Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

DEPENDENCE OF THE KINETIC ISOTOPE EFFECT ON THE STRUCTURE OF THE ORGANOLITHIUM METALATING REAGENT IN THE METALATION OF TRIPHENYLMETHANE*

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(Received December 1st, 1968; in revised form July 3rd, 1969)

SUMMARY

Measurements have been made of k_H/k_D kinetic isotope effects associated with the metalation of a series of triarylmethanes (α-H and α-D) by six organolithium reagents (RLi) in tetrahydrofuran at 22°. The substantial variation in k_H/k_D value observed with benzyllithium, allyllithium, phenyllithium, vinyllithium, n-butyllithium and methyllithium, is attributed to different transition state geometries, dependent on the structures of the organolithium compounds. Hammett σ ρ plots for each RLi metalating reagent yield ρ values within the range 2.2 to 3.0, suggesting appreciable negative charge occurs on the triarylmethyl moiety in the transition states. It is inferred from k_H/k_D values measured with (*p*-methylphenyl)diphenylmethane, (*p*-methoxyphenyl)diphenylmethane, and triphenylmethane, that the effective basicity of organolithiums towards these substrates increases in the series n-butyllithium < vinyllithium < methyllithium < benzyllithium < phenyllithium.

INTRODUCTION

Measurements of kinetic isotope effects occurring on metalation of triphenylmethane by six organolithium (RLi) reagents are reported herein. The findings illustrate the dependence of k_H/k_D ratio on the structure of the organolithium reagent. Isotope effects which illustrate the effect of variations in structure of the substrate being metalated are known[1-4] for a number of metalation reactions. A recent report[5] examines the effect of metalating reagent structure on k_H/k_D values determined using a comparative technique. The k_H/k_D values reported here are derived from direct reaction rate measurements. The goal of these experiments was to provide opportunity to relate variation of transition state for metalation, as assessed from kinetic isotope effects, with structure of metalating reagent. Metalation studies are also reported on substituted triphenylmethanes with the aim of utilizing substituent effects to gain additional information about the transition states and their dependence on metalating reagent structure. The kinetic behavior and relative

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* This paper was reported in part at the Symposium on Hydrocarbon Ions, Abstracts, 152nd National Meeting, American Chemical Society, New York, N.Y., September 1966, p. U41.
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reactivities of the same six RLi reagents as metalating reagents towards triphenylmethane are discussed elsewhere[6,7].

EXPERIMENTAL

Rates of formation of triphenylmethyllithium and substituted triphenylmethyllithiums were followed spectrophotometrically at 500 mμ using a Cary 14 spectrophotometer, and the recorded kinetic data were processed as reported previously[8]. All product triarylmethyllithiums were found, within experimental error, to have the same extinction coefficient at 500 mμ ($\varepsilon = 3.5 \times 10^4$ $M^{-1} \cdot \text{cm}^{-1}$), although the shapes of the absorption envelopes were not identical. The spectroscopic cell employed in this work, and the experimental techniques have been described earlier[9]. All reactions were conducted under an atmosphere of dry argon in tetrahydrofuran (THF) at $22 \pm 1°$, generally using $[\text{substrate}]_i \simeq 0.002$ M and excess RLi. Colligative property measurements were done by established techniques[10]. THF was preliminarily dried over calcium hydride, stirred with lithium benzophenone ketyl, and distilled from the blue-green ketyl just prior to use. Diethyl ether and hexane were distilled from lithium metal dispersion.

Precursors for organolithium reagents purchased and used without further purification were $(CH_3)_2Hg$ (Eastman Organic Chemicals), $(CH_2{=}CHCH_2)_2Hg$ (Orgmet, Inc.), $(CH_2{=}CHCH_2)_4Sn$ and $(CH_2{=}CH)_4Sn$ (M and T Chemicals, Inc.), whereas $(C_6H_5CH_2)_2Hg$ (Metallomer Laboratories) was recrystallized from methylene chloride/ethanol mixture. n-Butyllithium in hexane was obtained from Foote Mineral Company and used as received.

Preparation of organolithiums

The organolithiums were prepared using halide free procedures, since such salts effect reactivity[11-13]. Methyllithium, benzyllithium and allyllithium were prepared in diethyl ether from the corresponding bis-organomercury compounds and excess lithium metal[9,14]. Vinyllithium and allyllithium were made from tetraorganotins via transmetalation with n-butyllithium[8,15]. Formal organolithium concentrations {RLi} were determined by titration with 0.10 M HCl using phenolphthalein as indicator. When using fresh reagents, total alkalinity is, within analytical capabilities, equivalent to the active organolithium concentration {RLi}[16].

*Triarylmethanes**

Triphenylmethane. Triphenylmethane (Eastman Organic Chemicals) was recrystallized from ethanol prior to use; m.p. 92.5° (lit. m.p. 92.5°).

Triphenylmethane-α-d. To a solution of 17 mmoles of $(C_6H_5)_3CH$ in 5 ml THF was added, in 5 ml aliquots, 25 ml of 1.56 F n-butyllithium (39 mmoles) in hexane. The first aliquot was added dropwise giving initially a clear red solution and later a two-phase system (orange over red solution layers). Addition of the remaining aliquots, during stirring of the system, produced a solid orange precipitate. The supernatant was transferred to another vessel and 1.0 ml THF added with no perceptible change in color. A small amount of orange precipitate was found on the

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* The elemental analyses were done by Galbraith Laboratories, Inc.

addition of 2.5 ml n-butyllithium/hexane solution after cooling. The main batch of orange precipitate was washed several times with hexane, dried under vacuum, and 10 ml THF added yielding a deep red homogeneous solution, $\{(C_6H_5)_3CLi\} = 0.80\ F$. The solution was cooled to 0° and 0.1 ml D_2O added dropwise with stirring. Work up of the solution together with recrystallization of the product from methanol produced 0.836 g $(C_6H_5)_3CD$, m.p. 92.5°. A further 0.040 g was recovered from the mother liquors after D_2O treatment. Total yield 0.876 g (21%). The material was analyzed for deuterium content (Josef Nemeth, Urbana, Illinois 61801) and found to be 97% pure. NMR and mass spectral analyses confirmed this finding.

Tris-p-tolylmethane. This compound, m.p. 61–62° (lit.[17] m.p. 61–63°), was kindly supplied by Dr. Arnold E. Young, The Dow Chemical Company.

(Substituted-phenyl)diphenylmethanes. The commercially available intermediates used in the synthesis of these compounds were *m*-fluorobromobenzene and *m*-(trifluoromethyl)benzoyl chloride (Pierce Chemical Co.), *p*-bromotoluene and *p*-bromoanisole (Columbia Organic Chemicals), lithium aluminum hydride and lithium aluminum deuteride (Metal Hydrides, Inc.) and triply sublimed magnesium (The Dow Chemical Co.).

The appropriate triarylmethanols were prepared by reaction of benzophenones or arylesters with aryl Grignard or organolithium reagents usually in THF or diethyl ether. The reaction products were isolated in crude form and then, unless otherwise stated, converted into the corresponding triarylmethyl chlorides by refluxing for approximately 30 min with an excess of acetyl chloride or thionyl chloride in petroleum ether. The desired chlorides were isolated either as oils or solids, recrystallized from benzene/petroleum ether or hexane containing a few drops of acid chloride. These triarylmethyl chlorides were dissolved in diethyl ether to which was added excess lithium aluminum hydride (or deuteride). The reaction was allowed to proceed for approximately 1 h prior to quenching with an isopropanol/water mixture. Rochelle salt $(NaKC_4H_4O_6 \cdot 4\ H_2O)$ was added to complex the aluminum salts and the organic material extracted with diethyl ether, dried over sodium sulphate and stripped of solvent. The resultant materials were usually oils which crystallized out on standing. The products were recrystallized from methanol and all were indicated to be of $\gtrsim$95% purity by mass spectrometry, NMR and infrared spectroscopy.

(p-Methoxyphenyl)diphenylmethane, m.p. 60–61° (lit.[18] m.p. 60–61°)
(p-Methoxyphenyl)diphenylmethane-α-d, m.p. 59.5–60.5°
p-Tolyldiphenylmethane, m.p. 69–70° (lit.[19] m.p. 70–71°)
p-Tolyldiphenylmethane-α-d, m.p. 69–70°
(m-Fluorophenyl)diphenylmethane, m.p. 40–41° (Found: C, 86.84; H. 5.71; F, 7.07. $C_{19}H_{15}F$ calcd.: C, 86.99; H, 5.76; F, 7.24%.)
(m-Fluorophenyl)diphenylmethane-α-d, m.p. 40–41°

[m-(Trifluoromethyl)phenyl]diphenylmethane. This compound was prepared by formic acid/sodium formate reduction of the corresponding carbinol. Work up of this reaction mixture produced a light yellow oil, which on high-vacuum distillation gave a clear viscous oil that crystallized upon standing. This material was recrystallized from methanol giving a product with m.p. 35–36°. (Found: C, 77.13; H, 4.70; F, 18.07. $C_{20}H_{15}F_3$ calcd.: C, 76.91; H, 4.84; F, 18.25%.)

[m-(Trifluoromethyl)phenyl]diphenylmethane-α-d, m.p. 34–35°.

RESULTS

The six RLi reagents examined were n-butyllithium, methyllithium, phenyllithium, vinyllithium, benzyllithium and allyllithium. Reactions were generally run using excess RLi, with $[\text{substrate}]_i \simeq 0.002\ M$. This procedure minimized possible influence of product triphenylmethyllithium/reactant RLi interactions. From measurements of the initial increase in optical density at 500 mμ with time, the quantity:

$$\left(\frac{\text{RATE}}{S}\right)_i = \left(\frac{\mathrm{d}\{(C_6H_5)_3CLi\}/\mathrm{d}t}{[\text{substrate}]}\right)_i$$

was evaluated for each RLi metalating reagent over a range of $\{\text{RLi}\}_i$ concentrations, using triarylmethanes (α-H and α-D) as substrate. Plots of log $(\text{RATE}/S)_i$ *vs.* log $\{\text{RLi}\}_i$ are given in Fig. 1. Least-square lines were drawn through each set of data.

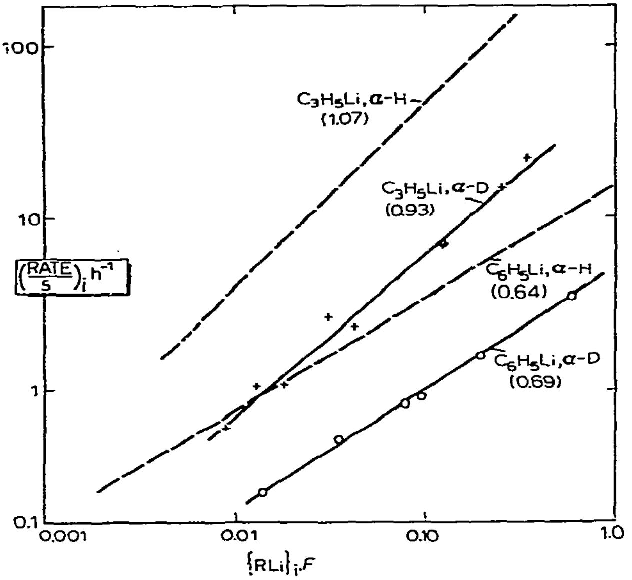


Fig. 1. Variation in RLi reaction orders in the metalation of $(C_6H_5)_3CH$ and $(C_6H_5)_3CD$ by allyllithium and phenyllithium in THF at 22°.

The slope of each line (given in Table 1) is the effective reaction order in organolithium reagent over the concentration range examined[8]. Both $(C_6H_5)_3CH$ and $(C_6H_5)_3CD$ yield effectively the same reaction order in $\{\text{RLi}\}_i$, although experimental variations are evident. No significant changes in these {RLi} reaction orders were observed in the metalation of substituted triarylmethanes both for α-H and α-D compounds.

Values of k_H/k_D for metalation of $(C_6H_5)_3CH(D)$ by the six RLi reagents at $\{\text{RLi}\}_i = 0.08\ F$ are given in Table 2. The relative reactivities exhibited by these metalating reagents at $\{\text{RLi}\}_i = 0.08\ F$ towards substituted triarylmethanes (α-H and α-D) were also determined. Hammett σ ρ plots of log Relative Rate *vs.* substituent σ yield ρ values between 2.2 and 3.0 for n-butyllithium, methyllithium, phenyllithium

TABLE 1

REACTION ORDERS IN INITIAL FORMAL ORGANOLITHIUM CONCENTRATION $\{RLi\}_i$, F, FOR METALATION OF $(C_6H_5)_3CH(D)$ IN THF AT 22 ± 1°

Organolithium (RLi)	$(C_6H_5)_3CH$[7]			$(C_6H_5)_3CD$		
	$\{RLi\}_i$ F range studied	Number of expts.	Least square slope[a]	$\{RLi\}_i$ F range studied	Number of expts.	Least square slope[a]
n-Butyllithium	0.006–1.0	19	0.33 ± 0.05	0.01 –0.5	7	0.27 ± 0.08
Methyllithium	0.010–0.7	9	0.28 ± 0.08	0.02 –0.6	8	0.25 ± 0.05
Phenyllithium	0.003–2.0	25	0.64 ± 0.07	0.01 –0.6	6	0.69 ± 0.04
Vinyllithium	0.005–1.0	16	0.24 ± 0.04	0.02 –0.7	4	0.30 ± 0.16[b]
Benzyllithium	0.007–0.04	6	0.90 ± 0.27	0.007–0.1	8	0.90 ± 0.16
Allyllithium	0.005–0.3	24	1.07 ± 0.05	0.009–0.4	9	0.93 ± 0.10

[a] 95% confidence limits. [b] Large error because only have four points for regression analysis.

(Fig. 2), vinyllithium and benzyllithium. In addition, kinetic isotopic values (k_H/k_D) were computed for each RLi reagent at $\{RLi\} = 0.08$ F with a series of substituted triarylmethanes (α-H and α-D) (Fig. 3).

In metalations where $[\text{substrate}]_i \gg \{RLi\}_i$, an initial major optical density increase was observed at 500 mμ which was equivalent to substantially less than 100% yield of triphenylmethyllithium based on the quantity of RLi employed. Sub-

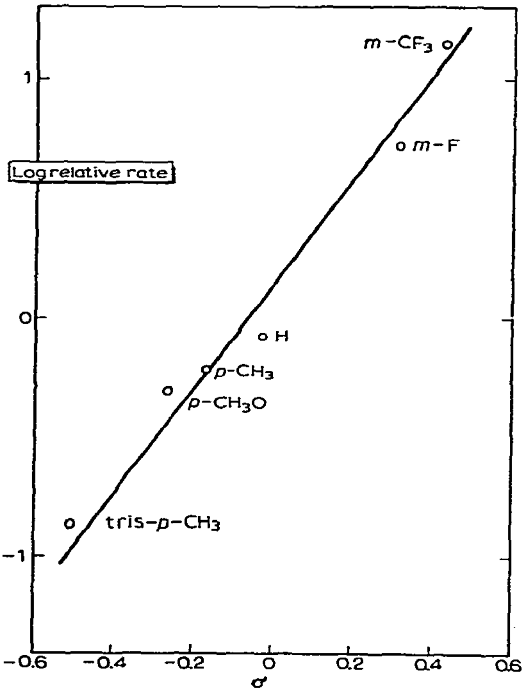


Fig. 2. Hammett $\sigma\rho$ plot for metalation of monosubstituted triphenylmethanes and tri-p-tolylmethane with 0.08 F phenyllithium in THF at 22° ($\rho = 2.2$).

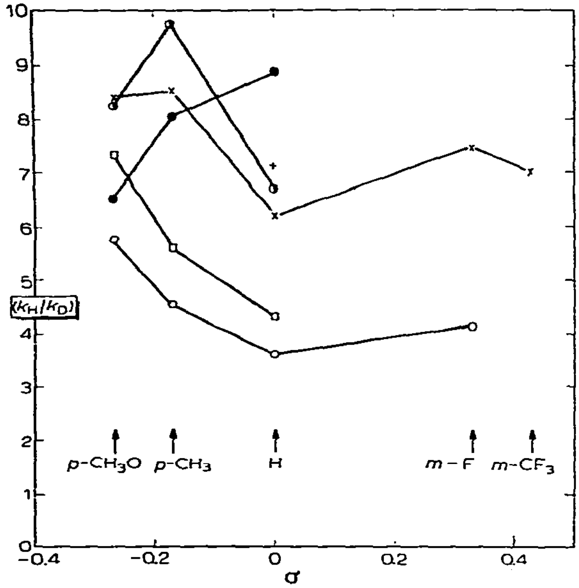


Fig. 3. Kinetic isotopic effects associated with the metalation of substituted triphenylmethanes in THF at 22° by various organolithium reagents at $\{RLi\}_i = 0.08$ F (○ phenyllithium, □ benzyllithium, × methyllithium, ◑ vinyllithium, + allyllithium, ● n-butyllithium).

sequent aliquots of RLi produced incremental increases in optical density. This behavior is considered[7] to result from multimetalation of the substrate.

DISCUSSION

Values of k_H/k_D listed in Table 2 are substantial and establish that rupture of the α-carbon–hydrogen bond is rate-determining in the metalation of $(C_6H_5)_3CH$ by organolithium reagents in THF solution.

Experimentally measured k_H/k_D values as read from plots of log $(RATE/S)_i$ *vs.* log $\{RLi\}_i$ (*e.g.* Fig. 1), vary slightly with $\{RLi\}_i$. This is due to difference in slope of least-square lines drawn through the two data sets derived from $(C_6H_5)_3CH$ and $(C_6H_5)_3CD$. The difference between the reaction orders determined with the α-H and α-D compounds for a particular RLi reagent is not statistically significant. The 95% confidence limits of the individual reaction orders are given in Table 1.

The organolithium reagents in Table 2 exemplify three structural classes: (1) alkyl, n-butyl and methyl, (2) sp^2-carbon σ-bonded, phenyl and vinyl, and (3) resonance stabilized, benzyl and allyl. Notably, k_H/k_D values *within each class* of reagents vary substantially. Thus, a relationship between k_H/k_D value and relative base strength of the metalating reagents, as judged by pK_a of their conjugate acids, is lacking.

The transition state for this metalation reaction, following Hammond's postulate[24], should strongly resemble reactants. Relative amounts of $\geq$C–H bond rupture and R–H bond formation would be expected to relate to the relative stabilities of the product triphenylmethyllithium and the reactant RLi. The amount of bond breakage/formation in the transition state should, therefore, vary in a direct manner with the structure of R, presuming the transition state structures are similar.

TABLE 2

KINETIC ISOTOPE VALUES FOR METALATION OF $(C_6H_5)_3CH(D)$ BY ORGANOLITHIUM REAGENTS IN TETRAHYDROFURAN

Organolithium (RLi)	(k_H/k_D) ± 0.5[a]	Approximate pK_a of conjugate acid RH[b]	Predominant RLi species[c]
n-Butyllithium	8.9	42	Tetramer
Methyllithium	6.2	40	Tetramer
Phenyllithium	3.6	37	Dimer
Vinyllithium	6.7	36.5	Tetramer
Benzyllithium	4.3	35	Monomer
Allyllithium	7.1	35.5	Monomer + dimer
$(C_6H_5)_3CH$		32.5	

[a] Values taken at {RLi} = 0.08 *F*. Values change slightly with RLi concentration (0.005 to 0.5 *F*) owing to small differences in least-squares effective reaction orders in RLi for Ph_3CH and Ph_3CD (Table 1). $[(C_6H_5)_3CH(D)]_i = 0.002$ *M*. [b] See ref. 22. Absolute values are in doubt; relative values are of significance here[23]. [c] Results applicable at {RLi} = 0.1 *F* in THF at 25°, procedure as in ref. 10.

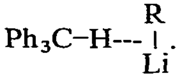
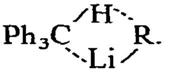
Fundamental principles predict a maximum k_H/k_D value for a transition state symmetrical with respect to proton transfer, *i.e.*, force constant of the breaking bond is equal to the force constant of the forming bond[25,26]. Hence, decreasing k_H/k_D values for more reactant-like or more product-like transition states are expected[27]. Sensitivity of k_H/k_D values to transition state symmetry is uncertain, but it is believed to be a smooth function and is suggested to have a sharp rather than a broad maximum[28,29].

For the case involving free ions and presumably non-crowded transition states, the above concepts are demonstrated by recent experiments[30-32]. Correlation between pK_a and k_H/k_D was found for proton transfer between substituted pyridines and 2-nitropropane[33]. It was shown that, when the pK_a of reactant hydrocarbon and product hydrocarbon are equal, a maximum k_H/k_D value is obtained. The behavior expected in the present studies would, therefore, be for organolithiums within each class of reagent, the conjugate acids of which have similar pK_a's, to have k_H/k_D values of similar magnitude. The anticipated order of increasing k_H/k_D value should be n-butyl $\lesssim$ methyl $<$ phenyl $\lesssim$ vinyl $<$ allyl $\lesssim$ benzyl. The order of the values in Table 2 deviate substantially from this prediction.

The anticipated variation in k_H/k_D value requires that the basicity of each of the organolithium species in solution relate to the acidity of its corresponding hydrocarbon in the same manner. This is apparently true for free ions[30-32], but doubtful for ion pairs (for example see ref. 34). The reactive organolithium species in these studies are believed to be ion pairs and/or ion aggregates[7].

The deviation of these k_H/k_D values from expectation indicates that the basicity of each RLi may not relate to the acidity of RH in the same manner throughout the series of organolithium reagents or even *within each class* of species. This may arise from the intrinsic anion–cation interaction of the reactant organolithium not following a regular behavior with changes in structure of the organolithium species, as a consequence of such factors as differences in solvation, anion size and inherent anion stabilities.

The observation that the pK_a of weak acids differ in mediums in which free ions are existing from those found in mediums favoring ion pairing[34] supports this suggestion. The influence of ion-pair interaction is illustrated by sensitivity of k_H/k_D to cation keeping the same anion[35].

Two other important considerations are transition state geometry and tunneling. Most theoretical treatments presume linear C–H---X transition states in proton transfer reactions, which in these studies could be visualized as  $Ph_3C{-}H{\cdots}\overset{R}{\underset{Li}{|}}$. Most likely the transition states in these reactions are not linear but take the form,  $Ph_3C\overset{H}{\underset{Li}{\langle\ \rangle}}R$. Such transition states are no doubt crowded.

Transition states for each metalation reaction may be expected to differ because of dissimilar steric requirements of the organolithium reagents. The degree of loss in vibrational and bending modes in the transition states could, then, depend on factors other than the base strength of the organolithium species[28]. Differences in attenuation of force constants between the transition states would result in variation in k_H/k_D values[27] (considering C–H stretch max. $k_H/k_D \sim 6.6$, but considering loss of bending modes max. $k_H/k_D \sim 14$–17)[36].

The contribution of tunneling may vary substantially with the various organolithium reagents owing to different energetics and transition state geometries. Tunneling is predicted to be most pronounced in sterically hindered transition states for which the high thin barrier is the ideal situation[33]. Because k_H/k_D is increased by tunneling from what it would be in the absence of tunneling, the trends in the data do not seem to be in accord with this being a significant factor. The experimental values are substantially less than the theoretical k_H/k_D value of ~ 14 attainable in the absence of tunneling[36].

It is important, however, to note that the gross nature of these organolithium species in solution differ substantially[10] (see Table 2). Consequently, some species show first order kinetic dependence and others show fractional reaction orders[7,37,38]. Of importance to the isotope measurements, though, is the nature of the organolithium species in the rate determining step, which may or may not correspond to the form of the bulk reagent in solution. Correlation of colligative property measurements with kinetic behaviors[7], indicates that in some instances aggregated organolithium species (*e.g.* dimers, tetramers) are sufficiently reactive to be responsible for appreciable product formation, relative to that from monomeric RLi species.

To further enlarge understanding of the transition states of these metalation reactions, relative reaction rates and isotope effects were evaluated for metalation of substituted triphenylmethanes by most of these organolithium reagents. Reaction orders in $\{RLi\}_i$ obtained with different substituted triphenylmethanes and a particular organolithium reagent are, within experimental error, the same as those derived for unsubstituted triphenylmethane. Data obtained at $\{RLi\}_i = 0.08$ *F* with phenyllithium (Fig. 2), vinyllithium, methyllithium, n-butyllithium, and benzyllithium, when plotted in the form of log Relative Rate *vs.* σ yield Hammett ρ values between 2.2 and 3.0. The sizable positive ρ values, independent of the nature of the organolithium reagent, indicate substantial negative charge density on the triphenylmethyl moiety in the transition states. This situation is directly comparable with the carbanionic character of transition states involved in both the detritiation of ring-substituted toluene-α-*t* compounds with lithium cyclohexylamide in cyclohexylamine ($\rho = 4.0$)[39], and the copolymerization of *p*-substituted styrenes with living polystyrene ($\rho = 5.0$)[40]. In the foregoing instances larger ρ values are observed than in the metalation of the triarylmethanes. This behavior is predictable since ring substitution in benzyl anionic moieties would be expected to produce greater percentage change in reaction rate than similar substitution in a single phenyl ring of triphenylmethyl anionic species.

A feature of note is that substantial variations in k_H/k_D value occur with different substituted triphenylmethanes and the same metalating reagent. Plots of k_H/k_D *vs.* σ for such systems (Fig. 3) contain sections of negative, zero, and/or positive slope, such behavior being associated with variations in the degree of proton transfer in the transition states. An increase in k_H/k_D value resulting from *p*-methyl or *p*-methoxy substitution of a phenyl ring in triphenylmethane is observed with phenyllithium and benzyllithium (Fig. 3), indicating that the transition states are reactant-like in accord with Hammond's postulate[24]. A maximum in kinetic isotope effect is expected when the transition state is of symmetrical configuration with respect to hydrogen transfer. When an increase in substrate pK_a within a series of substituted triphenylmethanes (*e.g.* *p*-methyl and *p*-methoxy) results in a decrease in k_H/k_D value as observed with the n-butyllithium (Fig. 3), the occurrence of more product-like transition states for metalation by this RLi reagent is indicated. Consideration with confidence can not be given to k_H/k_D values measured for (*m*-fluorophenyl)diphenylmethane and [*m*-(trifluoromethyl)phenyl]diphenylmethane, since analytical data on the reaction of these substrates with different organolithium reagents indicate that undesirable side reactions occur*.

The k_H/k_D value obtained from our direct rate measurements for the phenyllithium/triphenylmethane system in THF at 22° is not significantly different from that evaluated by product analysis of competitive metalation[5] of triphenylmethane and triphenylmethane-α-*d* by phenyllithium in THF at 15°. On the other hand, the comparative technique gives a k_H/k_D value of 10.8 ± 1 for triphenylmethane metalation by benzyllithium at 15°, which is substantially higher than the 4.3 ± 0.5 value derived from initial rate measurements on the same system at 22°. The small difference in

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* The treatment of $(p\text{-CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CH}$ and $(p\text{-CH}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CH}$ with methyllithium or n-butyllithium in THF appears to lead dominantly to monometalation. This is indicated by NMR and GLC studies of trimethylsilyl derivatives of the reacting products. Extensive metalation of the *p*-anisyl ring does not seem to occur within the allowed 30 min reaction time**. On the other hand, a multitude of GLC bands are observed after trimethylsilyl chloride has been reacted with the products obtained on mixing benzyllithium in THF with either $(m\text{-FC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CH}$ or $(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CH}$ over a 30 min period***.

** It should be noted here that n-butyllithium, however, does metalate anisole[4] and $(m\text{-CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CH}$ (mol.wt. 274). In the latter instance, mass spectrometric analysis of the D_2O quenched metalation products shows mono-, di- and tri-deutero compounds (mol.wt. 275, 276 and 277 respectively)[41].

*** This behavior is in contrast to the stability exhibited by *m*-(trifluoromethyl)toluene towards lithium cyclohexylamide in cyclohexylamine. Only proton exchange at the α-carbon atom occurs, and this at a rate in accord with that expected for $\sigma(m\text{-CF}_3)$[39].

ambient temperatures employed in the separate studies is not expected to be responsible for this difference in k_H/k_D values.

A possible explanation is that in the comparative experiments benzyllithium in THF was slowly added over a 5–30 minute period to at least a tenfold excess of triphenylmethane (50/50, α-H/α-D) in THF, with subsequent analysis for α-H and α-D toluene. Benzyllithium is not stable as a dilute solution in THF[6], and reaction with the solvent, or impurities, could bias the derived k_H/k_D value to the high side. In addition, in the comparative experiments product triphenylmethyllithium is present in appreciable quantity relative to reactant RLi as the reaction proceeds, and the effective reactivity of reactant RLi may be appreciably affected by interaction with triphenylmethyllithium, the importance of such an interaction perhaps varying with RLi structure. The significance of measured k_H/k_D values under such circumstances is consequently questionable.

From the work presented here on the metalation of substituted triphenylmethanes by phenyllithium, it is concluded that the transition state involved in the reaction of phenyllithium with triphenylmethane at 22° resembles reactants. In contrast to this, comparative studies[5] involving phenyllithium in THF and a series of hydrocarbons—phenylacetylene, fluorene, indene, *p*-biphenylyldiphenylmethane and triphenylmethane—were interpreted as indicating that the phenyllithium/triphenylmethane transition state resembles products. Since our findings do not support the latter conclusion, a likely explanation is that the influence of different steric factors, as considered earlier[5] by the authors of the competition studies, may be important within the series of acids examined in the comparative experiments.

The observation of a range of k_H/k_D values for metalation of triarylmethanes by different organolithium reagents in tetrahydrofuran is significant. Variable transition state geometries are considered to have a significant influence upon the relative magnitude of k_H/k_D kinetic isotope effects. From the kinetic isotope effects (k_H/k_D) recorded for *p*-tolyldiphenylmethane, (*p*-methoxyphenyl)diphenylmethane, and triphenylmethane itself (Fig. 3), it is inferred that the effective basicity exhibited by the different RLi reagents toward the triarylmethyl substrates increases in the order n-butyllithium < vinyllithium < methyllithium < benzyllithium < phenyllithium.

The absence of a relationship between k_H/k_D values and relative reactivities of these organolithium species is also significant; the latter change dramatically with RLi concentration[37,38], whereas the former are much less dependent on this parameter, see Fig. 1 and footnote[a], Table 2.

ACKNOWLEDGEMENTS

The authors wish to thank Mary A. Doran for the preparation of triphenylmethane-α-*d* and Arnold E. Young for the preparation of tris-*p*-tolylmethane. Appreciation is also expressed to Elliott Richelson and Mary C. Woodville for assistance in some of the kinetic experiments, and to Thomas W. Shannon and Philip R. Briggs for the mass spectrometric analyses.

REFERENCES

1 A. Streitwieser, Jr., R. G. Lawler and C. Perrin, *J. Amer. Chem. Soc.*, 87 (1965) 5385.
2 E. A. Kovrizhnykh, F. S. Yakushin and A. I. Shatenshtein, *Org. Reactivity*, 3 (1966) 209.

3 H. F. EBEL AND G. RITTERBUSCH, *Justus Liebigs. Ann. Chem.*, 704 (1967) 15.
4 D. A. SHIRLEY AND J. P. HENDRIX, *J. Organometal. Chem.*, 11 (1968) 217.
5 Y. POCKER AND J. H. EXNER, *J. Amer. Chem. Soc.*, 90 (1968) 6764.
6 R. WAACK AND P. WEST, *J. Amer. Chem. Soc.*, 86 (1964) 4495.
7 P. WEST, R. WAACK AND J. I. PURMORT, submitted for publication.
8 R. WAACK AND P. E. STEVENSON, *J. Amer. Chem. Soc.*, 87 (1965) 1183.
9 R. WAACK AND M. A. DORAN, *J. Amer. Chem. Soc.*, 85 (1963) 1651.
10 P. WEST AND R. WAACK, *J. Amer. Chem. Soc.*, 89 (1967) 4395.
11 R. WAACK AND M. A. DORAN, *Chem. Ind. (London)*, (1964) 496.
12 R. WAACK, *Symposium on New Concepts in Anionic Polymerization*, Am. Chem. Soc. Polymer Preprints, 7 (1966) 56.
13 R. WAACK, M. A. DORAN, E. B. BAKER AND P. WEST, *Abstracts, 3rd Inst. Conf. Organometal. Chem.*, Munich, Germany, 1967.
14 G. WITTIG, F. J. MEYER AND G. LANGE, *Justus Liebigs Ann. Chem.*, 571 (1951) 167.
15 D. SEYFERTH AND M. A. WEINER, *J. Amer. Chem. Soc.*, 83 (1961) 3583.
16 R. WAACK AND M. A. DORAN, *J. Amer. Chem. Soc.*, 91 (1969) 2456.
17 A. G. BROOK AND H. GILMAN, *J. Amer. Chem. Soc.*, 76 (1954) 2338.
18 L. D. McKEEVER, Ph.D. Thesis, University of California, Irvine, 1966.
19 S. G. MEL'KANOVITSKAYA AND I. P. TSUKERVANIK, *Zh. Obsch. Khim.*, 28 (1958) 11.
20 R. STEWART, *Can. J. Chem.*, 35 (1957) 766.
21 N. C. DENO, H. J. PETERSON AND G. S. SAINES, *Chem. Rev.*, 60 (1960) 7.
22 D. J. CRAM, *Fundamentals of Carbanion Chemistry*, Academic Press, New York, 1965, p. 19.
23 A. STREITWIESER, JR., E. CIUFFARIN AND J. H. HAMMONS, *J. Amer. Chem. Soc.*, 89 (1967) 63.
24 G. HAMMOND, *J. Amer. Chem. Soc.*, 77 (1955) 334.
25 F. H. WESTHEIMER, *Chem. Rev.*, 61 (1961) 265.
26 J. BIGELEISEN, *Pure Appl. Chem.*, 8 (1964) 217.
27 A. V. WILLI AND M. WOLFSBERG, *Chem. Ind. (London)*, (1964) 2097.
28 R. A. MORE O'FERRALL, *J. Chem. Soc., B*, (1967) 985, 988.
29 R. P. BELL, *Discussions Faraday Soc.*, 39 (1965) 16.
30 D. J. CRAM AND W. D. KOLLMEYER, *J. Amer. Chem. Soc.*, 90 (1968) 1791.
31 R. P. BELL AND D. M. GOODALL, *Proc. Roy. Soc.*, A294 (1966) 273.
32 J. L. LONGRIDGE AND F. A. LONG, *J. Amer. Chem. Soc.*, 89 (1967) 1292.
33 E. S. LEWIS AND L. H. FUNDERBURK, *J. Amer. Chem. Soc.*, 89 (1967) 2322; 86 (1964) 2531.
34 C. D. RITCHIE AND R. E. USCHOLD, *J. Amer. Chem. Soc.*, 89 (1967) 1721.
35 A. STREITWIESER, JR., AND R. A. CALDWELL, *J. Amer. Chem. Soc.*, 87 (1965) 5394.
36 L. MELANDER, *Isotope Effects on Reaction Rates*, Roland Press, New York, 1960.
37 R. WAACK AND P. WEST, *J. Organometal. Chem.*, 5 (1966) 188.
38 R. WAACK, P. WEST AND M. A. DORAN, *Chem. Ind. (London)*, (1966) 1035.
39 A. STREITWIESER, JR., AND H. F. KOCH, *J. Amer. Chem. Soc.*, 86 (1964) 404.
40 M. SHIMA, D. N. BHATTACHARYYA, J. SMID AND M. SZWARC, *J. Amer. Chem. Soc.*, 85 (1963) 1306.
41 P. WEST AND W. P. WEBER, unpublished data.