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KINETIC STUDY OF ADDITION OF *p*-t-AMYLBENZYLLITHIUM TO 1,1-DIPHENYLETHYLENE IN TOLUENE

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SUMMARY

p-t-Amylbenzyllithium (I) is found to be appreciably soluble in toluene, in contrast to the very limited solubility of benzyllithium in this solvent. The reaction order in organolithium, for addition of I to 1,1-diphenylethylene, is 0.5. This kinetic behavior and reaction rate are compared to the behavior of benzyllithium in ether solutions and to the behavior of other organolithium reagents in hydrocarbon solution.

Kinetic studies of addition of the hydrocarbon soluble alkyllithium reagents to 1,1-diphenylethylene (DPE) were reported in benzene[1]. Lack of sufficient hydrocarbon solubility precluded reactivity studies of other structural types of organolithium reagents in hydrocarbon solution. Reported here is the preparation of a hydrocarbon-soluble odd alternant organolithium, *p*-t-amylbenzyllithium (I) and kinetic studies for addition of this reagent to DPE in toluene. Electronic spectral measurements and ^{7}Li NMR measurements are also reported. Kinetic studies of the odd alternant benzyllithium to DPE were reported for tetrahydrofuran[2] and diethyl ether[3] solutions.

The capability of an alkyl substituent to enhance hydrocarbon solubility of odd alternant organolithiums was suggested by the substantial hydrocarbon solubility of 1,1-diphenyl-n-hexyllithium[4] contrasted with the relative insolubility of diphenylmethyllithium. The limiting solubility of benzyllithium in aromatic hydrocarbons, *e.g.* benzene, is approximately 0.1 molar. The *p*-alkyl substituent of I imparts hydrocarbon solubility to >0.8 molar. The hydrocarbon solubility of polystyryllithium is an extreme example of this substituent effect. The kinetic behavior of polystyryllithium addition to styrene in benzene[5] corresponds to the kinetic behavior found here.

EXPERIMENTAL

The experimental procedures were identical to those reported previously[2]. Kinetic measurements were done in the closed spectroscopic cell[6]. Reagents were handled with gas-tight syringes. Solvents were distilled from lithium dispersion in argon. Reac-

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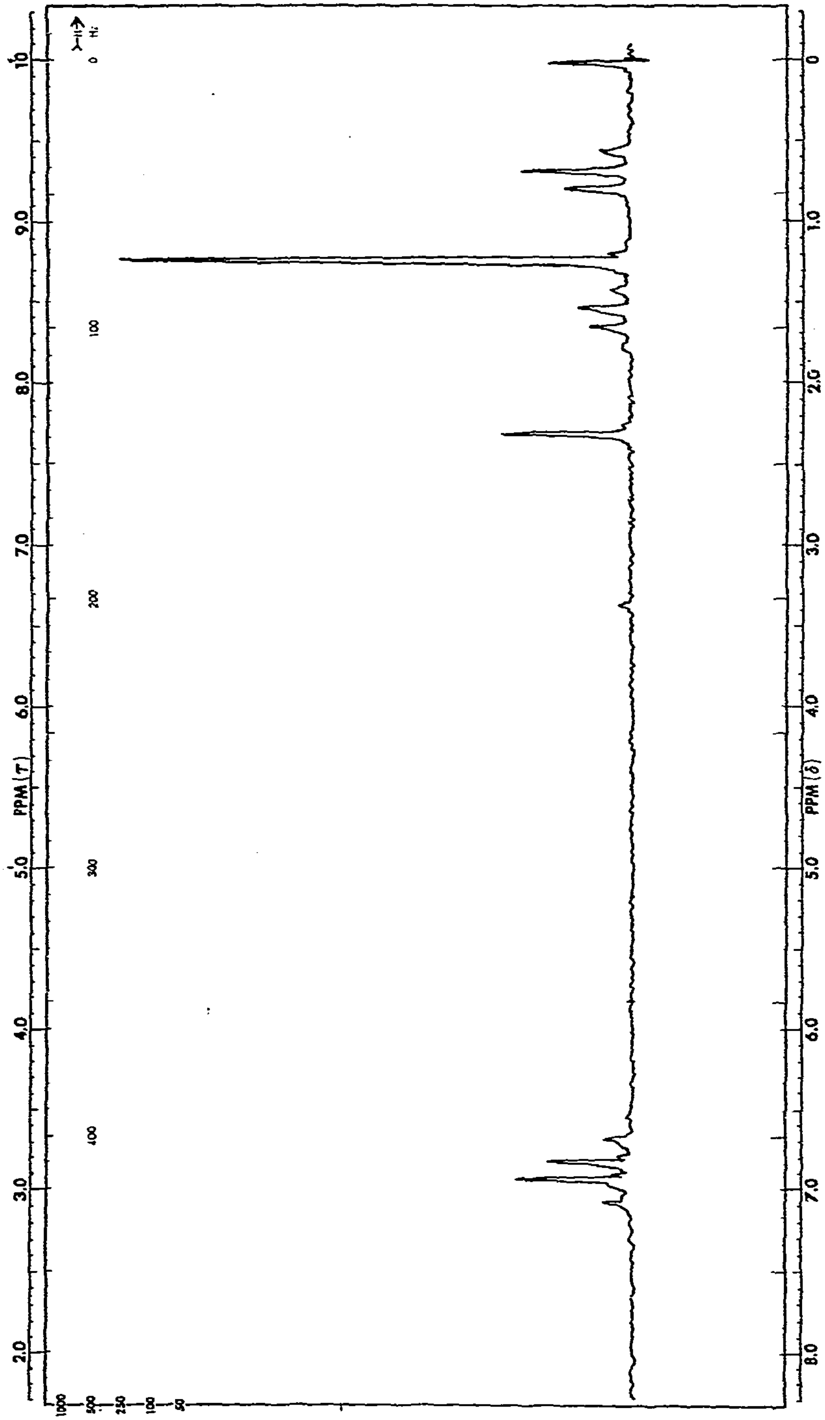

Fig. 1. Varian A60, PMR spectra of bis(p-t-amylbenzyl)mercury in CCl_4.

tion rates were determined by monitoring the rate of adduct formation spectroscopically, using a Cary-14 recording spectrophotometer.

Preparation of p-t-amylbenzyllithium

p-t-Amylbenzyllithium was prepared from lithium and the corresponding bismercury compound (*i.e.* bis(*p*-t-amylbenzyl)mercury), (II), in diethyl ether[2] or toluene solution, or in toluene containing THF at 2 molar equivalents to the mercury compound. Preparation in ether is rapid and straightforward. The mercury compound II (1.8 mmoles) was degassed to "hard" vacuum, blanketed with argon and several pieces of clean lithium wire and 6 ml diethyl ether were added. Reaction was evident after ten minutes stirring, magnetically, at room temperature. In two hours the molarity of soluble lithium was 0.43. This did not change in 4½ hours. Centrifuging gave a clear red-brown solution, yield 72%. Recovery of mercury ~78%.

A portion of this reagent (2.5 ml) was evaporated to dryness at 50° in vacuum. Addition of 3 ml toluene gave a clear solution. This was evaporated to dryness in vacuum at 60° giving first a yellow oil and then a crystalline yellow solid having the appearance of frozen benzene. One ml of toluene gave a clear solution. This was evaporated to dryness in vacuum at 60° with pumping for an extensive period of time. Addition of 1 ml of toluene gives a clear brown solution 1.1 molar in soluble lithium. Only a trace of diethyl ether remains. GLC analysis shows the ether to lithium molar ratio to be one to ten.

It was found that with more forcing conditions this lithium reagent could be prepared in aromatic hydrocarbon solvents. One and three-tenths mmoles of the mercury compound II was degassed on the vacuum line. Excess lithium wire cut into small pieces (the surface was scraped clean and shiny) and 2 ml toluene was added to the degassed II under argon purge. The reaction mixture was heated to 75° for 4 hours and then 3 ml toluene was added.

The clear supernate after centrifuging is 0.3 molar in soluble lithium. This represents 67% conversion. Recovery of mercury was 75%. This procedure has subsequently been found to permit preparation of unsubstituted benzyllithium in hydrocarbon solution[7].

Preparation and characterization of bis(p-t-amylbenzyl)mercury (II)

t-Amylbenzene (Aldrich) was chloromethylated with chloromethyl ether and zinc oxide to give *p*-t-amylbenzyl chloride (b.p. 103–112°/2mmHg). The chloride was converted to the dimethylsulfonium chloride salt by reaction with dimethyl sulfide in aqueous methanol. Titration of chloride ion with silver nitrate indicated a yield of 91.5%. The sulfonium salt was not isolated but converted directly to the mercury compound by reduction at the mercury cathode of a divided electrolytic cell*. The crude product, obtained from benzene extraction of the cathode compartment contents, was recrystallized from benzene–ethanol to give white needles, m.p. 82–84° in 87% yield.

Bis(*p*-t-amylbenzyl)mercury is an unreported compound. Identification was established by elemental analysis and NMR and electronic spectra. Found Hg, 38.0.

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* We are indebted to Dr. William Settineri for equipment use and procedural assistance in this preparation.

$C_{24}H_{34}Hg$ calcd.: Hg, 38.2%. The PMR spectrum (Varian A60, CCl_4) shown in Fig. 1 is interpreted as follows. The t-amyl group gives rise to a triplet, singlet and quartet at δ 0.67, 1.23 and 1.60 respectively. The aromatic protons show a A_2B_2 quartet at δ 6.9 and the α-CH_2 a singlet at δ 2.30. The α-CH_2 also is partially split into a doublet by ^{199}Hg ($J(^1H-^{199}Hg)$ 126Hz) only half of which is clearly visible at δ 3.36. Integration gives the appropriate relative intensities.

The electronic spectrum of the mercury compound in THF is a single absorption at 260 nm, $\varepsilon = 2.64 \times 10^4$. This compares with dibenzylmercury having a single absorption at 258 nm with $\varepsilon = 2.2 \times 10^4$.

The A_2B_2 PMR pattern for the aromatic protons, and the absence of signals not explained by the above interpretation, is good evidence that the isolated compound is the pure *para* isomer. Bis(*p*-t-amylbenzyl)mercury shows noticeable decomposition at room temperature under laboratory light after several days but appears stable for several months when stored in a refrigerator at 0°.

Lithium[7] NMR spectra were taken on the spectrometer of Baker and Burd[8] in sealed tubes prepared on the vacuum line.

RESULTS

p-t-Amylbenzyllithium reacts with 1,1-diphenylethylene (DPE) in toluene, diethylether or THF by addition of the organogroup to the methylene to give the substituted diphenylmethyllithium, III. This was established by GLC analysis of the protonated product. Identity of the adduct, III, was indicated by comparison with the benzyllithium adduct[3]. The electronic spectrum of the adduct, III, summarized in Table 1, is the same as that observed for analogous organolithium reagents[2,3]. The position of absorption maximum of the adduct is strongly solvent sensitive, in accord with reported detailed studies for the n-butyllithium–DPE adduct[4].

The effective extinction coefficients of the adduct, III, are less in hydrocarbon solution than in ethers, a result of the absorption bands being typically broader in the

TABLE 1

ELECTRONIC ABSORPTION SPECTRUM OF *p*-t-AMYLBENZYLLITHIUM AND DPE ADDUCT III

Solvent	λ_{max} *(nm)*	
	p-t-amylbenzyllithium[a]	*DPE adduct, III*[b]
Toluene	292[c]	422 (4900 cm^{-1})[d]
Et_2O	326	435 —
THF	330	494 (3700 cm^{-1})[d]
THF/Toluene[e]	330	494 (4200 cm^{-1})[d]

[a] $\varepsilon \sim 1 \times 10^4$ in toluene and 1.3×10^4 in THF. [b] p-t-$C_5H_{11}C_6H_4CH_2CH_2CPh_2Li$, $\varepsilon \sim 2 \times 10^4$ in toluene, 2.9×10^4 in Et_2O and 3.3×10^4 in THF. [c] Spectrum is the same in presence of 1/10 mole % Et_2O per mole lithium reagent. The absorption maximum is superimposed on increasing absorption due to the weak 261 nm absorption of toluene. [d] Absorption band width at half height. [e] 2/1, THF/toluene by volume.

former solvents than in the latter. In the THF/toluene mixture the breadth of the absorption band indicates a mixture of two etherates[4].

The position of the absorption maximum in the spectrum of *p*-t-amylbenzyllithium shows small changes with solvent as reported[7] for benzyllithium.

The lithium-7 chemical shifts of I show the same behavior as that of benzyllithium[7]. The chemical shift of I in toluene is + 1.65 ppm relative to n-butyllithium (in the same solvent but not examined as a mixture) for the reagent prepared in toluene or that prepared in diethyl ether and subsequent removal of the ether as described above. The reagent prepared in toluene gives a broad resonance having a width at half height of 24 Hz, whereas that prepared in ether (having a 10 mole % residual ether relative to I) is of half-width 7.4 Hz. The resonance in both samples shows an asymmetry on the low field side. In the toluene preparation this skewness is more pronounced. The lithium chemical shift of I in THF (prepared in ether and solvent removed) is at + 1.06 ppm relative to n-butyllithium, identical to that of benzyllithium[7].

The results of kinetic studies of addition of I to DPE in toluene are given in Table 2. The *p*-t-amylbenzyllithium used in these studies was that prepared in diethyl ether, which was removed as described in the preceding section and dissolved in toluene. The small amount of residual diethyl ether is considered to have no effect on the kinetic behavior; *i.e.* reaction order, but may increase the reaction rate, although probably not appreciably[9,10].

TABLE 2

INITIAL RATES OF ADDITION OF *p*-t-AMYLBENZYLLITHIUM TO 1,1-DIPHENYLETHYLENE IN TOLUENE AT 22±1°

$(RLi)_i$	$(DPE)_i$	$R_i/(DPE)_i$[a]	k[b] (*Effective rate constant*)
0.22	0.272	0.030	0.064
0.060	0.272	0.016	0.065
0.033	0.228	0.012	0.066
0.008	0.054	0.0049	0.055

[a] Units are moles$\cdot l^{-1}\cdot h^{-1}$, using $\varepsilon_{(adduct)} = 2.0 \times 10^4$. The ε value is uncertain and might be as low as $\sim 1.6 \times 10^4$. [b] $k = k'K(1/n)^{1/n}$, using $1/n = 0.5$ in the rate expression: rate $= k(\mathrm{RLi})^{1/n}\cdot(\mathrm{DPE})$.

Figure 2 is the log–log plot of initial rate *versus* formal organolithium concentration. The slope of line A in Fig. 2 shows that the effective reaction order in organolithium is 0.5. Data for the reaction of n-butyllithium with DPE in benzene[11], adjusted to 22°, is shown by the upper line, C, in Fig. 2. The dashed line, B, in Fig. 2 shows the effect of using an absorptivity value for adduct III of 1.6×10^4 as mentioned in Table 2.

A single kinetic experiment in diethyl ether indicates the reaction rate of I with DPE is ~1.8 times faster than that of benzyllithium in ether. Reaction of I with DPE in THF gives immediate red color as found for benzyllithium–DPE reaction in this solvent[2].

The reaction order in DPE was not determined but by analogy with previous work[11,12], is likely unity.

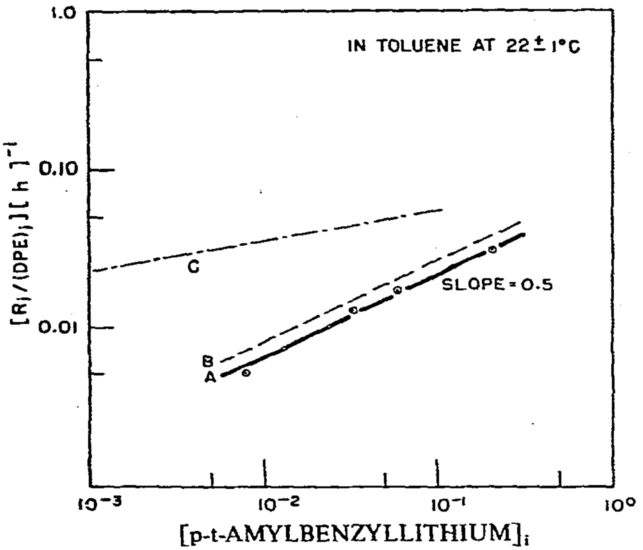

Fig. 2. Log–log differential rate plot for addition of *p*-t-amylbenzyllithium to 1,1-diphenylethylene in toluene at 22°.

DISCUSSION

The odd alternant organolithium reagent *p*-t-amylbenzyllithium has substantial hydrocarbon solubility. By comparison with the limited solubility of benzyllithium[7], it is apparent that the alkyl group has a pronounced influence on solubility behavior.

The electronic spectrum and ^{7}Li NMR spectrum of I in hydrocarbon and in ether solvents correspond to the behavior found for benzyllithium[7]. The changes in these properties with solvent are indicative of stronger ion-pair interaction in less polar solvents.

The 0.5 kinetic order shown by I in toluene is in agreement with the reaction order reported for polystyryllithium in the polymerization of styrene in benzene solution[5].

The line drawn in Fig. 2 through the points is of slope 0.50. The line best fitting all four points would be of slope 0.54. The lower concentration point presumably has more error, favoring the smaller value of the slope as representative of the true effective reaction order.

The 0.5 reaction order is attributed to the reagent being primarily dimeric, but that monomeric reagent predominates as the kinetically reactive species. In ether solutions, *i.e.*, THF[2] and diethylether[3], the effective reaction order for addition of benzyllithium to DPE is ~ unity. Hence, the solvation energy of interaction of these ethers with the dipolar benzyllithium (the positively polarized lithium is presumably the site of solvent interaction) is sufficient to overcome association energies, whereas in aromatic hydrocarbons the dipolar lithium reagent forms dimers, *i.e.*, self solvates. With other organolithium reagents, *e.g.*, n-butyllithium, the solvation energy gain between hydrocarbon and ether solvents is insufficient to disrupt the aggregates, although an average hexameric structure indicated in benzene[11] is reduced to approximately tetrameric aggregates in either[3]. These different behaviors presumably come about as a result of different energies of association or differences in solvation energies for the two reagents. The ability of the odd alternant molecule to delocalize negative charge into the π system is no doubt a factor favoring strong interaction of the donor solvents with the positively polarized lithium.

Rates of addition of n-butyllithium to DPE in benzene are illustrated in Fig. 1 for comparison with those of I in toluene. Relative reactivities of these two species are seen to be strongly concentration dependent owing to the different effective reaction orders. Nevertheless, the relative reactivity order for these reagents in aromatic hydrocarbon solution is not greatly different to that found in diethyl ether[3] and THF[2] solutions. For example, the relative reactivities between n-butyllithium and benzyllithium at 10^{-2} formal organolithium concentration is ~ 5 in aromatic hydrocarbon solution, 33 in diethylether and 3 in THF. At about one molar organolithium concentration, the reactivity of n-butyllithium and I in toluene become equivalent. The reactivities of n-butyllithium and benzyllithium also converge in diethyl ether and THF at approximately this same concentration[2,3].

On the other hand, there is an enormous difference in absolute reaction rates as a function of these three solvents for each of the above organolithium reagents. For example, rate constants (*i.e.* calculated at 1.0*F* organolithium concentration) in units $l^{1/n} \cdot \text{mole}^{-1/n} \cdot \text{sec}^{-1}$ are 1.8×10^{-5} for addition of I to DPE in toluene and for addition of benzyllithium to DPE in diethyl ether[3] is 1.8×10^{-2} and in THF is 3.0×10^{-1}. The reaction rate spread is $> 10^6$. The differences in effective reaction orders in these solvents cause the relative reactivity relation with solvent to be concentration dependent. To illustrate, at 0.01*F* organolithium the respective rates are 1.8×10^{-6}, 8.3×10^{-5} and 1.9×10^{-1}. In view of this enormous reaction rate difference induced by solvent for a particular reagent, the maintaining of the same relative reactivity order (and approximate magnitude of difference) between two reagents in each of these three solvents is significant.

REFERENCES

1 R. A. H. Casling, A. G. Evans and N. H. Rees, *J. Chem. Soc. B*, (1966) 519 and ref. therein.
2 R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, 91 (1969) 2456.
3 R. Waack and M. A. Doran, *J. Organometal. Chem.*, 29 (1971) 329.
4 R. Waack, M. A. Doran and P. E. Stevenson, *J. Amer. Chem. Soc.*, 88 (1966) 2109.
5 D. J. Worsfold and S. Bywater, *Can. J. Chem.*, 38 (1960) 1891.
6 R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, 85 (1963) 1651.
7 R. Waack, L. D. McKeever and M. A. Doran, *Chem Commun.*, (1969) 117, L. D. McKeever and R. Waack, *J. Organometal. Chem.*, 28 (1971) 145.
8 E. B. Baker and L. W. Bard, *Rev. Sci. Instr.*, 28 (1957) 313; 34 (1963) 238.
9 M. van Beylen, D. N. Bhattacharyya, J. Smid and M. Szwarc, *J. Phys. Chem.*, 70 (1966) 157.
10 R. Waack and M. A. Doran, *J. Organometal. Chem.*, 3 (1965) 481.
11 A. G. Evans and D. B. George, *J. Chem. Soc.*, (1961) 4653.