

# Studies in Nuclear Magnetic Resonance Spectroscopy. XI. Proton Spectroscopy of Lithioisobutyrophenone and Its Complexes with Lithium Chloride and Bromide<sup>1,2</sup>

L. M. Jackman\* and R. C. Haddon

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received July 19, 1972

**Abstract:** The proton magnetic spectra of lithioisobutyrophenone in various ether solvents have been determined. The barrier to rotation about the carbon-carbon double bond is  $>27$  kcal mol<sup>-1</sup>. Two species, believed to be ion-pair aggregates of the same stoichiometry but with different structures, coexist in dioxolane in the temperature range  $-40$  to  $+50^\circ$  with  $\Delta H = -10.3 \pm 0.3$  kcal mol<sup>-1</sup> and  $\Delta S = -38.7 \pm 1.0$  eu for the equilibrium between the low- and high-temperature species. In the presence of either LiCl or LiBr, lithioisobutyrophenone forms a complex,  $\text{Li}_3(\text{OCPh}=\text{CMe}_2)_4\text{X}$ , X = Cl or Br, in dioxolane. The exchange between the complexes and lithioisobutyrophenone has been studied by dnmr line-shape analysis, and the observed kinetics are consistent with a mechanism involving an enolate ion as an intermediate. The exchange processes have free energies of activation of the order of 16 kcal mol<sup>-1</sup>.

In part X<sup>2</sup> we demonstrated that proton nmr spectroscopy is a powerful method for detecting equilibria between contact and solvent separated ion pairs, and we later showed<sup>3</sup> that the analysis of chemical shift data for contact ion pairs can be utilized to derive information regarding the average structures of these species in solution. The examples considered were simple carbanions of little practical interest. In this paper we describe some preliminary studies of chemically much more important anions, *viz.*, enolate ions.

In general, the reactions of both carbanions and enolate ions are sensitive to ion pairing and related phenomena.<sup>4,5</sup> In particular, the orientation in reactions of the ambident enolate ions appear to be subject to the same factors that influence the nature of ion pairs.<sup>6</sup>

Apart from many systematic and casual investigations of the reactions of enolate ions, there have been several physico-chemical studies of these species. These have included molecular weight determina-

tions,<sup>6d-f</sup> conductance measurements,<sup>6d-f,m-o</sup> and infrared spectroscopy.<sup>5f,i,k,7</sup>

The initial aims of this study were firstly to examine the proton chemical shifts of enolate ions<sup>6f,g,i</sup> with a view to detecting solution phenomena such as ion pairing or aggregation and, secondly, to determine, if possible, the barrier to rotation about the partial carbon-carbon double bond of the enolate ion since its value might also depend on the same phenomena. The systems chosen for study were solutions of lithioisobutyrophenone in ether solvents.

During the course of this investigation we discovered the existence of an entirely novel type of complex between lithioisobutyrophenone and lithium halides. Since such species might be of considerable importance in alkylations and acylations of enolate ions by alkyl and acyl chlorides, respectively, we include here some preliminary results concerning their nature.

## Experimental Section

All liquids were purified by distillation using nmr and/or glc as criteria of purity. Ether solvents with boiling points in excess of  $100^\circ$  were refluxed with calcium hydride prior to distillation. The remaining ethers were refluxed over fresh sodium wire. All solvents were stored over sodium wire.

**Isobutyrophenone Trimethylsilyl Enol Ether.** Sodium hydride (32 g of a 57% oil dispersion) and dimethoxyethane (500 ml) were placed in a three-necked flask equipped with a mechanical stirrer, reflux condenser, and a pressure-equalized dropping funnel. Water (0.1 ml), followed by isobutyrophenone (75 ml), was added over a period of 1 hr and the mixture was refluxed overnight by which time the nmr of an aliquot indicated the absence of ketone.

Trimethylsilyl chloride (100 ml) was added to the cooled reaction mixture which was then stirred for 1 hr. Light petroleum (bp  $30-60^\circ$ , 250 ml) was added. The resulting mixture was filtered in an argon atmosphere and the residue was washed with a further quantity of light petroleum (500 ml). The solvent was removed on a rotary evaporator and the residue was shown to contain less than 5% of starting ketone (it is not practical to purify product containing greater than 5% ketone). The product was fractionated twice with a 10-in. Nester-Faust spinning band column (reflux ratio: 100/1) to yield pure isobutyrophenone trimethylsilyl enol ether (66 g, 60%), bp  $98^\circ$  (11 mm),  $n_D^{25}$  1.4936. *Anal.* Calcd for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : mol wt, 220.128. Found: mol wt, 220.133 (Picker

(1) (a) From the Ph.D. Thesis of R. C. Haddon, Pennsylvania State University, 1971. (b) Supported by Grant No. GP-33903 from the National Science Foundation.

(2) Part X: J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *J. Amer. Chem. Soc.*, **94**, 2306 (1972).

(3) L. M. Jackman and J. B. Grutzner, unpublished results.

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

(5) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968.

(6) (a) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965; (b) H. D. Zook and W. L. Rellahan, *J. Amer. Chem. Soc.*, **79**, 881 (1957); (c) W. L. Rellahan, W. L. Gumby, and H. D. Zook, *J. Org. Chem.*, **24**, 709 (1959); (d) H. D. Zook and W. L. Gumby, *J. Amer. Chem. Soc.*, **82**, 1386 (1960); (e) H. D. Zook and T. J. Russo, *ibid.*, **82**, 1258 (1960); (f) H. D. Zook, T. J. Russo, E. F. Ferrand, and D. S. Stotz, *J. Org. Chem.*, **33**, 2222 (1968); (g) H. D. Zook, W. L. Kelly, and I. Y. Posey, *ibid.*, **33**, 3477 (1968); (h) H. O. House, *Rec. Chem. Progr.*, **28**, 99 (1967); (i) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969); (j) G. Stork and P. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462, 4464 (1968); (k) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **89**, 1153 (1970); (l) K. L. Shepard and J. I. Stevens, *Chem. Commun.*, 951 (1971); (m) A. L. Kurts, A. Macias, I. P. Beletskaya, and O. A. Reutov, *Tetrahedron*, **27**, 4759 (1971); (n) A. L. Kurts, P. I. Dem'yanov, A. Macias, J. P. Beletskaya, and O. A. Reutov, *ibid.*, **27**, 4769 (1971); (o) A. L. Kurts, N. K. Genkina, A. Macias, I. P. Beletskaya, and O. A. Reutov, *ibid.*, **27**, 4777 (1971); (p) H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971); (q) A. G. Pinkus, J. G. Lindberg, and A.-B. Wu, *Chem. Commun.*, 1350 (1969); (r) A. G. Pinkus, A.-B. Wu and J. G. Lindberg, *ibid.*, 859 (1970).

(7) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas.*, **86**, 807, 1345 (1967); **89**, 300 (1970).

MS9 mass spectrometer). Nmr ( $\text{CCl}_4$ ):  $\delta$  0.07 (9 H, singlet,  $\text{Si}(\text{CH}_3)_3$ ), 1.64, 1.74 (6 H, singlets,  $=\text{C}(\text{CH}_3)_2$ ), 7.22 (5 H, broad singlet, Ar protons).

The purified material was stored in 1-ml glass ampoules, and the refractive index was checked immediately prior to use.

**Preparation of Lithioisobutyrophenone Solutions.** The enolate ion solutions were prepared by vacuum line techniques. The reaction vessel had four side arms comprised of nmr tubes separated from the main flask by medium porosity sintered glass septa. A typical experiment is described below.

Appropriate quantities (1–40 mg) of lithium halides were weighed directly into four, argon filled, nmr tubes which had been carefully dried. The four tubes were then sealed onto the reaction vessel. Each tube and its contents was then heated for 12 hr at  $110^\circ$  and 2 mm pressure to remove any water introduced during the attachment of the tubes. Argon was then admitted and a steady stream of argon was directed to the bottom of the reaction flask. A dried magnetic stirrer bar was placed in the flask together with a length of glass tubing sufficient to protrude above the mouth of the vessel. Butyllithium (2.8 ml of 1.6 M solution in hexane) was introduced by a syringe through the glass tubing which was then removed. The reaction vessel was then rapidly attached to a vacuum line manifold.

The contents of the reaction vessel were degassed three times by freezing and thawing and degassed diethyl ether (10 ml, from lithium aluminum hydride) followed by isobutyrophenone trimethylsilyl enol ether (1.1 ml) were transferred to the reaction vessel. The resulting solution was stirred overnight.

The volatile components were removed by pumping for 24 hr. Degassed dioxolane (10 ml, from lithium aluminum hydride) was transferred onto the residue and then removed by pumping. The process was repeated and finally dioxolane (8 ml) and tetramethylsilane (0.05 ml) were transferred to give the solution of the enolate ion.

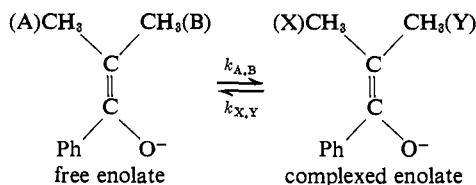
The evacuated vessel was removed from the manifold. The enolate ion solution was filtered into the nmr tube by inclining the vessel so as to pour approximately 1 ml onto the sintered disk and cooling the nmr tube in ice-water. The tube was sealed off and removed.

Solutions prepared by the above technique are completely colorless. Usually the concentration of enolate ion in the first sample was determined by comparison of the nmr integrals of the methyl absorptions with the integral of one of the  $^{13}\text{C}$  satellites of the solvent. The volumes added to the remaining three tubes could then be adjusted to give the desired halide/enolate ratios.

**Nmr Spectroscopy.** Routine spectra were obtained with a Varian A-60A spectrometer. All spectra for line-shape analysis were recorded on a Varian HA-100 spectrometer and the spectra were calibrated with a frequency counter ( $\pm 0.1$  Hz). Temperatures of samples were measured using Varian methanol and ethylene glycol standards and were then corrected by the method of Van Geet.<sup>8</sup>

The spectra for dynamic nuclear magnetic resonance (dnmr) analysis were digitized with a Calma 302 Digitizer. The magnetic tape outputs from the digitizer were then processed to give cards with a format suitable for input to the dnmr programs.

**Dnmr Analysis.** Reaction rates were obtained by total line-shape analysis of the methyl absorptions which correspond to two unequally populated AX(BY) exchange cases with common reaction rates.



For this system the line-shape function takes the following form.<sup>9</sup>

$$v = \omega_1 M_0 [(O_{AX} P_{AX} + Q_{AX} R_{AX}) / (P_{AX}^2 + R_{AX}^2) + (O_{BY} P_{BY} + Q_{BY} R_{BY}) / (P_{BY}^2 + R_{BY}^2)]$$

$$O_{AX} = 1 + \tau(p_X R_A + p_A R_X)$$

$$P_{AX} = R_A p_A + R_X p_X + \tau(R_A R_X - \Delta\omega_{AX}^2 + \delta\omega_{AX}^2/4)$$

(8) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968); **42**, 679 (1970).

(9) (a) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); (b) H. S. Gutowsky and A. Saika, *ibid.*, **21**, 1688 (1953); (c) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

$$Q_{AX} = \tau[\Delta\omega_{AX} + \delta\omega_{AX}(p_X - p_A)/2]$$

$$R_{AX} = \Delta\omega_{AX}[1 + \tau(R_A + R_X)] +$$

$$\delta\omega_{AX}[p_A - p_X + \tau(R_X - R_A)]/2$$

and analogous expressions for  $O_{BY}$ ,  $P_{BY}$ ,  $Q_{BY}$ , and  $R_{BY}$

$$\Delta\omega_{AX} = 1/2(\omega_A + \omega_X) - \omega$$

$$\tau = \frac{\tau_{A,B}\tau_{X,Y}}{\tau_{A,B} + \tau_{X,Y}} = \frac{1}{k_{A,B} + k_{X,Y}}$$

In these expressions the symbols have their usual meaning:  $v$ , the transverse magnetization in the absorption mode which is proportional to the intensity;  $\omega_1$ , the radiofrequency field;  $M_0$ , the equilibrium value of the longitudinal magnetization;  $\Delta\omega_A$ , the resonance frequency of a nucleus at site A;  $\omega$ , the frequency of the applied radiofrequency field;  $\delta\omega_{AX}$  the resonance frequency difference between sites A and X;  $p_A$ , the fractional population of sites A;  $R_A$ , the line width at half height of component A in the absence of exchange;  $k_{A,B}$ , the first-order rate constant for enolate complexation (inverse of the lifetime  $\tau_{A,B}$ ).

The line widths at half height for the two molecular species were found to be temperature dependent. At elevated temperatures these bands could be partially resolved as quartets ( $J \sim 0.3$  Hz) due to coupling between the two methyl groups so that the minimum observable line width is approximately 1.4 Hz. This coupling is neglected in the line-shape analysis since it is not affected by the exchange process.

These line-shape equations were subjected to a nonlinear regression analysis and the resulting algorithms were programmed for iteration on populations and lifetimes.<sup>1b,10</sup> Also incorporated into the programs was an option for introducing the four chemical shifts into the iterative procedure (improvement of these parameters is not feasible above coalescence). Line widths and chemical shifts at each temperature for the pure enolate and pure complex were obtained from spectra of lithioisobutyrophenone in the absence of lithium halide and in the presence of a substantial excess, respectively.

## Results and Discussion

**Rotational Barrier in the Enolate Ion.** The proton spectra of lithioisobutyrophenone in a variety of ether solvents at ambient temperature exhibit two singlets in the region  $\delta$  1.0–2.0 (Table I), the nonequivalence being

**Table I.** Chemical Shifts ( $\delta$ ) of the Protons of the Methyl Groups of Lithioisobutyrophenone in Various Solvents

| Solvent | $\delta_A$ , ppm | $\delta_B$ , ppm |
|---------|------------------|------------------|
|         | 1.600            | 1.491            |
|         | 1.557            | 1.522            |
|         | 1.483            | 1.395            |
|         | 1.467            | 1.423            |
|         | 1.661            | 1.553            |
|         | 1.551            | 1.351            |

due to a substantial barrier to rotation about the partial carbon-carbon double bond of the mesomeric anion (1). This nonequivalence persists up to  $200^\circ$  in the

(10) L. M. Jackman, T. E. Kavanagh, and R. C. Haddon *Org. Magn. Resonance*, **1**, 109 (1969).

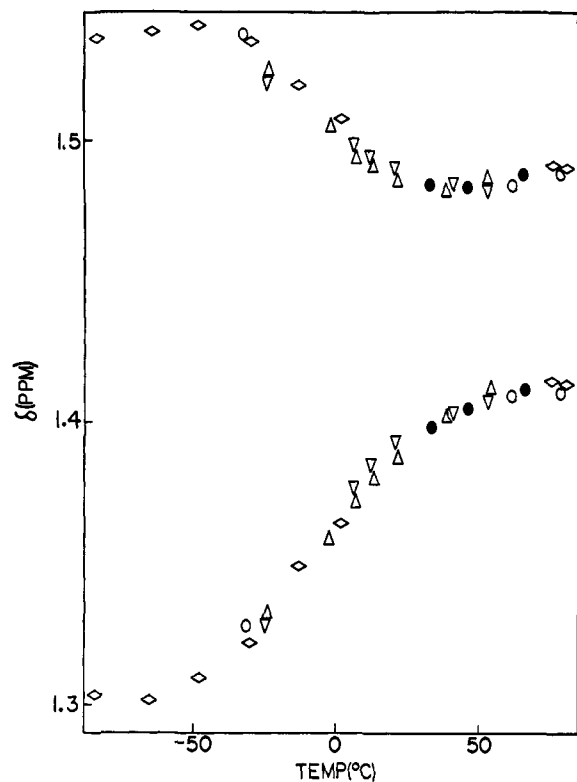
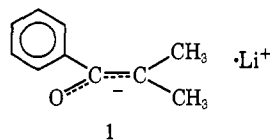


Figure 1. The temperature dependence of the chemical shifts of protons of the methyl groups of lithioisobutyrophenone in dioxolane: ( $\diamond$ ) 1.12 M; ( $\circ$ ) 0.47 M; ( $\nabla$ ) 0.52 M; ( $\triangle$ ) 0.08 M; ( $\bullet$ ) all four points coincident.



solvent triglyme.<sup>11</sup> Assuming a minimum value<sup>12</sup> of  $10^{13}$  for the preexponential term of the Arrhenius equation and that a 30% broadening of the absorptions would have been observable, a lower limit of 27 kcal mol<sup>-1</sup> is calculated for the rotational barrier. This value indicates appreciable localization of the negative charge on oxygen and that species involving a carbon-lithium bond, if present at all, are at kinetically insignificant concentrations.

**Temperature Dependence of Chemical Shifts for Lithioisobutyrophenone.** Nmr evidence for ion-pair equilibria generally takes the form of a sigmoidal dependence of chemical shift on temperature.<sup>13</sup> The chemical shifts of the protons of the two methyl groups of lithioisobutyrophenone exhibit such behavior in the range  $-50$  to  $+50^\circ$  (Figure 1). The observed temperature dependence is evidently independent of the concentration of enolate in the range 0.08–1.12 M. The presence or absence of lithium chloride or bromide, provided uncomplexed (see below) lithioisobutyrophenone is still present, also had no effect. This is consistent with an equilibrium between two species having the same stoichiometry in lithioisobutyrophenone. The

(11) Preliminary studies with the corresponding sodium and potassium salts revealed the same behavior, and the same is true for lithio-pinacolone in triglyme.

(12) (a) R. C. Neuman and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965); (b) R. C. Neuman, D. N. Roark, and V. Jonas, *J. Amer. Chem. Soc.*, **89**, 3412 (1967).

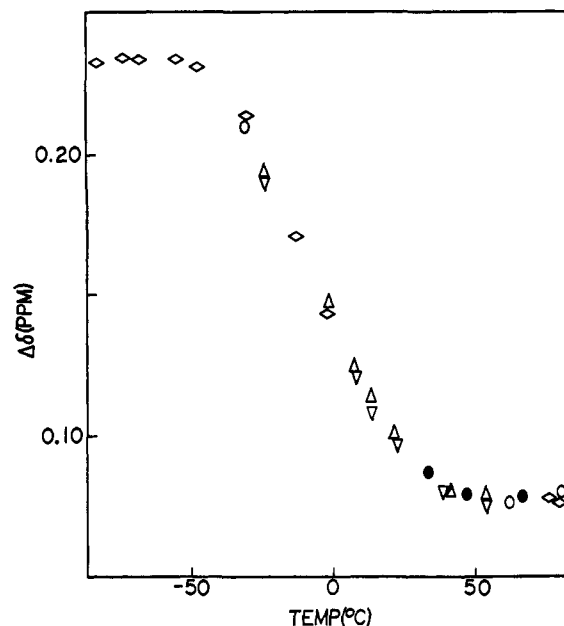


Figure 2. The temperature dependence of the difference ( $\Delta\delta$ ) in chemical shifts of the two methyl groups of lithioisobutyrophenone in dioxolane: ( $\diamond$ ) 1.12 M; ( $\circ$ ) 0.47 M; ( $\nabla$ ) 0.52 M; ( $\triangle$ ) 0.08 M; ( $\bullet$ ) all four points coincident.

simplest explanation would involve an equilibrium between monomeric, contact, and solvent separated ion pairs. However, the data do not exclude equilibria between aggregated species containing the same or nearly the same (in the case of high degrees of aggregation) numbers of lithioisobutyrophenone.

Figure 2 is the analogous plot of the difference ( $\Delta\delta$ ) between the chemical shifts of the protons of the two methyl groups *vs.* temperature. Using the limiting values 23.3 and 7.6 Hz at the low- and high-temperature limits and assuming their temperature invariance, the values of the equilibrium constants ( $\Delta\delta = 23.3$  species  $\rightleftharpoons$   $\Delta\delta = 7.6$  species) between the two species were calculated for 19 data points in the temperature range  $-31$  to  $41^\circ$ . The corresponding free energies and reciprocal temperatures were subjected to a linear regression analysis. The correlation coefficient was found to be 0.994 and the following values for the thermodynamic parameters were obtained:  $\Delta F(25^\circ) = 1.26$ ;  $\Delta H = -10.3 \pm 0.3$  kcal mol<sup>-1</sup>;  $\Delta S = -38.7 \pm 1.0$  kcal mol<sup>-1</sup> deg<sup>-1</sup>.

The chemical shifts of the methyl protons of lithioisobutyrophenone in dimethoxyethane exhibit only a small, monotonic variation with temperature in the range  $-70$  to  $70^\circ$ , and  $\Delta\delta$  was essentially invariant.

While the present study gives no indication of the degree of association of lithioisobutyrophenone in dioxolane, published data on related systems suggest that metalloenolates are not monomeric. Zook and his co-workers<sup>6d,e</sup> have found association numbers of approximately 3 for sodio- and potassiobutyrophenone in both diethyl ether and dimethoxyethane. Lithium 2,6-dimethylphenoxide in dioxane appears to be a dimer,<sup>13</sup> and lithium alkoxides are highly associated in solvents such as benzene and cyclohexane<sup>14,15</sup> as well as in the

(13) K. Shobatake and K. Nakamoto, *Inorg. Chim. Acta*, **4**, 485 (1970).

(14) M. S. Bains, *Res. Bull. Punjab Univ.*, **15** (III-IV), 303 (1964).

(15) G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, **5**, 1257 (1966).

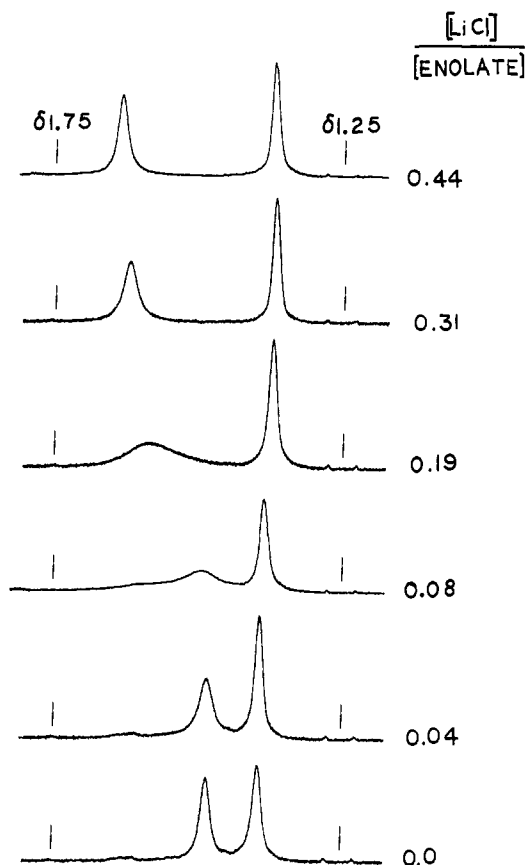


Figure 3. The effect of varying concentrations of lithium chloride on the nmr spectrum of 0.50 *M* lithioisobutyrophenone in dioxolane at 33°.

vapor phase.<sup>15</sup> The chemical process responsible for the behavior observed in Figures 1 and 2 may therefore involve a change in structure and/or solvation of an aggregate. Certainly the entropy change is much more negative than observed for equilibria between contact and solvent separated ion pairs which involve monomeric carbanion salts.<sup>1a</sup>

**Proton Spectra of Lithioisobutyrophenone-Lithium Halide Solutions.** The addition of either lithium chloride or lithium bromide profoundly affects the appearance of the absorptions of the methyl protons of lithioisobutyrophenone in dioxolane. This is illustrated in Figure 3 for various ratios of lithium chloride to lithioisobutyrophenone. The effect of temperature at a constant chloride-enolate ratio is shown in Figure 4. These spectra clearly indicate that the system is undergoing exchange of enolate ions between two sites, the populations of which are dependent on the halide-enolate ratio. Further, in the temperature range for which slow exchange is observed, the chemical shifts of two of the absorptions correspond in line positions to those of the methyl protons of pure lithioisobutyrophenone solutions at the same temperatures. Thus at -65° (Figure 4) the two more intense peaks correspond to lithioisobutyrophenone; at higher temperatures (e.g., 1.0°) the high-field absorptions of the two species coincide. The second species is evidently a complex involving lithium chloride and lithioisobutyrophenone. Lithium bromide produces a similar effect. The line broadening observed on reducing the temperature from -30 to -65° (and lower) is probably due to the in-

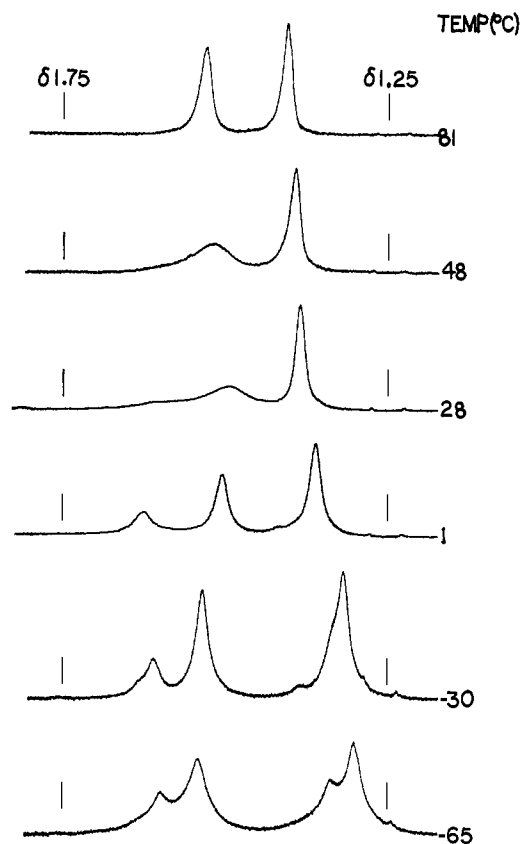


Figure 4. The effect of temperature on the spectra of a solution of lithioisobutyrophenone (0.05 *M*) and lithium chloride (0.04 *M*) in dioxolane.

creased viscosities of the solutions at the lower temperatures.

Information regarding the stoichiometry and formation constant for the halide complexes is, in principle, available over the entire temperature range investigated. In the slow exchange limit, the proportions of enolate and halide complex can be obtained by direct integration. At temperatures for which rapid exchange prevails, the averaged chemical shifts yield the same information, provided the values for the pure components are known. Finally, in the region of intermediate exchange, dnmr line-shape analysis can be used to obtain the populations of the two sites. Actually the line-shape analysis programs with suitable input data may be used to give populations over the entire temperature range studied.

It is convenient to define an apparent stoichiometry ( $n_{app}$ ) as

$$n_{app} = \frac{[\text{complexed enolate ion}]}{[\text{total lithium halide}]} \\ = \frac{p_X [\text{total lithioisobutyrophenone}]}{[\text{total lithium halide}]}$$

If the formation constant of the complex is sufficiently large,  $n_{app}$  will be invariant to changes in temperature and concentration and will then be equal to  $r/s$  corresponding to the formula  $[\text{LiOCPh}=\text{CMe}_2]_r[\text{LiX}]_s$ . Table II lists values of  $n_{app}$  for the lithium chloride complex, obtained mainly by dnmr methods but including some obtained by instrumental integration. It should be noted that the values of  $n_{app}$  obtained at high temperatures depend critically on the values of the chemical

**Table II.** Values of  $n_{app}$  for Various Concentrations of Lithioisobutyrophenone and Lithium Chloride at Various Temperatures

| [Enolate] | [Enolate]/<br>[LiCl] | Temp, °C |     |                  |                  |     |     |     |     |     |    |     |     |     |     |     |     |     |     |     |
|-----------|----------------------|----------|-----|------------------|------------------|-----|-----|-----|-----|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|           |                      | -31      | -24 | -13              | -4               | -2  | 7   | 13  | 20  | 21  | 25 | 27  | 33  | 41  | 46  | 53  | 54  | 62  | 65  | 70  |
| 0.54      | 4.2                  |          |     |                  |                  |     |     |     |     | 2.7 |    |     |     |     |     |     |     |     |     |     |
| 0.47      | 5.3                  | 3.1      |     | 3.3              |                  |     |     |     |     |     |    | 3.1 | 3.1 |     | 2.8 |     |     | 3.0 | 3.0 |     |
|           |                      |          |     | 3.3 <sup>a</sup> |                  |     |     |     |     |     |    |     |     |     |     |     |     |     |     |     |
| 1.12      | 6.1                  |          | 3.6 |                  |                  | 3.5 | 3.4 | 3.5 |     | 3.5 |    |     | 3.3 | 3.5 | 3.5 | 3.5 | 3.5 |     | 3.3 | 3.5 |
| 0.39      | 6.1                  |          | 3.6 |                  |                  | 3.5 | 3.5 | 3.6 | 3.5 | 3.5 |    | 3.6 | 3.4 | 3.3 | 3.3 | 3.3 | 3.4 | 3.2 |     |     |
| 0.17      | 6.1                  |          | 3.5 |                  |                  | 3.6 | 3.5 | 3.7 |     |     |    |     | 3.5 | 3.5 | 3.6 | 3.4 | 3.2 |     | 3.3 | 3.4 |
| 0.10      | 6.1                  |          | 3.4 |                  |                  | 3.5 | 3.5 | 3.7 |     | 3.6 |    |     | 3.6 | 3.6 | 3.6 | 3.5 |     | 3.5 |     |     |
| 0.08      | 8.1                  |          |     |                  |                  | 3.5 | 3.3 | 3.5 |     | 3.5 |    |     | 3.5 | 3.4 | 3.6 | 3.2 | 3.4 |     |     | 3.4 |
| 0.52      | 8.4                  |          | 3.7 |                  |                  | 3.6 | 3.6 | 3.6 |     | 3.7 |    |     | 3.5 | 3.6 | 3.3 | 3.6 | 3.5 | 3.5 |     | 3.4 |
| 0.50      | 12.2                 | 4.0      |     | 4.1              | 4.1              |     |     |     |     |     |    |     |     | 4.0 |     | 3.6 |     |     | 3.7 | 3.9 |
|           |                      |          |     | 4.0 <sup>a</sup> | 3.9 <sup>a</sup> |     |     |     |     |     |    |     |     |     |     |     |     |     |     |     |
| 0.54      | 15.2                 |          |     |                  |                  |     |     |     |     | 3.9 |    |     |     |     |     |     |     |     |     |     |
| 0.54      | 19.8                 |          |     |                  |                  |     |     |     |     | 4.3 |    |     |     |     |     |     |     |     |     |     |
| 0.47      | 24.0                 |          |     | 3.2              |                  |     |     |     |     |     |    | 3.6 |     | 2.3 |     |     |     | 2.2 | 2.4 |     |

<sup>a</sup> Determined by instrumental integration. All other values obtained by dnmr analysis.

**Table III.** Values of  $n_{app}$  for Various Concentrations of Lithioisobutyrophenone and Lithium Bromide at Various Temperatures

| [Enolate] | [Enolate]/<br>[LiCl] | Temp, °C |                  |                  |     |                  |                  |     |     |     |     |     |  |
|-----------|----------------------|----------|------------------|------------------|-----|------------------|------------------|-----|-----|-----|-----|-----|--|
|           |                      | -36      | -20              | -10              | -6  | 4                | 13               | 33  | 50  | 61  | 65  | 75  |  |
| 0.57      | 3.5                  | 2.3      | 2.5              |                  | 2.5 | 2.5              | 2.4              | 2.5 | 2.3 | 2.2 | 2.2 | 2.1 |  |
|           |                      |          | 2.5 <sup>a</sup> | 2.5 <sup>a</sup> |     | 2.5 <sup>a</sup> | 2.5 <sup>a</sup> |     |     |     |     |     |  |
| 0.57      | 6.3                  | 3.3      | 3.3              |                  | 3.4 | 3.3              | 3.3              | 3.3 | 3.0 | 2.9 | 3.0 | 2.8 |  |
|           |                      |          | 3.4 <sup>a</sup> | 3.3 <sup>a</sup> |     | 3.4 <sup>a</sup> | 3.3 <sup>a</sup> |     |     |     |     |     |  |
| 0.57      | 13.0                 | 3.1      | 3.4              |                  | 2.9 | 2.9              | 3.0              | 3.3 | 2.7 | 2.5 | 2.4 | 2.3 |  |
|           |                      |          | 3.6 <sup>a</sup> | 3.4 <sup>a</sup> |     | 3.4 <sup>a</sup> |                  |     |     |     |     |     |  |

<sup>a</sup> Determined by instrumental integration. All other values obtained by dnmr analysis.

**Table IV.** Reciprocal Lifetimes (sec<sup>-1</sup>) at 25° for Exchange of Enolate Ion between Free and Halide Complex Sites

|        | [Enolate] | [Eno-<br>late]/<br>[LiX] | $1/\tau_{A,B}$ |          | $1/\tau_{X,Y}$ |          |
|--------|-----------|--------------------------|----------------|----------|----------------|----------|
|        |           |                          | $1/\tau_{A,B}$ | $r^a$    | $1/\tau_{X,Y}$ | $r^a$    |
| X = Cl | 0.54      | 4.2                      | 35.5           | <i>b</i> | 19.6           | <i>b</i> |
|        | 0.47      | 5.3                      | 26.0           | 0.986    | 18.8           | 0.988    |
|        | 0.515     | 8.3                      | 16.4           | 0.983    | 22.4           | 0.985    |
|        | 0.50      | 12.2                     | 9.4            | 0.986    | 19.8           | 0.990    |
|        | 0.54      | 15.2                     | 9.9            | <i>b</i> | 28.7           | <i>b</i> |
|        | 0.54      | 19.8                     | 7.2            | <i>b</i> | 25.5           | <i>b</i> |
| X = Br | 1.12      | 6.1                      | 31.7           | 0.979    | 24.5           | 0.975    |
|        | 0.39      | 6.1                      | 26.0           | 0.977    | 19.7           | 0.983    |
|        | 0.17      | 6.1                      | 21.1           | 0.987    | 15.2           | 0.986    |
|        | 0.10      | 6.1                      | 20.4           | 0.961    | 14.0           | 0.970    |
|        | 0.57      | 3.5                      | 30.2           | 0.989    | 13.9           | 0.987    |
|        | 0.57      | 6.3                      | 14.7           | 0.989    | 14.5           | 0.990    |
|        | 0.57      | 13.0                     | 4.7            | 0.990    | 16.7           | 0.986    |

<sup>a</sup>  $r$  is the correlation coefficient for  $\ln(1/\tau)$  vs.  $1/T$  used for interpolating the values of  $1/\tau$  at 25°. <sup>b</sup> Single measurements at 25°.

shifts for the two components and those for the complex are difficult to obtain with certainty.

Figure 5 indicates that, for lithium chloride,  $n_{app}$  is a function of [enolate]/[LiCl] but attains a limiting value of 4 at large ratios. Measurements on the lithium bromide system show similar trends (Table III).

The halide complex can be envisaged as  $\text{Li}_5^+[(\text{LiOCPh}=\text{CMe}_2)_4\text{X}]^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ), in which the halide ion is located at the center of a tetrahedron of lithium ions with four enolate ions symmetrically disposed at the faces or apices of the inner cluster. Such a structure is reminiscent of that found for  $\text{Be}_4\text{O}(\text{OOCCH}_3)_6$  in which the four beryllium atoms are distributed tetrahedrally about the oxygen atom.<sup>16</sup> The present structure requires one lithium ion external to the complex.

(16) (a) W. Bragg and G. T. Morgan, *Proc. Roy. Soc., Ser. A*, **104**, 437 (1923); (b) W. Bragg, *Nature*, **111**, 532 (1923).

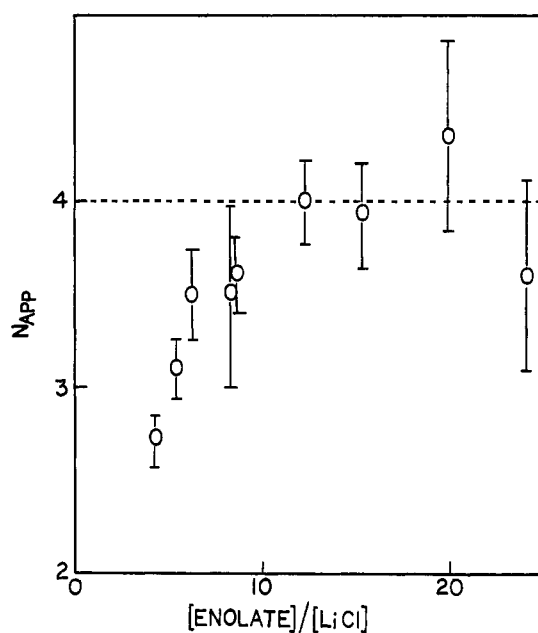


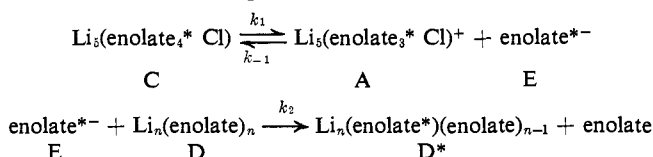
Figure 5. The dependence of  $n_{app}$  on [enolate]/[LiCl].

Attempts to observe multiple species of  $^7\text{Li}$  by nmr at 14.1 kG have been inconclusive as only asymmetric, but unresolved bands are observed for lithium bromide-lithioisobutyrophenone solutions at low temperatures.<sup>17</sup>

**Kinetics of the Exchange Process.** The dnmr studies afford the rates of exchange ( $1/\tau_{A,B}$  and  $1/\tau_{X,Y}$ ) of the enolate ion between the halide free aggregate and halide complex sites. Some selected values for the chloride and bromide systems are given in Table IV. Although

(17) We are indebted to Dr. M. Melchior of Esso Engineering and Research, Linden, N. J., for obtaining some  $^7\text{Li}$  spectra with a Jeolco C-60 HL spectrometer.

these measurements are subject to rather large errors, particularly at high values of [enolate]/[LiX], certain trends are immediately obvious. The rates of the forward reaction (A,B → X,Y) are relatively insensitive to changes in absolute concentrations, provided [enolate]/[LiX] is maintained constant, but they are sensitive to this ratio. In contrast, the back reaction (X,Y → A,B) is insensitive to both these factors. These observations are consistent with the mechanism given below, in which the exchange of magnetization between the two sites is effected through the intermediacy of a free enolate ion. The data in Table IV can be analyzed in terms of this mechanism in a manner which follows closely that developed by Williams and Brown<sup>18</sup> for exchange of <sup>7</sup>Li and <sup>1</sup>H between (CH<sub>3</sub>Li)<sub>4</sub> and Li<sub>2</sub>Zn(CH<sub>3</sub>)<sub>4</sub>. We note that the data refer to 25° at which temperature only the "high temperature" form of the halide free enolate is present.



Employing the steady state assumption for E

$$\begin{aligned} d(\text{E})/dt &= k_1(\text{C}) - k_{-1}(\text{A})(\text{E}) - k_2(\text{E})(\text{D}) \\ &= k_1(\text{C}) - k_{-1}(\text{E})^2 - k_2(\text{E})(\text{D}) = 0 \\ (\text{E}) &= k_1(\text{C})/[k_{-1}(\text{E}) + k_2(\text{D})] \end{aligned}$$

$$d(\text{D}^*)/dt = k_2(\text{E})(\text{D}) = k_1 k_2 (\text{C})(\text{D})/[k_{-1}(\text{E}) + k_2(\text{D})]$$

(18) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4132, 4140 (1966).

If  $k_{-1}(\text{E}) \ll k_2(\text{D})$

$$d(\text{D}^*)/dt = k_1(\text{C})$$

If (T) is the total enolate concentration in all forms

$$(\text{C}) = p_X(\text{T})/4, (\text{D}) = p_A(\text{T})/n$$

$$1/\tau_{A,B} = (1/n(\text{D}))(d(\text{D}^*)/dt) =$$

$$k_1(\text{C})/n(\text{D}) = k_1 p_X/4 p_A \quad (1)$$

$$1/\tau_{X,Y} = (1/4(\text{C}))(d(\text{D}^*)/dt) = k_1/4 \quad (2)$$

The data in Table IV can be used to test eq 1 and 2. For the chloride system  $1/\tau_{A,B}$  correlates well ( $r = 0.993$ ) with  $p_X/p_A$  and leads to  $k_1 = 71 \pm 4 \text{ sec}^{-1}$ .  $1/\tau_{X,Y}$  is reasonably constant and corresponds to  $k_1 = 91 \pm 14 \text{ sec}^{-1}$ . For bromide systems the corresponding values are  $46.4 \pm 3.6$  and  $60 \pm 8 \text{ sec}^{-1}$ . In both cases a small upward trend in  $1/\tau_{X,Y}$  with increasing halide concentration is apparent and similar trends are seen in the somewhat analogous systems studied by Williams and Brown.<sup>18</sup> It is possible that this is the result of increasing ionic strength, and certainly the values of  $k_1$  calculated from  $1/\tau_{X,Y}$  and  $1/\tau_{A,B}$  are in better agreement at low halide concentrations.

The free energies of activation for dissociation of an enolate ion from these complexes are of the order of 15–16 kcal mol<sup>-1</sup>, most of which is attributable to the enthalpies of activation. Effects of this magnitude are clearly capable of influencing the reactions of enolate ions in the presence of halide ions, a possibility which we are currently investigating.

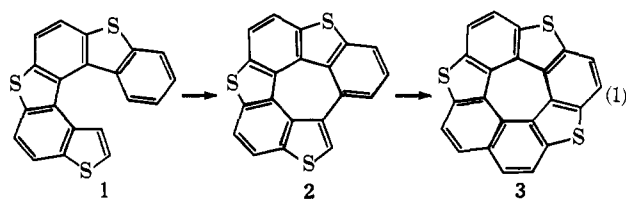
## Use of Thieno[2,3-*b*]thiophene in the Synthesis of Heterohelicenes by Double Photocyclizations

J. H. Dopfer, D. Oudman, and Hans Wynberg\*

Contribution from the Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands. Received October 2, 1972

**Abstract:** Five new heterohelicenes were prepared. Two new elements in heterohelicene synthesis have been introduced: (a) double photocyclizations and (b) the use of thieno[2,3-*b*]thiophene (4) as a building block for helicenes. In the nmr spectrum of one of the helicenes (6) "through-space coupling" is observed. The unusual spectral properties of helicenes containing the thiophene moiety are discussed.

Ever since the discovery and preparation of hexahelicene,<sup>1</sup> this compound has fascinated many chemists. Groen and Wynberg developed the chem-



(1) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

istry and determined the absolute configuration of the heterohelicenes.<sup>2</sup> Recently we reported the first synthesis of a [7]heterocirculene 3.<sup>3</sup> We wish to draw attention to the fact that with the preparation of this circulene 3 use has been made for the first time of the unique structural properties of the helicenes in the preparatively useful synthesis of other interesting com-

(2) (a) H. Wynberg and M. B. Groen, *ibid.*, **90**, 5339 (1968); **92**, 6664 (1970); (b) *Chem. Commun.*, 964 (1969); (c) M. B. Groen, H. Schadenberg, and H. Wynberg, *J. Org. Chem.*, **36**, 2797 (1971); (d) M. B. Groen and H. Wynberg, *J. Amer. Chem. Soc.*, **93**, 2968 (1971); (e) M. B. Groen, G. Stulen, G. J. Visser, and H. Wynberg, *ibid.*, **92**, 7218 (1970).

(3) J. H. Dopfer and H. Wynberg, *Tetrahedron Lett.*, 763 (1972).