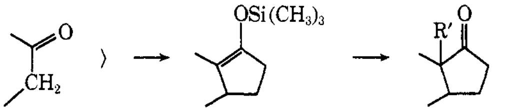
[7] W. G. Williams, R. J. Pritchett, and G. K. Frankel, *J. Chem. Phys.*, 52, 5584 (1970).

[8] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 138.

New Synthetic Reactions. Cyclopentane Annelation

Sir:

The discovery of many important natural products containing five-membered rings such as the prostaglandins,[1] several sesquiterpene antibiotics,[2] and various flavor and fragrance principles[3] requires new methods for cyclopentane synthesis. We wish to report a method of annealing a cyclopentane ring onto a carbonyl compound possessing an adjacent methyl or methylene unit with the further ability to introduce additional alkyl groups regiospecifically as illustrated in eq 1.



(1)

Condensation of diphenylsulfonium cyclopropylide[4] with carbonyl groups generates oxaspiropentanes in isolated yields of approximately 90% in most cases (see Scheme I).[5,6] For example, use of 1.0 equiv of sulfonium salt per 1.0 equiv of cyclopentanone with a reaction time of 3 hr produced the corresponding oxaspiropentane in 94% yield. Treatment of this compound with lithium diethylamide in hexane at room temperature effected ring opening with formation of 1-cyclopentenyl-1′-cyclopropanol.[7,8] Work-up of the

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[1] For some recent synthetic efforts see T. K. Schaaf and E. J. Corey, *J. Org. Chem.*, 37, 2921 (1972), and references therein; M. P. L. Caton, E. C. J. Coffee, and G. L. Watkins, *Tetrahedron Lett.*, 773 (1972); E. J. Corey and T. Ravindranathan, *ibid.*, 4753 (1971); C. J. Sih, R. G. Salomon, P. Price, R. Sood, and G. Peruzzotti, *ibid.*, 2435 (1972), and references therein; H. L. Slates, Z. S. Zelawski, D. Taub, and N. L. Wendler, *Chem. Commun.*, 304 (1972); J. Fried, C. H. Lin, J. C. Sih, P. Dalven, and G. F. Cooper, *J. Amer. Chem. Soc.*, 94, 4342 (1972); J. Fried, J. C. Sih, C. H. Lin, and P. Dalven, *ibid.*, 94, 4343 (1972), and references therein; P. Crabbe, A. Cervantes, and A. Guzman, *Tetrahedron Lett.*, 1123 (1972).

[2] For example, hirsutic acid [F. W. Comer, F. McCapra, I. H. Oureshi, and A. I. Scott, *Tetrahedron*, 23, 4761 (1967); F. W. Comer and J. Trotter, *J. Chem. Soc. B*, 11 (1966)] and pentalenolactone [D. G. Martin, G. Slomp, S. Mizsak, D. J. Duchamp, and C. G. Chidester, *Tetrahedron Lett.*, 4901 (1970); S. Takeuchi, Y. Ogawa, and H. Yonehara, *ibid.*, 2737 (1969)]. For recent efforts toward hirsutic acid, see P. T. Lansbury, N. Y. Wang, and J. E. Rhodes, *Tetrahedron Lett.*, 2053 (1972); F. Sakan, H. Hashimoto, and A. Ichihara, *ibid.*, 3703 (1971).

[3] For some recent synthetic efforts see J. A. Marshall, W. F. Huffman, and J. A. Ruth, *J. Amer. Chem. Soc.*, 94, 4691 (1972); J. A. Marshall and A. E. Greene, *J. Org. Chem.*, 37, 982 (1972); J. E. McMurry and T. E. Glass, *Tetrahedron Lett.*, 2575 (1971); G. Büchi and B. Egger, *J. Org. Chem.*, 36, 2021 (1971); J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, 93, 5309 (1971).

[4] B. M. Trost and M. J. Bogdanowicz, *ibid.*, 93, 3773 (1971).

[5] M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, 887 (1972).

[6] Complete spectral characterization and elemental composition confirm the structural assignment. Copies of spectra are available upon request from the authors.

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[8] For other methods of preparation of 1-vinylcyclopropanols see H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, 91, 2375 (1969); H. H. Wasserman, H. W. Adickes, and O. Espejo de Ochoa, *ibid.*, 93, 5586 (1971); J. R. Conia and J. M. Conia, *Tetrahedron Lett.*, 2849 (1972).