

# Studies in Magnetic Resonance. X.<sup>1</sup> The Spectroscopy of Carbanions and the Effect of Ion Pairing on Chemical Shifts

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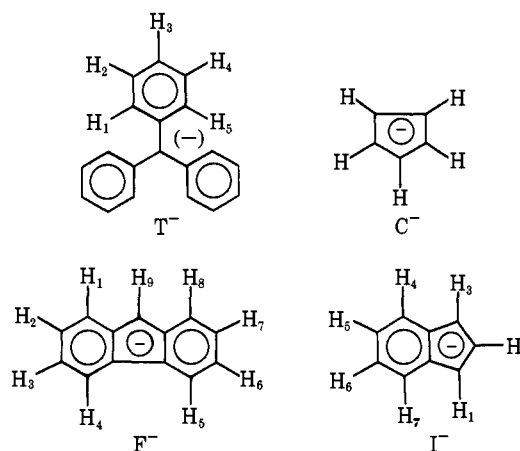
**Abstract:** The nmr spectra of the triphenylmethanide, fluorenone, indenide, and cyclopentadienide ions have been investigated over the temperature range  $-40$  to  $80^\circ$  with each of the alkali metal cations in diethyl ether, THF, and DME. Chemical shift differences detected in the anion spectra with changing conditions have been interpreted in terms of an equilibrium between contact and solvent-separated ion pairs. The factors controlling the equilibrium have been studied and the enthalpy and entropy of the process evaluated in favorable cases. The interpretation of these quantities is discussed.

Until quite recently, the role of the alkali metal cation and the solvent in controlling the course of carbanion reactions has been little understood.<sup>3</sup> The present study was undertaken in an attempt to establish the importance of these factors and to try to find a general method for investigation of this problem. The findings described here are concerned with the determination of the environment of the carbanion in these solutions and how it is altered by the cation, the solvent, the temperature and the type of carbanion. The results clearly show that what had often been considered as "sleeping partners" can control the form of the carbanion in solution. Nmr spectroscopy has been used extensively in this investigation and has proved to be a very useful and general tool for studying these systems.

While this work was in progress, other investigators,<sup>4-11</sup> using a variety of techniques, have contributed greatly to our knowledge of carbanion solutions. Particular mention must be made of the pioneering work of Szwarc and his school<sup>4</sup> which established the presence of an equilibrium between contact and solvent-separated ion pairs in similar systems and hence rationalized many diverse observations scattered through the literature. Our results are very much in accord with this theory.

The aromatic carbanions triphenylmethanide ( $T^-$ ), fluorenone ( $F^-$ ), indenide ( $I^-$ ), and cyclopentadienide ( $C^-$ ) were selected for this investigation since they could be prepared cleanly in several solvents with each of the alkali metal cations, have a wide range of basicities,

and were stable over extended periods when protected from the atmosphere.



## Results

### Carbanion Nmr Spectra. (i) Triphenylmethanide Ion.

The spectrum of the triphenylmethanide ion shown here (Figure 1) is essentially the same as that reported by Sandel and Freedman.<sup>12</sup> There are small differences between the reported coupling constants and those given here, which probably arise from a comparison of first order and complete analysis results. It is possible that this ion could exist in a number of conformers, e.g., a symmetric propellor, two rings and the center carbon atom planar and the third ring tilted out of this plane, etc. Work on the related fluorine-substituted carbonium ion<sup>13</sup> reveals that such forms can exist but are interconverting rapidly on the nmr time scale. In addition, the triphenylmethyl carbonium ion has been shown to prefer the symmetrical propellor conformation in the solid state.<sup>14</sup> Under all conditions used in the present study, the spectrum of the carbanion was only consistent with a structure in which all phenyl rings were equivalent on the nmr time scale. The six ortho protons [ $H(1)$  and  $H(5)$ ] and the six meta protons [ $H(2)$  and  $H(4)$ ] were also equivalent on the nmr time scale. Thus the carbanion must exist as the symmetrical propellor form or be rapidly interconverting between

(1) (a) Part IX, *Org. Magn. Resonance*, **1**, 103 (1969); (b) from the Ph.D. Thesis, J. B. Grutzner, University of Melbourne, Australia, 1967. This work was presented at the International Symposium on Nuclear Magnetic Resonance, Birmingham, July 1969 (abstracted by Zentralstelle für Atom kern energie).

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(3) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(4) (a) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968; (b) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

(5) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967).

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(8) N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968).

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Table I. Spectral Analysis Results for Carbanions<sup>a</sup>

	Cation	Solvent <sup>b</sup>	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$	$\delta_5$	$\delta_9$	$J_{12}$	$J_{13}$	$J_{14}$	$J_{15}$	$J_{23}$	$J_{24}$	
Triphenylmethanide	Li	Et <sub>2</sub> O	7.2815	6.798	6.312				8.19	1.17	0.47	2.27	7.16	1.67	
	Na	Et <sub>2</sub> O	7.3375	6.705	6.175				8.18	1.18	0.46	2.27	7.06	1.68	
	Na	DME	7.260	6.513	5.951				8.18	1.18	0.46	2.25	6.95	1.68	
Fluorenone	Li	Et <sub>2</sub> O	7.3995	6.9685	6.672	7.982		5.815	8.17	1.06	0.83	6.67	1.17	7.99	0.08
	Na	THF	7.381	6.861	6.509	7.9655		5.993	8.03	1.05	0.77	6.59	1.19	7.71	0.90
	Na	THF <sup>c</sup>	7.376	6.899	6.546	8.004		6.035	8.16	1.08	0.81	6.65	0.94	7.85	0.68
	Li	THF <sup>c</sup>	7.209	6.728	6.353	7.816		5.819	8.05	1.04	0.66	6.60	0.91	7.74	0.63
	Li	DME	7.2465	6.741	6.361	6.840		5.9275	8.06	1.01	0.76	6.55	1.19	7.71	0.70
Indenide	Na	THF	5.932	6.5985		7.308	7.3965		3.30	0.75	0.75	8.05	1.14	0.82	6.46
	Na	THF <sup>d</sup>							3.23			7.97	1.13	0.80	6.17

<sup>a</sup> All chemical shifts are in parts per million downfield from TMS and all coupling constants are in hertz. The final analyses gave the sum of squares of residuals less than 0.05, and all lines were assigned to better than 0.1 Hz. <sup>b</sup> DME = 1,2-dimethoxyethane, THF = tetrahydrofuran, Et<sub>2</sub>O = diethyl ether. <sup>c</sup> Reference 7. <sup>d</sup> W. B. Smith, W. H. Watson, and S. Chiranjeeri, *J. Amer. Chem. Soc.*, **89**, 1438 (1967).

such structures as will result in the same symmetrical form. The spectra were analyzed using the computer program LAOCN3,<sup>15</sup> as an AA'MM'Y spin system, and the results are given in Table I. The assignment of the chemical shifts to the appropriate protons was readily made on the basis of multiplicities and intensities.

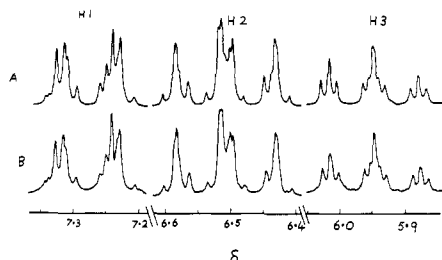


Figure 1. Nmr spectrum (100 MHz) of sodium triphenylmethanide in DME: (A) calculated, (B) experimental.

(ii) **Fluorenone Ion.** There have been several reports of the fluorenone ion spectra in the literature<sup>7,16,17</sup> which are in general agreement with the data presented here (Table I) (Figure 2). In the past, electron density arguments have been used to assign chemical shifts, and these are now confirmed by a rigorous argument employing the observed coupling constants. For the purpose of analysis, the ion can be treated as two equivalent AMRX systems with one proton of each group coupled to an external proton [H(9)] and no other interaction between the two groups. Multiplicities produce an initial assignment, and then the observation that each of the vicinal and allylic couplings in the six-membered ring are different permitted the determination of the sequence of protons around the ring. Finally, the detection of the well-known<sup>18</sup> five-bond inter-ring coupling between H(4) and H(9) allowed the unambiguous assignment of each of the resonances. The spin analysis results are given in Table I. No other long-range coupling greater than 0.3 Hz could be detected in the spectrum. Our results for the sodium

salt in tetrahydrofuran are in fair agreement with those reported by Cox<sup>7</sup> for the same system (see Table I).

(iii) **Indenide Ion.** The present report of the indenide spectrum (Figure 3) is in close agreement with those published previously.<sup>16,19</sup> The spin analysis of the ion was performed using two separate systems, an AA'XX' and an AA'X, with a long-range interaction between

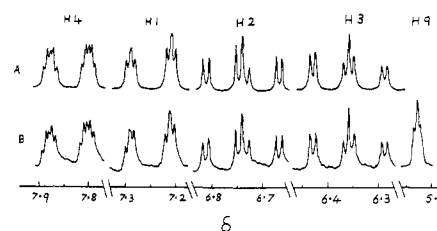


Figure 2. Nmr spectrum (100 MHz) of lithium fluorenone in DME: (A) calculated, (B) experimental.

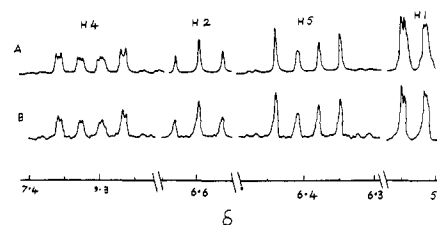


Figure 3. Nmr spectrum (100 MHz) of sodium indenide in THF: (A) calculated, (B) experimental.

the two. Owing to the large number of overlapping lines and the symmetry of the spectrum, a complete iterative analysis was not possible. However, after initial analysis of the three- and four-spin systems separately, the whole spectrum was calculated for a number of possible values of the long-range inter-ring and cross-ring couplings, and the final values given in Table I were chosen on the basis of the close agreement between the calculated and observed spectra. Smith, *et al.*,<sup>19</sup> obtained similar results, and these are given in the table for comparison. Once again the five-bond inter-ring coupling between H(1) and H(4) allowed the unambiguous assignment of the six-membered ring

(15) S. Castellano and A. A. Bothner-By, Mellon Institute, Pittsburgh, Pa., 1966.

(16) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(17) J. A. Dixon, P. A. Gwinner and D. C. Lini, *J. Amer. Chem. Soc.*, **87**, 1379 (1965).

(18) S. Sternhell, *Quart. Rev. Chem. Soc.*, **23**, 236 (1969).

(19) W. B. Smith, W. H. Watson, and S. Chiranjeeri, *J. Amer. Chem. Soc.*, **89**, 1438 (1967).

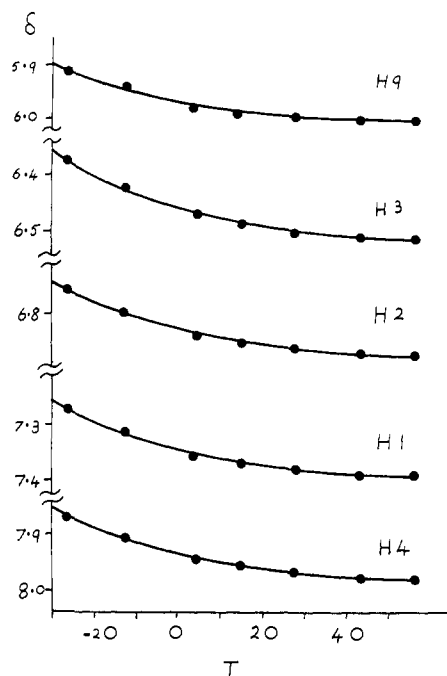


Figure 4. Chemical shift of sodium fluorene in THF as a function of temperature.

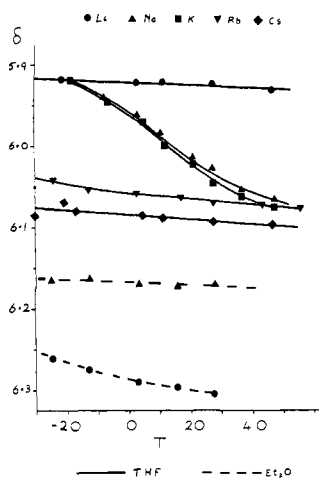


Figure 5. Chemical shift of H(3) of triphenylmethanide ion in THF and  $\text{Et}_2\text{O}$  as a function of cation and temperature.

protons. In several cases the multiplets due to H(2) and to H(5) and H(6) overlapped and since in all cases the observed spectra were the simple superposition of these multiplets, the coupling constant between these groups must be very close to zero (as was assumed in the analysis).

**(iv) Cyclopentadienide Ion.** The spectrum of the cyclopentadienide ion has been reported by several authors.<sup>16, 20, 21</sup> It consisted of a single sharp line for all samples studied. The observed line width was never greater than the limit set by instrumental inhomogeneities (usually *ca.* 0.3 Hz.).

**Coupling Constants.** The coupling constant differences between samples of the ion with different cations and solvents are real and are readily observed by compari-

(20) J. R. Leto, F. A. Cotton, and J. S. Waugh, *Nature (London)*, **180**, 978 (1957).

(21) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

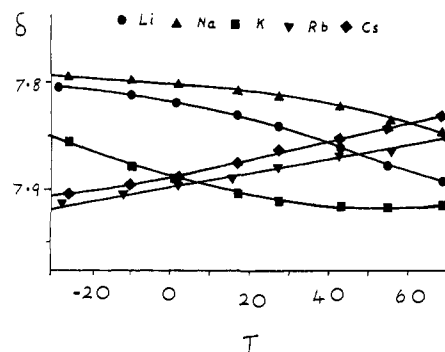


Figure 6. Chemical shift of H(4) of fluorene ion in DME as a function of cation and temperature.

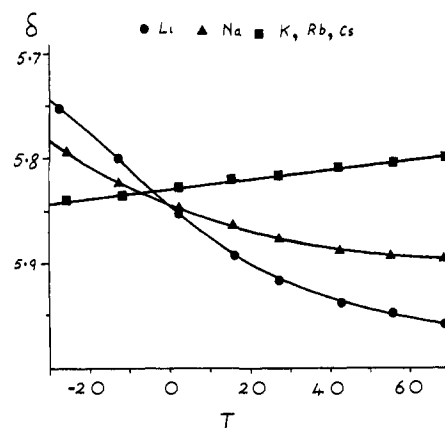


Figure 7. Chemical shift of H(1) of indenide ion in DME as a function of cation and temperature.

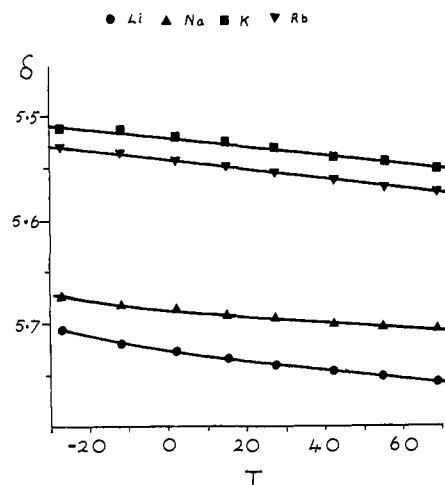


Figure 8. Chemical shift of cyclopentadienide ion in DME as a function of cation and temperature.

son of the appropriate spectra. These differences appear to correlate with the distance between the cation and the anion (see below) so that as the separation of the ions increases, the vicinal coupling constants decrease. Similar observations have been made by other workers<sup>22</sup> and suggest that the coupling constants are determined at least in part by local electric fields.

(22) J. B. Merry and J. H. Goldstein, *ibid.*, **88**, 5560 (1966).

Table II. Chemical Shifts for Triphenylmethide Ion

Cation	DME					THF					Et <sub>2</sub> O				
	Temp, °C	$\delta_1$	$\delta_2$	$\delta_3$	% <sup>a</sup>	Temp, °C	$\delta_1$	$\delta_2$	$\delta_3$	% <sup>a</sup>	Temp, °C	$\delta_1$	$\delta_2$	$\delta_3$	% <sup>a</sup>
Li	56.0	7.277	6.507	5.9425	100	46.6	7.271	6.494	5.9325	100	27.3	7.2855	6.7955	6.306	0
	27.3	7.268	6.5125	5.945	100	27.3	7.275	6.484	5.925	100	-24.9	7.332	6.747	6.2625	~5
Na	68.5	7.2605	6.533	5.9595	~80	47.3	7.292	6.6165	6.067	21	27.3	7.336	6.708	6.171	0
	27.3	7.266	6.508	5.9405	~95	27.3	7.296	6.580	6.029	38	-24.9		6.695	6.165	0
K	-28.4	7.2825	6.501	5.933	100	-7.7	7.301	6.497	5.940	77					
	68.5	7.235	6.601	6.034	41	46.9	7.288	6.6205	6.076	22	27.3	7.225	6.673	6.110	
Rb	27.3	7.262	6.5465	5.9815	68	27.3	7.299	6.598	6.048	32					
	-27.5	7.2745	6.495	5.928	94	-18.0	7.295	6.471	5.918	78					
Cs	68.1	7.249	6.6435	6.0775	15	55.5	7.2205	6.634	6.078	0					
	27.3	7.2755	6.6145	6.051	24	27.3	7.277	6.6275	6.0715	0					
Cs	-28.1	7.3005	6.5395	5.975	55	-24.3	7.2855	6.605	6.049	0					
	57.0		6.662	6.1045	0	46.2		6.6445	6.098	0					
	27.3	7.265	6.647	6.0915	0	27.3	7.225	6.638	6.0935	0					
	-17.2		6.6305	6.075	~5	-31.0	7.2575	6.6255	6.075	0					

<sup>a</sup> Per cent solvent-separated ion pairs.

A correlation of vicinal coupling constants in aromatic systems with  $\pi$ -bond orders has been given by several authors.<sup>19,23</sup> A discussion of the reasons behind this dependence has been given by Smith, *et al.*<sup>19</sup> The coupling constants obtained here support the correlation. While the results fall within the limits set by the equation of Smith, *et al.*, the original equation of Dailey, *et al.*,<sup>23</sup> provides a better fit of the present data; *i.e.*,  $J = 12.7P - 1.1$ , where  $P$  is the  $\pi$ -bond order determined from VESCF calculations.<sup>26</sup>

**Chemical Shifts.** The chemical shifts used in the following discussion were all determined from the center of gravity of multiplets. The shifts estimated in this manner differ from the more exact spin analysis values by at most a small constant amount (<0.02 ppm) and do not affect the arguments presented. Proton chemical shifts were determined for each anion over a range of conditions and were found to be dependent on temperature, cation, and solvent, but essentially independent of concentration. An individual proton resonance changed by up to 0.3 ppm as the conditions were varied. The most important feature is that all the shifts for a given carbanion proton, irrespective of the cation, solvent, temperature, or concentration employed, follow a simple sigmoid-type curve of chemical shift *vs.* temperature. The actual scaling of the curve and the portion of it observed in each case are governed by the conditions. Furthermore, each proton of a given carbanion shows the same behavior and differs only in the maximum change of the chemical shift axis. Some examples of these changes are shown in Figures 4-8, and an example of one set of data used to construct these figures is shown in Table II. These observations indicate that there is a rapid equilibrium between two distinct structures of the carbanion and that the position of the equilibrium is governed by the factors mentioned above. In the discussion it will be shown that the upfield form corresponds to a solvent-separated ion pair and the downfield form to a contact ion pair. These terms will be used in the remainder of this section for convenience. The H(1) proton of triphenylmethanide and the H(9) proton of fluorenyl ion have been excluded from these overall comments, since they

represent special cases which will be explained in the Discussion.

**Concentration Effects.** Detailed studies of the effect of concentration were carried out for the triphenylmethanide ion. This propellor-shaped ion should be essentially free of the concentration-dependent shifts observed for planar aromatic solutes (the other ions studied fall in this category), since intermolecular ring current effects will be minimized. It was found that the chemical shifts were only slightly dependent on concentration in the range of 0.02-0.8 *M*, and the observed changes were an order of magnitude smaller than those caused by changes of temperature. This rules out any concentration-dependent mechanism for the explanation of the temperature-dependent phenomena.

Systematic studies of the effects of changing concentration were not carried out with the other carbanions. However, some random observations of these planar aromatic ions showed a greater dependence on concentration than for triphenylmethanide ion, which still was less than that associated with the cation, solvent, and temperature. Concentration effects with the planar ions were greater when they existed as contact ion pairs and may possibly be related to the formation of triple ions or higher sandwich-like aggregates. Generally, an upfield shift with increasing concentration was observed, in accord with the idea that the changes are due to intermolecular ring current effects.<sup>24,25</sup> This observation has also been made for the cyclopentadienide ion in THF by Schaefer and Schneider.<sup>16</sup>

**Temperature Effects.** Over the available temperature range (upper limit was set by the boiling point of solvent and lower limit by the carbanion solubility or instrumental difficulties) the samples could be divided essentially into two classes: those that were markedly affected by temperature and those that were not. In the former class, decreasing temperature caused an upfield shift along a section of the sigmoid curve (Figures 5 and 6). In other words, lower temperatures favor solvent separation of the ion pairs. In every instance, the shift changes were completely reversible and only dependent on the temperature. Thus, the observed

(24) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962), and references cited therein.

(25) D. J. Blears and S. S. Danyluk, *J. Amer. Chem. Soc.*, **89**, 21 (1967).

(23) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

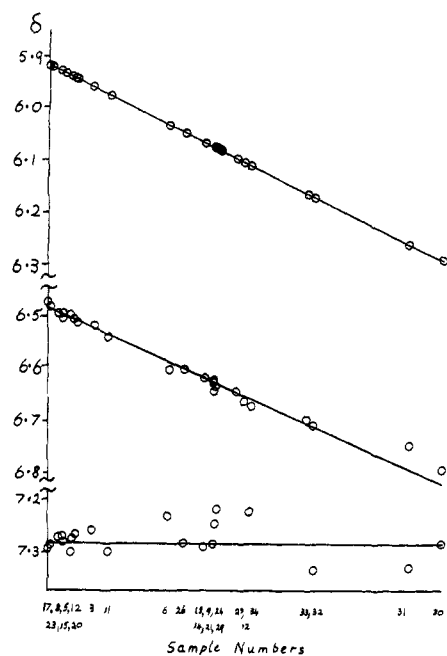


Figure 9. Correlation diagram for triphenylmethanide ion.

chemical shift can be used to determine the position of the equilibrium between the two forms of the carbanion and its dependence on temperature.

In the latter class there was little or no alteration of chemical shift, and one form of the carbanion predominated within the available temperature range. The decision whether the dominant species was the contact or solvent-separated pair was made from the observed chemical shift. Although the changes were small, an approximately linear downfield shift with decreasing temperature was detected for some members of this class. The effect was most clearly evident for those planar aromatic ions, especially as their cesium salts, which existed as contact ion pairs throughout. This was the same group that was most sensitive to the concentration changes noted above.

**Cation Effects.** There is a marked relationship between the size of the cation and the position of the equilibrium between contact and solvent-separated ion pairs—the smaller the cation, the greater the proportion of solvent-separated pairs. This is clearly shown in the figures. In addition, the size of the cation within the ion pair determines the proton shifts of the anion, so that the smaller the cation, the more downfield the proton shift. This is demonstrated for triphenylmethanide ion in Table III. The radii of the cations were assumed to be the Pauling ionic radii, and those of the solvated ions were taken from conductivity data. The change

Table III. Chemical Shifts of Triphenylmethanide as a Function of Cation Size

Cation	Radius, Å	$\delta_2$ , ppm	$\delta_3$ , ppm
Li	0.60	6.795	6.306
Na	0.95	6.707	6.170
Cs	1.67	6.641	6.089
M (DME) <sup>a</sup>	3.3	6.502	5.935
M (THF) <sup>a</sup>	4.1	6.485	5.928

<sup>a</sup> DME and THF solvated cations, respectively.

in chemical shift with cation size has been interpreted in terms of a polarization mechanism.<sup>7</sup> However, if this mechanism is operative, the changes induced in the triphenylmethanide ion by changing cation would require a change of 0.3 of an electron in the density of the central carbon. This does not seem reasonable. The shifts for each of the carbanions discussed here can be accounted for with a simple electrostatic model based on the Buckingham equation.<sup>26, 27</sup>

**Solvent Effects.** There is practically no solvent-induced shift, as such, between the ether solvents in these carbanion spectra. The lack of solvent shift is shown by the cases where the same form of the carbanion is present in each solvent (with the appropriate cation) and almost identical carbanion shifts are observed. The observed changes in chemical shift with changes in solvent, where they do occur, can be traced to solvent-induced changes in the position of the ion-pairing equilibrium. The equilibrium position changes (at constant cation and temperature) so that the order  $\text{Et}_2\text{O} < \text{THF} < \text{DME}$ , for the solvent-separated form, is observed.

## Discussion

**Nature of the Equilibrium.** The first point that must be established is that the observed changes in chemical shift have a common origin. One means of accomplishing this, for the triphenylmethanide and fluorenone ions at least, is through correlation diagrams (Figures 9 and 10). The conclusions deduced for these ions are reasonably carried over to the indenide and cyclopentadienide ions, where the data are not as extensive. The correlation diagram was constructed as follows: H(3) of the triphenylmethanide ion and H(4) of the fluorenone ion were chosen as "reference" protons which exemplify the overall trends. The particular samples of the carbanions in which each of these "reference" protons showed their extreme upfield and downfield shifts were selected and the shifts plotted at opposite ends of the abscissa, the scale of which was arbitrarily chosen. In effect, the arbitrary scale of the abscissa is proportional to the average separation (on the nmr time scale) of the cation and anion. A straight line was drawn between these selected reference points, and then all the other samples of each ion were ordered along the abscissa according to the shift of H(3) for triphenylmethanide or H(4) for fluorenone. In the triphenylmethanide case, the meta proton [H(2)] shifts follow the para proton [H(3)] shifts quite closely, and hence we conclude that the observed changes arise from a common source. On the other hand, the ortho proton [H(1)] shift shows very little variation. This anomaly, which has its origin in the small separation between this proton and the cation, is discussed in a subsequent paper.<sup>26</sup> A least-squares plot of the meta proton shifts *vs.* the para proton shifts gave a slope of 0.84, with a correlation coefficient of 0.990. On the other hand, the plot for the ortho protons showed essentially no correlation, as the correlation coefficient was 0.11. Similarly, for the fluorenone ion, the H(1), H(2), and H(3) shifts all correlate quite well with the H(4) shift, but the H(9) shift shows some variation. The results of the least-squares analysis for comparison with the H(4) shifts were: H(1)

(26) J. B. Grutzner and L. M. Jackman, *J. Amer. Chem. Soc.*, in press.

(27) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

slope 1.13, correlation coefficient 0.933; H(2) 0.99, 0.988; H(3) 1.14, 0.989; H(9) 1.46, 0.33.

Unfortunately, this presentation is not quite straightforward for the fluorenyl ion, since the H(2) and H(3) shifts also show a second correlation which is almost independent of the H(4) shift. Closer inspection shows that the samples which show this second correlation are just those which gave the anomalous concentration- and temperature-dependent shifts mentioned above. All these observations suggest that there is a second process occurring in these systems in addition to the main equilibrium under study here. This additional complication, which is favored by anion planarity, only interferes in those cases which exist as contact ion pairs (see below) over the available conditions. The present work was restricted to a detailed investigation of the equilibrium which gives rise to extensive chemical shift changes, and the secondary effect was not further studied. However, before leaving this question it is perhaps worth postulating some possible explanations for the phenomenon since it seems to be restricted to planar anions and contact ion pairs. An equilibrium involving triple ion or higher aggregate formation seems at present to be the most plausible explanation, but equilibria such as movement of the cation within the ion pair, change of the degree of solvation of the ion pair, or change in the vibrational structure of the ion pair cannot be ruled out. Hirota<sup>8</sup> has detected an equilibrium between two types of contact ion pair in esr studies of the sodium anthracene radical anion.

Now that it has been established that we are dealing with an effect which influences the anion as a whole, it is necessary to determine the equilibrium process which causes the observed sigmoid-type variation in chemical shift, controlled by cation, solvent, and temperature but not concentration. The arguments used to demonstrate that this is in fact an equilibrium between contact and solvent-separated ion pairs are essentially the same as those presented by Hogen-Esch and Smid<sup>4</sup> for the uv studies of the fluorenyl ion and will not be repeated here. It is sufficient to add that these ideas have been verified and elaborated in several subsequent carbanion studies.<sup>5-10, 28-34</sup> Thus the observed nmr behavior may be explained as follows. There is a rapid equilibrium between contact ion pairs (the low-field form of the carbanion) and solvent-separated ion pairs (the high-field form) and the position of this equilibrium which is governed by cation, anion, solvent, and temperature determines the observed chemical shift. The time scale for the interconversion between ion pair forms has been shown by esr studies on related systems<sup>8, 35</sup> to be of the order of  $10^{-8}$  sec and hence only the population average can be observed on the nmr time scale. That the assignment of the form of the carbanion which absorbs at higher field corresponds to the solvent-separated ion pair can be inferred from calculations of the effect of

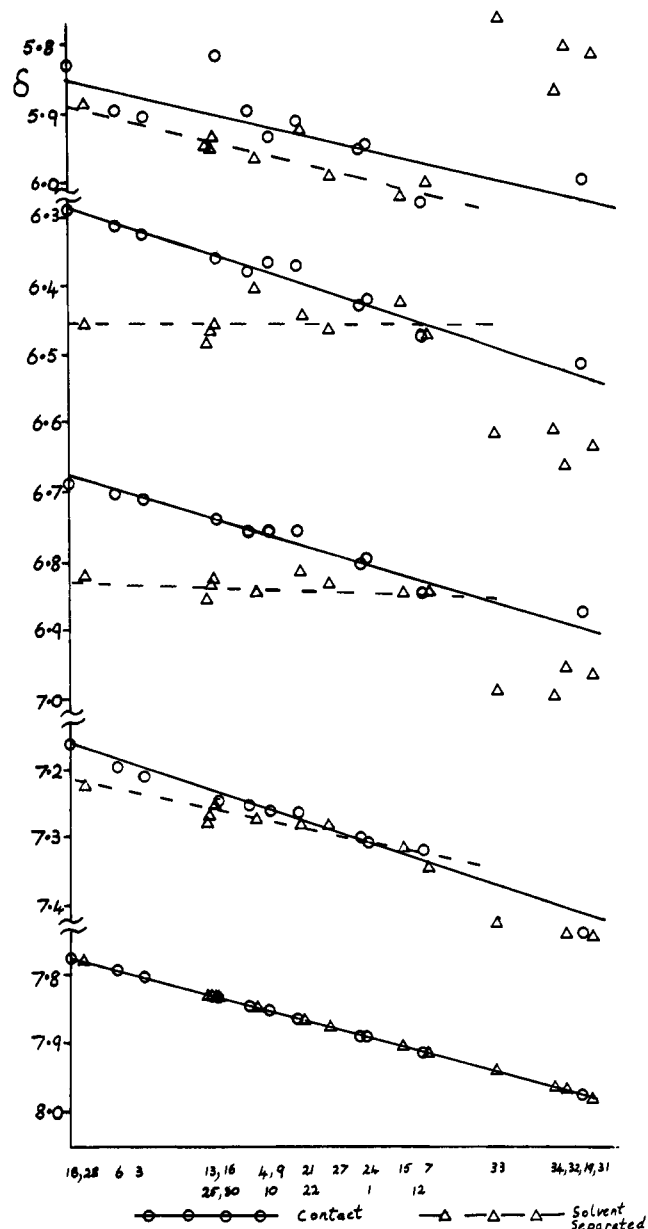


Figure 10. Correlation diagram for fluorenyl ion.

cationic size and charge on the chemical shift<sup>26</sup> and also by comparison with the uv results.

The equilibrium constant for the equilibrium between contact and solvent-separated ion pairs is given by

$$K = (\delta_0 - \delta_c) / (\delta_s - \delta_0) \quad (1)$$

where  $\delta_0$  is the chemical shift of a particular proton, and  $\delta_c$  and  $\delta_s$  are the limiting values for the contact and solvent-separated ion pairs, respectively. The enthalpy and entropy of ion pair interconversion were calculated from  $K$  vs.  $T$  data. This assumes that activity coefficients for the two species are similar, that only the two species of ion pairs exist under the conditions studied, and that  $\delta_c$  and  $\delta_s$  are temperature invariant. This last assumption was found to be valid in every system for which it could be tested. The accuracy of the chemical shift and temperature measurements is discussed in the Experimental Section.

In almost every case, the values of both  $\delta_c$  and  $\delta_s$  could not be obtained directly and had to be estimated. This

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(34) L. L. Chan and J. Smid, *ibid.*, **90**, 4645 (1968).

(35) R. Chang and C. S. Johnson, *ibid.*, **88**, 2338 (1966).

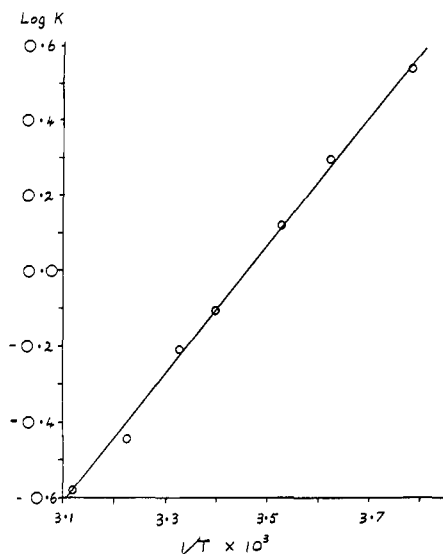


Figure 11. Plot of  $\ln K$  vs.  $1/T$  for contact  $\rightleftharpoons$  solvent-separated ion pair equilibrium shown by H(2) of sodium triphenylmethanide in THF.

estimate was very subjective in several cases, so a computational method was used to provide these values. Equilibrium constants were calculated from the data for each proton in the following manner. The input quantities required were the observed chemical shift, the temperature, and the estimated range of possible values of  $\delta_c$  and  $\delta_s$  for each proton of the carbanion. The value of  $\log K$  at each temperature was then calculated from eq 1 for each combination of the series of possible values of  $\delta_c$  and  $\delta_s$  which fell within the estimated limits. The linearity of the  $\ln K$  vs.  $1/T$  plot was computed for each combination, and the errors were obtained together with the enthalpies and entropies. The acceptable values for  $\delta_c$  and  $\delta_s$  were then selected on the basis of the standard deviation of the straight line. In most cases a limited range of combinations of  $\delta_c$  and  $\delta_s$  gave essentially the same minimum standard deviation, and the derived values of  $\Delta H$  and  $\Delta S$  were simply averaged to obtain their "best" values. An example of a  $\ln K$  vs.  $1/T$  plot obtained by this method is given in Figure 11. This procedure was performed for each proton in the carbanion, and the results were averaged to obtain  $\Delta H$  and  $\Delta S$  for each combination of cation, solvent, and carbanion. The final values for each cation and carbanion are given in matrix form in Table IV together with the results obtained by other workers.

Despite the approximations and uncertainties in this procedure, it has revealed several important trends and placed them on a quantitative scale. There are several reasons for believing that the results are valid within the limits of the experimental error of  $\pm 1$  kcal/mol and  $\pm 5$  eu. (1) The data obtained here by nmr and reported from uv studies by Hogen-Esch and Smid<sup>4</sup> for the fluorenone ion are in very good agreement (Table V). (2) Gaps for specific ion pairs in the enthalpy section of Table IV can be interpolated in several ways. When two different methods can be used for the same interpolation, they both yield similar values (e.g.,  $K^+F^-$  in THF; completing the square from other fluorenone cases gives 5.4 kcal/mol and, by comparison of all potassium samples, 5.45 kcal/mol). (3) Assuming a constant entropy change of  $-16$  cal/(deg mol) for DME

Table IV. Thermodynamic Quantities for Conversion of Contact into Solvent-Separated Ion Pairs

Anion <sup>a</sup>	Solvent	Cation			
		Li	Na	K	Rb
Enthalpy, kcal/mol					
T	THF		-8.2	-6.7	
T	DME			-5.3	-3.4
F	THF	<i>b</i>	-6.7 <sup>c</sup>		
F	DME	-5.6	-5.4	-4.1 <sup>d</sup>	
I	DME	-5.0	-3.5		
Entropy, cal/(deg mol)					
T	THF		-28	-23	
T	DME			-16	-13
F	THF		-27 <sup>c</sup>		
F	DME	-15	-17	-16	
I	DME	-20	-15		

<sup>a</sup> T = triphenylmethanide, F = fluorenone, I = indenide.  
<sup>b</sup> Lit.<sup>4</sup> -7.0 kcal/mol. <sup>c</sup> Lit.<sup>4</sup> -7.6 kcal/mol, -33 cal/(deg mol).  
<sup>d</sup> Lit.<sup>10</sup> -4.6 kcal/mol.

Table V. Comparison of Uv<sup>a</sup> and Nmr Results for Fluorenone Ion

Cation	Solvent	Temp, °C	% Solvent-separated pairs	
			Uv	Nmr
Li	THF	25	80	~90
K	THF	25	0	10
Cs	THF	25	0	0
Li	DME	25	100	~90
Na	DME	25	95	~90
K	DME	25	~10	~10
Cs	DME	25	0	0
Na	THF	24.2	5	8
Na	THF	14.7	8	11
Na	THF	1.8	11	18
Na	THF	-14.6	24	33
Na	THF	-21.8	32	43
Na	THF	-26.3	38	48

<sup>a</sup> Reference 4.

and  $-27$  cal/(deg mol) for THF and the interpolated enthalpy values, one can calculate the proportion of each form of ion pair that would be present at a given temperature. With the restriction that 10% of a given form is the detectable limit, these calculations confirm the assignment of the samples into classes i-iii above over the available temperature range. (4) The "best" values of  $\delta_c$  and  $\delta_s$  derived in this manner are internally consistent for the same anion with different cations. (5) The values obtained for  $\Delta H$  and  $\Delta S$  are similar to those found for several other closely related systems.<sup>5, 29, 33, 36</sup>

**Interpretation of Thermodynamic Results.** The values of the energy terms associated with the conversion of contact into solvent-separated ion pairs have been interpreted by several workers.<sup>4-7</sup> The major features of the theory will be briefly mentioned here so that the values in Table V can be put in perspective. The observed enthalpy change represents the energy balance between the coulombic energy required to separate two oppositely charged ions and the gain in energy due to the ion-dipole interaction between cation and solvent.

(36) The results obtained by Casson and Tabner<sup>29</sup> for sodium 4,5-methylenephenanthrene do not fall within the expected range although the other cations yield normal values. The explanation of this anomaly is unclear at present, but the sodium salts do give normal  $\Delta F$  values.

(37) C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **87**, 5548 (1965).

The entropy term is negative, as the formation of a solvent-separated ion pair freezes solvent molecules around the cation causing an overall loss of freedom in the system. The factors which favor the solvent-separated form of the ion pair have been demonstrated, and the values in Table V allow the interpretation of each of these factors in a rational way. They are (1) decreasing temperature (the sign of the entropy change is negative so that decreasing temperature reduces the magnitude of the entropy contribution and results in a more negative free energy change), (2) increasing anion delocalization (this reduces the coulombic energy required to separate the ions and leads to a more negative enthalpy change; this is the first time that thermodynamic quantities have been available to verify this point which was originally mentioned by Hogen-Esch and Smid),<sup>4</sup> (3) decreasing the cation size (this is the net result of the competition between the increase in the ion-dipole interaction and the more unfavorable ion-separation term; as various studies in THF and DME have shown, the polarization term is the dominant one), (4) increasing dielectric constant (it reduces the energy required to separate the ions as for anion delocalization), and (5) increasing coordinating ability of the solvent (this is determined by the entropy contribution of the solvent; the data in Table V show that the entropy values for each solvent are virtually independent of cation and anion but depend on the solvent).

The relative magnitude of the entropy change for the two solvents is also notable, as the THF value is almost twice the DME value [ $-27$  and  $-16$  cal/(deg mol)]. The relation to the number of oxygen atoms in the solvent molecule is immediately apparent. These facts strongly support the idea that the change in entropy on the formation of solvent-separated ion pairs is due to the freezing of solvent molecules around the cation. The size of the entropy change permits the speculation that two molecules of THF or one molecule of DME per cation is required for the conversion. In other words, the change from a contact ion pair to a solvent-separated ion pair releases two coordination sites on the cation which are taken up by the oxygen lone pairs of the solvent. The smaller size of the solvated sodium ion in DME as against that in THF adds further weight to the suggestion that one DME molecule is equivalent to two THF molecules for cation solvation. The results show that, to obtain the same proportion of solvent-separated ion pairs in THF as is present for the same salt in DME, the temperature must be lowered by about  $100^\circ$ . This should be borne in mind when synthetic applications of the different reactivities of ion pair forms are being considered.

**Conclusions.** Nmr spectroscopy has been shown to be a useful addition to the other techniques for the determination of carbanion structures in solution. The small chemical shift changes detected in these anions under a range of conditions have been fully interpreted in terms of a rapid equilibrium between contact and solvent-separated ion pairs.

The contact ion pair may be converted into the solvent-separated form by an appropriate change of conditions. This process involves the replacement of the anion by the solvent at two coordination sites on the cation. The exact number of solvent molecules involved in this process is governed by the number of

oxygen atoms in the ether with lone pairs available for coordination with the cation. The process is rapidly reversible, but each individual cation remains associated with its anion. The insertion of solvent molecules increases the separation of cation and anion within the ion pair, but does not otherwise affect the cation position.

The conversion of a contact ion pair into its solvent-separated form is an exothermic process. As it also involves freezing of solvent molecules around the cation, it has a negative entropy change. Solvent-separated ion pairing is favored by (1) decreasing cation size (the enthalpy change becomes more negative as the distance between the ions in the contact and solvent-separated ion pair increases), (2) decreasing temperature (the entropy change is negative, thus lower temperatures reduce the contribution of the entropy term to the free energy change), (3) increasing anion delocalization (this reduces the energy required to separate the ions and so leads to a more negative enthalpy change), (4) increasing dielectric constant (it affects the free energy in the same way as increasing anion delocalization), and (5) increasing coordination ability of the solvent (this reduces the magnitude of the entropy change).

### Experimental Section

**Materials.** Triphenylmethane (BDH) was recrystallized from ethanol and from petroleum ether, and finally sublimed. Fluorene (BDH) was recrystallized from ethanol and sublimed. Indene (Hopkins-Williams) was refluxed over sodium for 8 hr and distilled under nitrogen. It was stored in the dark under nitrogen for at most 2 weeks; aliquots were taken and redistilled under nitrogen immediately before use. Samples were checked for purity by glc. Cyclopentadiene was prepared immediately before use by cracking dicyclopentadiene (BDH). Biphenyl (BDH) was sublimed before use.

Lithium, sodium, and potassium were all BDH laboratory reagent grade materials which were used directly after removal of surface hydroxide and carbonate. Rubidium and cesium were initially obtained from Koch-Light and were used directly. For the indenide and cyclopentadienide preparations rubidium and cesium metals were prepared by thermal decomposition of their azides.<sup>38,39</sup>

The azide (K & K Laboratories, 1 g) was placed in a nickel tube sealed to a glass reaction vessel and evacuated to  $10^{-5}$  mm. The tube was slowly heated by an electric furnace to  $120^\circ$ , and that temperature was maintained until the required vacuum was again established. The tube temperature was then raised to ca.  $380^\circ$  (with continuous pumping), at which point the metal distilled into a side-arm which was then sealed off; yield ca. 0.5 g. Attempts to carry out the decomposition in Pyrex or silica tubes yielded only small quantities of metal, presumably because of prior reaction with the glass during the decomposition process.

Diethyl ether (May and Baker), tetrahydrofuran (THF, May and Baker), and 1,2-dimethoxyethane (DME, Hopkins and Williams) were all refluxed for 12 hr over sodium under nitrogen and then distilled, a central fraction being collected. The redistilled solvents were stored over sodium and aliquots taken as required. These aliquots were refluxed over lithium aluminum hydride under nitrogen and distilled directly into the vacuum line reservoir immediately before use. DME was contaminated with ca. 1% 1-methoxy-2-ethoxyethane which was not removed on distillation. Tetramethylsilane (TMS) (BDH) was used directly. All solvents were stored over lithium aluminum hydride in a reservoir on the vacuum line and degassed with freezing three times before use.

**Carbanion Preparation.** Since the direct reaction between the alkali metal and the hydrocarbons (except cyclopentadienide) occurred only slowly and incompletely and led to a variety of products, a method was developed which utilized the reaction between biphenyl radical anion and the appropriate hydrocarbon to generate

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(39) P. W. M. Jacobs and A. R. Tariq Kureishy, *J. Chem. Soc.*, 4718 (1964).



the required carbanions.<sup>40</sup> All operations were carried out on a vacuum line. The reaction vessel is shown in Figure 12. The hydrocarbon (6 mmol) and biphenyl (3 mmol) (the biphenyl was omitted in the cyclopentadiene preparation) were sealed into an ampoule under vacuum and placed in the reaction vessel. The alkali metal (6–8 mmol) was placed in its sidearm, and the reaction flask was evacuated with occasional flaming to a pressure of at most  $10^{-5}$  mm. Pressure was monitored on an Edwards' Penning gauge. The alkali metal was distilled out of the sidearm to form a film on the inside of the vessel (except lithium which was simply cut into small pieces before addition to the flask). The sidearm containing the metal dross was sealed off and removed. THF (ca. 25 ml) was distilled into the flask, and the whole vessel was sealed from the line

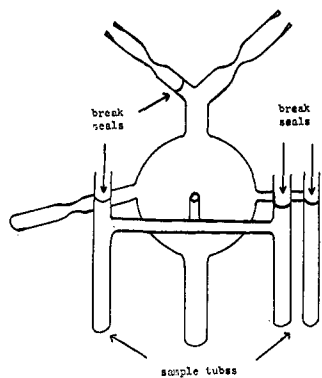


Figure 12. A diagram of the reaction vessel.

while still under vacuum. The seal of the ampoule containing the hydrocarbons was broken and reaction allowed to proceed. The blue-green color of the biphenyl radical anion was noted immediately and this gradually changed as reaction proceeded until only the color of the carbanion remained. The metal film had been consumed at this stage. Some hydrogen was apparently evolved in the indenide and cyclopentadienide preparations, but no gas evolution was observed in the fluorenone and triphenylmethanide cases. The indenide ion solutions all appeared green in color, the intensity varying from almost colorless for the lithium salts to emerald for the cesium salts. This observation is in contrast to that in the literature.<sup>16</sup> It was noted in the case of indenide that, when the solution was allowed to stand in the presence of excess metal, a red color developed—possibly due to the reversible formation of the dianion.

The solution was transferred to the six sample tubes and the flask replaced on the line *via* a second entry port protected with a break-seal. The solvent, unreacted hydrocarbons, and reduced biphenyls were then removed by evacuation. The tubes were flamed occasionally and pumping was continued overnight until the pressure had been reduced to less than  $10^{-5}$  mm. Each of the sample tubes, now containing solid salt (ca. 1 mmol), was sealed from the reaction flask and stored in the dark until required.

The nmr samples were prepared on the vacuum line using a simple bulb apparatus with nmr tubes, and a previously prepared sample tube was attached. The appropriate solvent (ca. 5 ml) and TMS (ca. 0.25 ml) were distilled onto the solid after evacuation of the system. The vessel was sealed from the line and nmr tubes were filled and sealed as required.

In a number of samples, small quantities (ca.  $10^{-8}$  M) of biphenyl radical anion were detected by esr,<sup>41</sup> but the nmr spectra obtained from these cases were identical in all respects with those obtained in the absence of the radical. Small amounts of the corresponding hydrocarbon were also present in some samples. No line broadening attributable to possible proton-exchange reactions was detected in the spectrum of any of these solutions. Samples prepared by the above procedure were quite stable for a considerable time and showed little sign of deterioration (formation of slight precipitate but no change in nmr spectrum) even after periods as long as 2 years.

During the early stages of this investigation, samples were prepared directly using DME as solvent throughout, and also without storage of the solid anions for extended periods, but no differences

could be detected between these samples and those prepared by the general method given above. THF must be employed initially as solvent for the preparations of the  $\text{Et}_2\text{O}$  solutions of the anion, since the biphenyl radical anion cannot be generated in diethyl ether under normal conditions. No residual THF could be detected by nmr in these  $\text{Et}_2\text{O}$  samples.

Attempts to study these ions in dioxane failed because of their low solubility in this solvent. Solubility also prevented the observation of potassium, rubidium, and cesium salts in  $\text{Et}_2\text{O}$ , all salts of cyclopentadienide in  $\text{Et}_2\text{O}$ , and the cesium salt in THF.

Samples used for concentration studies were prepared from a single solution. Dilutions were carried out by first pouring the required amount of concentrated solution into the nmr tube and then distilling the appropriate volume of solvent from the remainder of the solution into the tube by cooling with liquid air. Concentrations were determined by nmr integration of the carbanion signals using the downfield  $^{13}\text{C}$  side-band signals of the solvent as an internal intensity reference. The accuracy of the concentration determination was approximately  $\pm 10\%$  for the concentrated solutions and  $\pm 20\%$  for the more dilute cases. Attempts to study the effect of the addition of a common ion to the triphenylmethanide solutions using sodium tetraphenylboron failed. On addition of this salt to a number of solutions, radicals were formed which caused considerable line broadening and prevented the determination of accurate chemical shifts.

**Spectra.** Nmr spectra were determined on a Varian HA-100 spectrometer utilizing the field-frequency lock and normally operating in the field-sweep mode. All chemical shifts are given in terms of the  $\delta$  scale. Reported carbanion spectral data were obtained from the average of two 500-sec sweeps over a 50-Hz range with a frequency response of 0.5 Hz. Where possible, the TMS signal was used as the lock signal. In samples where the TMS concentration was too low to allow effective locking, a solvent band was used instead. In these instances, the TMS line position in the sample was measured relative to the same lock signal as that used for the carbanion spectra and was determined during the same spectral run. Carbanion line positions, measured using different lock signals, were identical within experimental error. Some of the samples for concentration studies were prepared without TMS, and the average solvent  $\delta$  values were used to obtain the carbanion shifts relative to TMS. Line positions were determined using a side-band technique, and frequencies were measured on a Hewlett Packard counter No. 5512A which could be read to  $\pm 0.1$  Hz. The largest difference between repeated scans (0.4 Hz) was observed while operating at nonambient temperatures. The accuracy of line positions within a single scan was  $\pm 0.1$  Hz, and the reproducibility was  $\pm 0.3$  Hz. The chemical shifts reported, except those given in Table I for the exact spin analysis, are taken as the center of gravity of each multiplet. Comparison of the chemical shifts obtained from spin analysis and center of gravity estimates showed only minor and uniform differences, hence the values used in the discussion are in error by, at worst, a small constant factor ( $< 0.02$  ppm).

Owing to solubility problems, the spectrum of potassium triphenylmethanide in  $\text{Et}_2\text{O}$  was obtained from 50 scans which were accumulated on a PDP-8 computer.<sup>42</sup>

**Temperature Control.** Variable-temperature operation was accomplished by use of the Varian temperature controller No. V-4343. Temperature was maintained to within  $\pm 2^\circ$  by a stream of preheated or cooled dry nitrogen. The probe temperature was determined from the separation of the hydroxyl and alkyl proton peaks of methanol from temperatures below  $40^\circ$  and of ethylene glycol for temperatures above  $25^\circ$ . The methanol and ethylene glycol samples used for this measurement were calibrated against a thermistor and independently against a thermocouple.<sup>43</sup> The calibrations obtained from the two procedures were self-consistent and agreed over the limited range where both samples could be used. However, they differed by up to  $10^\circ$  from the standard calibration curves supplied with the instrument.

**Spectral Analysis and Computation.** Calculations were carried out on the IBM 7094 computer. Spectral analyses were performed using the program LAOCN3 of Bothner-By and Castellano.<sup>15</sup> Spectra were simulated using the computed line positions and intensities together with a Lorentzian line-shape expansion of the appropriate line width (usually 0.35 Hz). The residual error in the analysis was

(42) We thank Dr. R. A. Craig of this department for making this technique available to us.

(43) We thank Dr. T. E. Kavanagh of this department and Mr. M. J. Saunders of CSIRO Division of Applied Chemistry for these calibrations.

(40) J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, **27**, 3745 (1962).

(41) N. Nishiguchi, *et al.*, *Mol. Phys.*, **9**, 153 (1965).

always less than 0.05, and coupling constants were accurate to  $\pm 0.05$  Hz.<sup>44</sup>

(44) Edgell, *et al.*, have recently published an infrared study of a series of inorganic salts in THF which provide additional insight into the structure of ion pairs in solution: W. F. Edgell, J. Lyford, R.

**Acknowledgment.** J. B. G. thanks the Commonwealth Scientific and Industrial Research Organization for the award of a Senior Studentship.

Wright, W. Risen, and A. Watts, *J. Amer. Chem. Soc.*, **92**, 2240 (1970).

## Chloride-Induced Elimination from 2-Phenylcyclopentyl, 2-Phenylcyclohexyl, and 2-Norbornyl Brosylates in Acetone

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**Abstract:** *cis*- and *trans*-2-phenylcyclopentyl and 2-phenylcyclohexyl *p*-bromobenzenesulfonates by reaction with *n*-Bu<sub>4</sub>NCl in acetone give variable amounts of olefinic products. The *cis* isomers (fraction of elimination  $F_E = 0.81$ – $0.99$ ) show a preference for Saytzeff elimination to the extent of 99.7% 1-phenylcyclopentene and 99.5% 1-phenylcyclohexene. The *trans* isomers ( $F_E = 0.55$ – $0.22$ ) have a >90% preference for Hofmann products, 3-phenylcyclopentene and 3-phenylcyclohexene. The ratio  $k_{cis}/k_{trans}$  of second-order rate constants for elimination at 50° is 48 for cyclopentyl derivatives and 1140 for cyclohexyl derivatives. *exo*-2-Norbornyl *p*-bromobenzenesulfonate under the same conditions gives, besides *endo*- and *exo*-norbornyl chlorides, nortricyclene and norbornene ( $F_E = 0.70$ ) with nortricyclene largely predominant. Kinetic measurements show that, while nortricyclene and norbornene are formed in a 9:1 ratio in ionization processes, the halide-induced elimination gives them in the ratio 99.4:0.6. *endo*-2-Norbornyl *p*-bromobenzenesulfonate reacts with *n*-Bu<sub>4</sub>NCl to give mainly *exo*-2-norbornyl chloride with no *endo* chloride and a small amount of elimination products ( $F_E = 0.05$ ).

Several years ago it was discovered that halide ions in acetone are effective in promoting elimination reactions.<sup>3</sup> Since then, a number of papers on the subject have been published. The substrates investigated were alkyl tosylates, brosylates, and halides; while primary derivatives give little or no elimination,<sup>4</sup> and tertiary derivatives present fractions of elimination close or equal to unity,<sup>4–6</sup> secondary substrates are more flexible in giving a blend of substitution and elimination products.<sup>3,4,7</sup> The most useful solvent-salt system for the study of these reactions seems to be acetone containing tetra-*n*-butylammonium halides, although other salts and dipolar aprotic solvents have been used.<sup>3,8</sup>

An interpretation of the halide-induced elimination has been advanced that requires an interaction of the halide ion with both  $\alpha$ -carbon and  $\beta$ -hydrogen atoms at the transition state (E2C-like transition state).<sup>7,9</sup> However, this suggestion has not been generally accepted,<sup>5,6,10,11</sup> and the whole question seems to be far from being solved.

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(2) CNR (Rome) Fellow, 1966–1967.

(3) S. Winstein, D. Darwish, and N. J. Holness, *J. Amer. Chem. Soc.*, **78**, 2915 (1956).

(4) S. Winstein, "Chimica teorica," Accademia naz. Lincei, Rome, 1965, p 327.

(5) J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **35**, 76 (1970).

(6) D. J. McLennan and R. J. Wong, *Tetrahedron Lett.*, 881 (1970).

(7) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).

(8) R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970).

(9) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

(10) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).

(11) See, however, D. Cook and A. J. Parker, *Tetrahedron Lett.*, 4901 (1969).

As a contribution to the understanding of the mechanism of this reaction, we present results obtained on 2-phenylcyclopentyl brosylates (I), 2-phenylcyclohexyl brosylates (II), and 2-norbornyl brosylates (III) reacting with *n*-Bu<sub>4</sub>NCl in acetone.

### Results

Rate coefficients  $k_{E+S}$  for the total reaction were obtained by adding the observed rates of chloride ion consumption and acid production. The ratio of acid produced to reacted substrate gave the fraction of elimination  $F_E$ . In some cases  $F_E$  was directly determined from product glc analysis. Rate coefficients  $k_E$  for elimination and  $k_S$  for substitution were calculated from the values of  $k_{E+S}$  and  $F_E$ . Results are given in Table I. Product analyses, by glc, gave the results summarized in Tables II and III.

Solvolyses, in the absence of chloride ion, were also studied, usually both in terms of rates and products. The results are gathered in Tables IV and V. An upward drift of first-order coefficients  $k_1$  was observed during the kinetic runs of compounds *cis*-I, *cis*-II, and *trans*-II, which was attributed to salt effects. A positive salt effect was ascertained for *exo*-III, by working at different concentrations of *n*-Bu<sub>4</sub>NClO<sub>4</sub>. The intervention of solvolysis in the reaction with chloride ion was estimated by comparing  $k_1$  values, corrected for salt effect, with the rates of bimolecular reactions, expressed as pseudo-first-order coefficients  $k' = k_{E+S} \times \text{average } [Cl^-]$ . Considerable intervention of solvolysis was found only in the case of *exo*-2-norbornyl brosylate (see later).

***cis*- and *trans*-2-Phenylcyclopentyl Brosylates.** The *cis* isomer (*cis*-I) is the most reactive with *n*-Bu<sub>4</sub>NCl of