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CARBANION MECHANISMS

VIII *. METALLATION OF ARYLMETHANES BY n-BUTYLLITHIUM. SPECTROPHOTOMETRIC STUDY OF ION PAIRING

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Summary

Results of a spectrophotometric study of the reaction of n-butyllithium are reported, in tetrahydrofuran (THF) medium, for triphenylmethane, diphenylmethane, di-*p*-tolylmethane, *p*-phenyltoluene and toluene. The temperature dependence of the absorption spectra for diphenylmethyllithium and di-*p*-tolylmethyllithium in THF gave evidence of an equilibrium between contact and solvent separated ion pair species, the latter predominating at low temperature. For di-*p*-tolylmethyllithium in THF this equilibrium is characterized by ΔH —5.9 kcal/mol and ΔS —18 e.u.

Introduction

Though the importance of organometallic compounds as reaction intermediates dictates that a variety of metallation procedures be readily accessible, systematic studies aimed at optimizing metallation of weak carbon acids have rarely been undertaken [2]. We reported recently on the use of the potassium amide and potassium methylamide/THF systems [1], as well as the potassium hydride/18-crown-6 ether/THF system [3], as effective metallating agents. While n-butyllithium has found wide use as a lithiating agent, the limits of its applicability in the direct metallation of weak carbon acids have not been established. In the present work the arylmethanes, of known acidities, have been found suitable for this purpose.

The arylmethanes which have been chosen for this study are triphenylmethane (TPM), diphenylmethane (DPM), di-*p*-tolylmethane (DPTM), *p*-phenyltoluene (PPT), and toluene (TOL). The pK_a values of these carbon acids, using Streitwieser's pK_a scale applicable to the cesium cyclohexylamide/cyclohexylamine

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* For Part VII, see ref. 1.

system, are 31.5, 33.1, 35.1, 38.6, and 41.0, respectively [4].

The available literature reports concerning the preparation of triphenylmethyllithium ($TPM^- Li^+$) from reaction of TPM with n-BuLi indicate that the extent of conversion is markedly dependent on the nature of the solvent employed. Thus, whereas Waack et al. [5] found that conversion to $TPM^- Li^+$ occurred in hexane/THF (85/15, v/v), Dietrich and Lehn [6] reported that in hexane alone no metallation took place. In the latter case, however, quantitative conversion to $TPM^- Li^+$ occurred on addition of cryptate. Similar behaviour was observed in the lithiation of DPM [6]. The lithiated derivatives of arylmethanes that are less acidic than DPM have generally been prepared by indirect routes, as for example by reaction of lithium with the dialkylmercury derivative [5].

Results and discussion

The reaction of n-BuLi with the series of arylmethanes, in THF solvent, was followed spectrophotometrically. It was found that TPM reacts with n-BuLi in THF solvent at room temperature yielding $TPM^- Li^+$ essentially quantitatively in ~15 min. A similar but somewhat slower reaction was found to occur between DPM and n-BuLi in THF (~30 min). Use of DME or Et_2O as solvents led to very much slower reactions and low extents of conversion (<25%), resulting probably in part due to reaction of n-BuLi with solvent [7], and in part due to the aggregation of n-BuLi in the low polarity solvents [8]. However, $TPM^- Li^+$ and $DPM^- Li^+$ in either DME or Et_2O solution could readily be obtained from the respective THF solutions by removal of THF under vacuum and transfer of the desired solvent to the residual organolithium. The concentrations of hydrocarbon used were in the range 10^{-4}—10^{-5} *M* and n-BuLi in hexane was added in 10-fold excess aliquot.

Addition of n-BuLi to DPTM in THF at room temperature and monitoring spectrophotometrically the $DPTM^- Li^+$ produced showed that a slow reaction was occurring, giving ~40% product after 1 h, based on the maximum absorbance value attained for $DPTM^- Li^+$. Since it appeared probable that n-BuLi was reacting competitively with the solvent, the experiment was repeated by mixing the reagents at —30°C, after 1 h allowing the temperature to rise gradually, but without significant improvement in the conversion. However, treatment with another aliquot of n-BuLi raised the yield of $DPTM^- Li^+$ to ~70%, and two further additions finally resulted in complete conversion to $DPTM^- Li^+$; following this no further increase in the carbanion absorbance was produced. Similarly, PPT required three additions of n-BuLi for complete conversion to $PPT^- Li^+$. Attempts to cause TOL to react under these conditions were largely unsuccessful, only low conversion to $TOL^- Li^+$ resulting after a number of additions of n-BuLi. Difficulty was experienced in ascertaining the extent of conversion to $TOL^- Li^+$ due to an interfering absorption, presumably caused by a side product from the reaction of n-BuLi with THF.

Examination of the carbanion systems at different temperatures revealed a variation in the spectral absorption bands which could be interpreted on the basis of ion pairing equilibria. It was found that the absorption spectra for $DPM^- Li^+$/THF and $DPTM^- Li^+$/THF showed changes on cooling to —60°C, but not those due to $TPM^- Li^+$ and $PPT^- Li^+$ in THF. The spectral changes for the former cases, i.e. for DPM$^-$ Li$^+$ a decreasing absorption at 418 nm and increasing at 448 nm while for DPTM$^-$Li$^+$ the absorption decreasing at 420 nm and increasing at 456 nm, have been found to be reversible, which indicates that the effect arises due to a shift in the equilibrium between two species. One can plausibly assign these species to the contact and the solvent separated ion pairs, the latter predominating at low temperature. Though no UV-vis spectral studies of these systems have previously been reported, analogy with the extensive studies on fluorenyl carbanion systems [9] and 1,1-diphenyl-n-hexyllithium [10] suggests that the shorter wavelength absorption is attributable in each case to the contact ion pair species and the longer wavelength absorption to the solvent separated ion pair species.

Ion pairing in diphenylmethylalkali-metal salts in ethereal solvents has been investigated by O'Brien et al. [11], using ^{13}C NMR spectroscopy. It was concluded that for DPM$^-$ Li$^+$ in THF a shift in equilibrium occurred on lowering the temperature and that at −50°C only solvent separated ion pairs were present. This is in overall agreement with our observations, so that the results of the UV-vis spectral study corroborate those obtained using the NMR method.

There has been no report of ion pairing in DPTM$^-$ Li$^+$ and we have therefore studied the DPTM$^-$ Li$^+$/THF system in detail. The spectra taken at various temperatures (Fig. 1) allow one to calculate the ΔH and ΔS parameters for the equilibrium:

$$\text{DPTM}^-, \text{Li}^+ + n\text{S} \rightleftharpoons \text{DPTM}^- \| \text{Li}^+$$

from the linear plot of log K vs. $1/T$ (Fig. 2). The equilibrium constant K at a given temperature is given by $K = [\text{S}]/[\text{C}] = (A - A_\text{C})/(A_\text{S} - A)$ where A is the

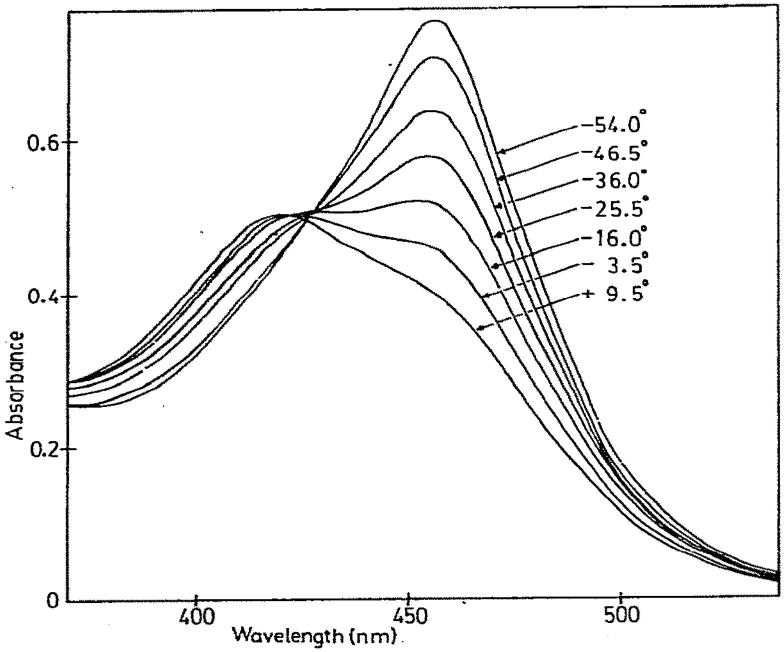

Fig. 1. Temperature dependence of the visible absorption spectra of di-p-tolylmethyllithium in tetrahydrofuran.

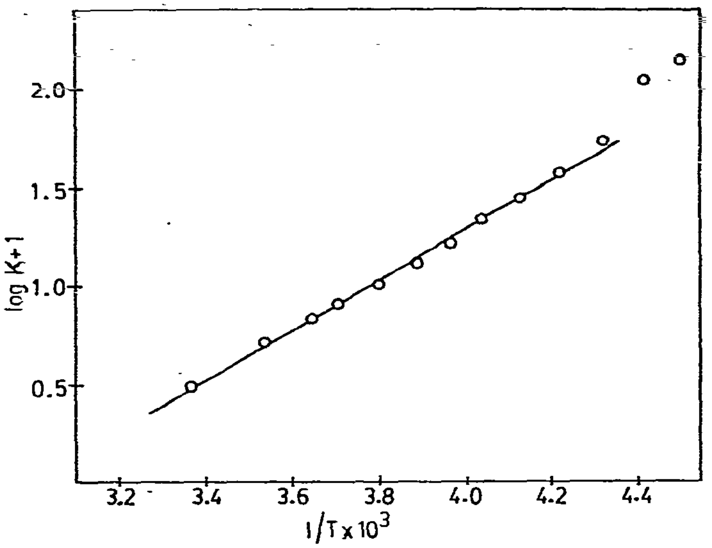

Fig. 2. Plot of log K versus $1/T$ for the contact solvent separated ion pair equilibrium (eq. 1).

density-corrected observed absorbance at 456 nm and A_C, A_S are the absorbance values at 456 nm due to 100% contact and solvent separated ion pairs, respectively. A_S and A_C are assumed to be equal [9], and A_S is taken from the spectrum at —54°C. The derived values of ΔH —5.9 kcal/mol, and ΔS — 18 e.u., are quite comparable to the results ΔH —6.3 kcal/mol, ΔS —20 e.u. for DPM^-/Li^+ in 2-methyltetrahydrofuran [11]. Negative enthalpies and entropies have generally been observed for contact to solvent separated ion pair equilibria [9], as a result of increased solvation and the concomitant immobilization of solvent molecules around the cation in this process.

Experimental

Materials

The arylmethanes used were recrystallized or distilled commercially available samples: TPM, m.p. 93.5—94.0°C; DPM, b.p. 125°C/10 mmHg, DPTM, b.p. 78°C/0.5 mmHg; PPT, m.p. 47—48°C. n-BuLi in hexane (Ventron) was standardized by titration (1.8 *M*). THF was distilled from calcium hydride, DME and Et_2O from lithium aluminium hydride, followed by treatment with n-BuLi, and were stored under vacuum in flasks fitted with greaseless Rotaflo stopcocks.

Procedure

The reactions between the arylmethanes and n-BuLi were carried out in a cylindrical vessel fitted with a 1 mm quartz cuvette and a Rotaflo stopcock attached to an "O" ring joint [12]. Solvent (~20 ml) was distilled into the flask from the storage vessel under vacuum and a known weight of the hydrocarbon (~1 mg) was introduced through the side arm under nitrogen, followed by addition of the n-BuLi with a syringe. The course of reaction was followed in a Unicam SP800B spectrophotometer, scanning periodically over the UV-vis region.

The spectral characteristics of the arylmethyllithium compounds in THF at ambient temperature, as obtained on successive additions of n-BuLi until maximum absorbance values resulted, are as follows: TPM$^-$ Li$^+$, 500, 435 (sh); DPM$^-$ Li$^+$ 418, 448; DPTM$^-$ Li$^+$, 420, 456; PPT$^-$ Li$^+$, 434 nm. In the case of DPM$^-$ Li$^+$ and DPTM$^-$ Li$^+$ the two absorption maxima are due to both contact and solvent separated ion pair species being present at equilibrium in appreciable proportions.

The temperature dependence of the ion pair equilibrium for DPTM$^-$ Li$^+$ in THF was performed after causing partial reaction between DPTM and n-BuLi (single aliquot) to occur in a vessel of the above design but fitted with a 10 mm cuvette which was sealed off for the spectrophotometric measurements, using a Beckman Acta IV instrument fitted with a low temperature accessory and a thermocouple attachment.

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References

1 E. Buncel and B.C. Menon, J. Organometal Chem., 141 (1977) 1.
2 H.O. House, Modern Synthetic Reactions, W.A. Benjamin, Menlo Park, Calif., 2nd ed., 1972.
3 E. Buncel and B.C. Menon, J. Amer. Chem. Soc., 99 (1977) 4457.
4 A. Streitwieser, Jr., J.R. Murdoch, G. Häfelinger and C.J. Chang, J. Amer. Chem. Soc., 95 (1973) 4248.
5 R. Waack, M.A. Doran, E.B. Baker and G.A. Olah, J. Amer. Chem. Soc., 88 (1966) 1272.
6 B. Dietrich and J.-M. Lehn, Tetrahedron Lett., (1973) 1225.
7 A. Maercker and W. Demuth, Liebigs Ann. Chem., (1977) 1909.
8 E. Buncel, Carbanions. Mechanistic and Isotopic Aspects, Elsevier, Amsterdam, 1975, Ch. 7.
9 J. Smid, in M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, Vol. 1, Wiley, New York, 1972.
10 R. Waack, M.A. Doran and P.E. Stevenson, J. Amer. Chem. Soc., 88 (1966) 2109.
11 D.H. O'Brien, C.R. Russell and A.J. Hart, J. Amer. Chem. Soc., 98 (1976) 7427.
12 E. Buncel and B.C. Menon, Can. J. Chem., 54 (1976) 3949.