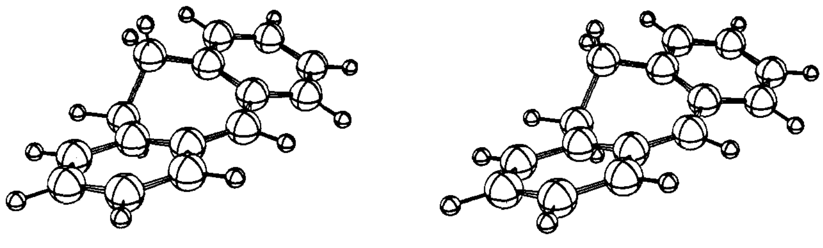

Figure 4. Stereoview of the chair-like conformation of carbanion from DCH.

significant difference between the methylene- or ethano-bridged series that could be attributed to a release or increase of ring strain on going from the hydrocarbon to the anion or to any differences in interactions between nonbonded atoms. The ethano bridge present in DCH leaves the two phenyl rings with some degree of torsional freedom and allows at least two accessible conformations for both the hydrocarbon and the anion.

In one possible conformation of the anion (Figures 1 and 2), the seven-membered ring of DCH is in a boat-shaped arrangement. This leaves the 5 position poorly conjugated to both benzo rings but a 5 substituent is well removed from the neighboring peri hydrogens. In this conformation the two benzo rings are twisted out-of-plane in the same direction relative to a plane that is perpendicular to the vertical axis of the p orbital of the 5 carbon. In another conformation (Figures 3 and 4), the benzo rings are twisted slightly out-of-plane in opposite directions, similar to diphenylmethyl anion, allowing excellent conjugation with the 5 position, but leaving the 5 substituent directly between the peri hydrogens, which are pointing essentially toward each other. We suggest that in DCH itself, where the 5 substitutent is hydrogen, the conformation in Figures 3 and 4 predominates; however, for a 5-substituted compound, interactions with the peri hydrogens are important and the conformation in Figures 1 and 2 now predominates. Consequently, the "anomaly" results from a change in reference. If DCH itself had the "boat" conformation, its p*K* value would be higher and methyl or phenyl substitution would produce a "normal" effect on p*K*.

A related situation occurs with diphenylmethane itself. In the corresponding methyl-substituted compound, 1,1-diphenylethane, the methyl substituent now interacts sterically with the ortho or "peri" hydrogen. The resulting ΔpK change of >2 units is more positive than for most methyl-substituted hydrocarbons (*e.g.*, 9-methylfluorene, $\Delta pK = 0.4$, TDA, $\Delta pK = 0.0$) but is comparable to the change for MDCH ($\Delta pK = 2.4$).

Acidity of Hydrocarbons. XLVII. Primary Kinetic Isotope Effects and Internal Return in Hydrogen Isotope Exchange of Toluene and Triphenylmethane with Lithium Cyclohexylamide[1]

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Abstract: Experimental primary isotope effects for LiCHA-catalyzed proton exchange are compared for toluene and triphenylmethane. For toluene at 25°, $k^{D}_{exptl}/k^{T}_{exptl} = 2.82$ in cyclohexylamine (CHA) and $k^{H}_{exptl}/k^{T}_{exptl} = 27.2$ in cyclohexylamine-*N*,*N*-d_2 (CHA-d_2). For triphenylmethane at 25°, $k^{H}_{exptl}/k^{T}_{exptl} = 2.79$ in CHA and $k^{H}_{exptl}/k^{T}_{exptl} = 19.2$ in CHA-d_2. Derived internal return values show that internal return is greater for triphenylmethane than for toluene. Mechanistic primary isotope effects for the proton transfer step are also derived. The resulting k_I^H/k_I^D value is about 11 for both hydrocarbons.

Base-catalyzed hydrogen isotope exchange reactions are frequently complicated by internal return phenomena[3,4] (eq 1). The primary hydrogen isotope

$$RL + B^- \underset{k_{-I}^L}{\overset{k_I^L}{\rightleftharpoons}} R^-LB \xrightarrow{k_{II}} RH \qquad (1)$$

effect has been a useful criterion for detecting the presence of significant amounts of internal return; k_{II} is a diffusion step which is expected to have but a weak isotope effect and, if k_{-I} becomes competitive with k_{II}, *low* isotope effects necessarily result (eq 2). In exchange reactions of methylarenes with lithium cyclo-

$$k^L_{exptl} = k_I^L/(1 + k_{-I}^L/k_{II}) \qquad (2)$$

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[2] (a) U. S. Public Health Predoctoral Fellow, 1968–1970; (b) National Science Foundation Postdoctoral Fellow, 1967–1968; (c) U. S. Public Health Predoctoral Fellow, 1964–1965; (d) National Science Foundation Postdoctoral Fellow, 1966–1967.

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Table I. Hydrogen Exchange with LiCHA in CHA

Run[a] no.	Temp, °C	[RH], M	$10^6k^D_{exptl}$, sec^{-1}	$10^6k^T_{exptl}$, sec^{-1}	$(k^D/k^T)_{exptl}$
			Toluene		
GRZ 41[b]	50.0	0.53	15.2 ± 0.3	6.02 ± 0.28	2.52 ± 0.13
PHO 6[c]	50.14	0.101	10.5 ± 0.1	3.98 ± 0.22	2.65 ± 0.15
WKS 6	25.0	0.045	3.34 ± 0.08	1.22 ± 0.03	2.75 ± 0.11
WKS 8	25.0	0.056	3.16 ± 0.01	1.09 ± 0.03	2.90 ± 0.15
			Triphenylmethane		
TLK 11[d]	25.0		2290 ± 80	787 ± 40	2.9 ± 0.2
HMN 9	25.07	0.0277	1110 ± 20	404 ± 7	2.75 ± 0.08
HMN 12[e]	24.97	0.0083	1630 ± 10	611 ± 44	2.67 ± 0.19
GS 11	25.0		1420 ± 30	497 ± 17	2.86 ± 0.16

[a] GRZ = G. R. Ziegler, PHO = P. H. Owens, WKS = W. K. Smith, TLK = T. L. Kruger, HMN = H. M. Niemeyer, GS = G. Sonnichsen. [b] Corrected for back reaction (ref 10), k^D_{exptl} (cor) = $(13.2 \pm 0.3) \times 10^{-6}$ sec^{-1}. LiCHA = 0.33 F; from model 2 for monomeric LiCHA (ref 12), $k_2^D = 17.5 \times 10^{-3}$ M^{-1} sec^{-1}. [c] k^D_{exptl} (cor) = $(9.9 \pm 0.1) \times 10^{-6}$ sec^{-1}; LiCHA = 0.0468 F; $k_2^D = 21.6 \times 10^{-3}$ M^{-1} sec^{-1}. [d] Run also contained diphenylmethane; $k^D_{exptl} = (620 \pm 10) \times 10^{-6}$ sec^{-1}. Hydrocarbons were separated by gc. [e] Run also contained benzotrifluoride-*2-d,t*; rate constants from Perrin's program (ref 8); LiCHA ≃ 0.01 F.

hexylamide (LiCHA) in cyclohexylamine (CHA), we have interpreted relatively high experimental k^D_{exptl}/k^T_{exptl} values[4] as demonstrating the absence of internal return in these reactions. We recently showed how the interrelationship of k^D_{exptl}/k^T_{exptl} and k^H_{exptl}/k^T_{exptl} in an exchange reaction can provide a quantitative assessment of the amount of internal return,[5] and we now apply this procedure to hydrogen exchange of toluene and triphenylmethane with LiCHA.

Experimental Section

Materials. Toluene-*α-d,t* was prepared from benzylmagnesium chloride by quenching with tritiated deuterium oxide. Benzyl-*α,α-d*$_2$ alcohol was prepared by reduction of methyl benzoate with lithium aluminum deuteride. This product was allowed to react with excess thionyl chloride. After refluxing for several hours, the benzyl chloride was distilled at reduced pressure, washed, dried, and redistilled. The Grignard reagent was quenched with tritiated water to yield toluene-*α,α-d*$_2$*-α-t*, bp 112–113°, 95.59% d_2 and 4.41% d_1, by low voltage mass spectroscopy.

Triphenylmethane-*α-d,t* is described in the next paper.[6]

Cyclohexylamine-*N,N-d*$_2$.[7] A mixture of 1.5 l. of cyclohexylamine, 200 g of deuterium oxide, and 250 ml of benzene was heated at reflux and the water was azeotropically distilled using a Dean-Stark trap. A new charge of 200 g of deuterium oxide was added and the procedure was repeated until 1400 g of deuterium oxide was used. After removal of benzene by distillation the cyclohexylamine-*N,N-d*$_2$ was distilled at 132–134°. Nmr analysis showed >99% *d*.

Kinetics. The kinetic runs followed our usual procedure.[8] The bifurcated reactor equipped with Teflon stopcocks was charged with the hydrocarbon in CHA in one arm and LiCHA in CHA in the other. After the reactor was pressurized with argon and equilibrated at bath temperature (25 or 50°), the contents were mixed and aliquots were taken at appropriate time intervals. For the triphenylmethane runs, the total reaction time was so short that a tape recorder was used to record the aliquot times. Bath temperatures were calibrated with a Hewlett-Packard quartz thermometer. From each aliquot the hydrocarbon was extracted into Spectrograde cyclohexane, assayed by uv absorbance on a Cary 14 spectrophotometer, and counted for tritium in a Nuclear-Chicago Mark I liquid scintillation counter. For the deuterium analyses a sample was isolated by gc and examined at low voltage on a CEC-130 or CEC-103 mass spectrometer.

Rate constants were evaluated using the LSKIN1 program.[9] No corrections were made for "back reaction"[10,11] because of the approximations required in the derivation of the corrections. These corrections are much the same for the two isotopes in the same run and are relatively small in the dilute solutions used for most of the runs. These runs each invoved 7–11 kinetic points.

Results and Discussion

Results of the kinetic runs are summarized in Tables I and II. The runs with toluene-*d,t* and LiCHA in CHA give an average k^D_{exptl}/k^T_{exptl} of 2.58 at 50° and 2.82 at 25°, a difference that corresponds to $\Delta\Delta H^{\ddagger} = 0.7$ kcal/mol, a value equal to the difference between C–D and C–T zero-point energies. In the 50° runs, the LiCHA concentration was also measured. LiCHA is known to be aggregated in CHA solution and only the monomer is kinetically significant;[10,12] hence, the concentration of monomeric LiCHA present was calculated according to our earlier treatment (model 2)[12] for the determination of the experimental second-order rate constant, k_2. The values so obtained, $k_2^D = 17.5 \times 10^{-3}$ (GRZ 41) and 21.6×10^{-3} (PHO 6) M^{-1} sec^{-1}, correspond well with the value of 19.1×10^{-3} M^{-1} sec^{-1} obtained in our earlier work.

The present values of k^D_{exptl}/k^T_{exptl} for toluene with LiCHA are close to the average of previously reported values ranging from 2.2 to 3.0.[10–12] The present values are expected to be more accurate and are preferred

Table II. Hydrogen Exchange with LiCHA in CHA-d_2

Run no.	Temp, °C	[RH], M	$10^6k^H_{exptl}$, sec^{-1}	$10^6 \cdot$ k^T_{exptl}, sec^{-1}	$(k^H/k^T)_{exptl}$
		Toluene-*α,α-d*$_2$*-α-t*			
PHO 8[a]	25.0	0.199	32.0 ± 1.5	1.18 ± 0.06	27.2 ± 2.0
PHO 7[b]	50.0	0.191	87.0 ± 1.6	3.99 ± 0.21	21.8 ± 1.2
		Triphenylmethane-*α-t*			
GS 14	25.0		14,500 ± 400	758 ± 8	19.2 ± 0.7

[a] LiCHA = 0.0500 F; $k_2^T = 2.42 \times 10^{-3}$ M^{-1} sec^{-1}. [b] LiCHA = 0.0429 F; $k_2^T = 8.83 \times 10^{-3}$ M^{-1} sec^{-1}.

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to the older ones for several reasons. Even though the simultaneous measurement of exchange of two isotopes during a single run is expected to remove some sources of systematic error, care is still required. Because of the relatively large value of the isotope effect, loss of deuterium is substantially complete before much loss of tritium has occurred. Such a system really consists of two kinetic runs within the same vessel and involving different time intervals. Any change in reaction conditions after most of the deuterium has exchanged, such as a reduction in active catalyst, will result in systematic error in comparing one experimental rate constant with another. In such cases careful inspection generally shows curved rather than linear kinetic plots. In most of our exchange kinetics we are primarily interested in the relative reactivities of two or more substrates and isotope effects are obtained as secondary results that serve to monitor the overall results. In the present runs, however, the isotope effects were the primary objectives and the kinetic points were spaced appropriately.

Reaction of $C_6H_5CD_2H(T)$ with LiCHA in cyclohexylamine-*N,N*-d_2 gives $k^{\mathrm{H}}_{\mathrm{exptl}}$ for replacement of H by D and $k^{\mathrm{T}}_{\mathrm{exptl}}$ for loss of T. These results are summarized in Table II. The $k^{\mathrm{T}}_{\mathrm{exptl}}$ rates provide a common denominator for both CHA and CHA-d_2 exchanges and allow the derivation of a solvent isotope effect for LiCHA kinetics. The rates for $C_6H_5CD_2T$ must first be corrected for the known secondary deuterium isotope effect of 1.31[13] to give $k^{\mathrm{T}}_{\mathrm{exptl}}$ values for reaction of $C_6H_5CH_2T$ in CHA-d_2: $k_2{}^{\mathrm{T}} = 3.17 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$ at 25°, $11.6 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$ at 50°. Note that these rate constants cannot be obtained directly by reaction of $C_6H_5CH_2T$ in CHA-d_2 because of the more rapid conversion of the α-H's to α-D's. Compared to the corresponding $k_2{}^{\mathrm{T}}$ in CHA (*vide supra*), we find $k(\text{CHA-}d_2)/k(\text{CHA}) = 3.17 \times 10^{-3}/2.02 \times 10^{-3} = 1.57$ at 25°, $11.6 \times 10^{-3}/7.4 \times 10^{-3} = 1.57$ at 50°. Although the CHA-d_2 results involve single kinetic runs this remarkable agreement provides a measure of confidence. This solvent isotope effect may seem surprisingly large for a reaction involving ion pairs in which the important solvation involves the cation and in which hydrogen bonding to the anion is probably not important. However, we should carefully note that in the above derivation we assumed that the dissociation of LiCHA aggregates to monomers is the same in CHA-d_2 as in CHA; that is, the experimental solvent isotope effect can pertain either to the proton transfer step or to the concentration of active catalyst or both. It is not implausible that CHA-d_2 could involve a secondary isotope effect to provide better solvation for Li^+ and increase the concentration of monomeric LiCHA ion pairs; in other cases deuterium is known to be effectively electron releasing relative to hydrogen.[14]

The rates in CHA-d_2 give values of $k^{\mathrm{H}}_{\mathrm{exptl}}/{}^{\mathrm{T}}_{\mathrm{exptl}}$ of 21.8 ± 1.2 at 50° and 27.2 ± 2.0 at 25°. If there is no appreciable solvent isotope effect on the primary isotope effect, these values can be related to the $k^{\mathrm{D}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}}$ results by the equation

$$k^{\mathrm{H}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}} = (k^{\mathrm{D}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}})^{y}$$

For a simple proton transfer process $y = 3.26$[15] or 3.344,[16] depending on some assumptions made in derivation. The experimental value of y found in the present work with toluene is 3.18 ± 0.08 at 25°, 3.25 ± 0.07 at 50°. These values are virtually within experimental error of theory and provide further evidence that internal return is negligible in this exchange reaction.

The same process has been applied to triphenylmethane. In this case the exchangeable hydrogen is tertiary and there are no complications of secondary substrate isotope effects and concurrent exchanges. $k^{\mathrm{D}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}}$ with LiCHA/CHA at 25° has the weighted average value of 2.79 ± 0.08, virtually the same as toluene. A single run in CHA-d_2 gives $k^{\mathrm{H}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}} = 19.2 \pm 0.07$, substantially less than that for toluene. For triphenylmethane, $y(\mathrm{exptl}) = \log (19.2 \pm 0.07)/\log (2.78 \pm 0.08) = 2.88 \pm 0.09$. This number is now significantly less than theory and indicates some internal return. The result was inherent in the $k^{\mathrm{H}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}}$ obtained from triphenylmethane which is much less than that for toluene (the difference is far greater than experimental error) compared with $k^{\mathrm{D}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}}$ which experimentally is much the same for both hydrocarbons. The amount of internal return is deduced by use of the equations derived previously.[5] For toluene, $a_{\mathrm{T}} = k_{-\mathrm{I}}{}^{\mathrm{T}}/k_{\mathrm{II}} \simeq 0.006$ whereas for triphenylmethane $a_{\mathrm{T}} \simeq 0.02$.[17] For tritium exchange, internal return is of little significance for both hydrocarbons. However, note that $k_{-\mathrm{I}}$ is subject to the same high primary isotope effect as the forward rate and internal return is greatest for proton exchange. Thus, for toluene, $a_{\mathrm{D}} = k_{-\mathrm{I}}{}^{\mathrm{D}}/k_{\mathrm{II}} \simeq 0.2$ for deuterium exchange but $a_{\mathrm{H}} \simeq 0.2$; that is, a negligible amount of return with tritium exchange still corresponds to substantial return with protium.

For triphenylmethane, $a_{\mathrm{D}} \simeq 0.06$ and $a_{\mathrm{H}} \simeq 0.6$–$0.9$. This amount of internal return is no longer negligible and demonstrates that even relatively large isotope effects can encompass substantial amounts of internal return; indeed, large isotope effects provide the means whereby internal reutrn can be of substantial magnitude for protium and of minor importance for deuterium and tritium.

The remarkable outcome of these experiments is that internal return is greater for triphenylmethyl anion than for benzyl anion even though the benzyl anion species is expected to have a shorter lifetime; that is, we expect $k_{-\mathrm{I}}(\text{benzyl anion}) > k_{-\mathrm{I}}(\text{triphenylmethyl anion})$. This assumed relationship then leads to $k_{\mathrm{II}}(\text{toluene}) > k_{\mathrm{II}}(\text{triphenylmethane})$. This result that the diffusion step is slower for the triphenylmethyl case must surely be associated with the greater bulk of this system. The steric constraints of the triphenylmethyl anion–solvated lithium cation ion pair are apparently such that rotation of the leaving solvent or replacement of this solvent molecule by another is

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[17] The treatment requires a value for the equilibrium distribution constant for hydrogen isotope between hydrocarbon and cyclohexylamine. This value is not known precisely but is close to unity[10] and is probably about 1.1–1.2; that is, deuterium and tritium are expected to concentrate slightly in solvent.

relatively difficult such that reaction with the original hydrogen is possible. In the benzyl anion–lithium cation case rotation around the primary CH_2 would render internal return with the original hydrogen less probable. A corollary of this rationalization is that loss of configuration is expected to be greater for toluene than the 18% racemization found previously in exchange of optically active ethylbenzene-*α-d* with LiCHA.[18] We see no practical way of testing this prediction, but the second corollary, that triarylmethanes show *less* racemization, is subject to experimental test.

Finally, these derived a^L values may be combined with the experimental isotope effects to produce the mechanistic isotope effects, $k_I^L/k_I^{L'}$; that is, the isotope effects for the proton transfer step itself. These values are summarized in Table III. The primary isotope effect, k_I^H/k_I^D, of about 11 is high for proton transfer reactions and suggests not only complete loss at the transition state of C–H stretching zero-point energy but that of some C–H bending zero-point energy as well. In the absence of a significant equilibrium isotope effect these values also apply to $k_{-I}^L/k_{-I}^{L'}$. Our entire analysis makes no allowance for tunneling. It is also surely noteworthy that the mechanistic isotope effects for toluene and for triphenylmethane are so similar in magnitude. This correspondence implies a similarity in transition-state structures despite a 10 p*K*-unit difference in equilibrium ion pair acidity. This further suggests that this equilibrium acidity difference is not fully manifest at the transition state and provides further evidence that the transition state in these reactions is highly pyramidal.[6]

Table III. Derived Isotope Effects at 25°

	k_I^D/k_I^T	k_I^H/k_I^T	k_I^H/k_I^D
Toluene	2.86	32	11
Triphenylmethane	2.90	30–36	10–12

Acknowledgment. We are indebted to D. Holtz for a preliminary mathematical analysis and helpful discussions.

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Acidity of Hydrocarbons. XLVIII. Kinetic Acidities of Mono-, Di-, and Triarylmethanes toward Lithium Cyclohexylamide[1]

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Abstract: Tritium exchange rates with lithium cyclohexylamide in cyclohexylamine have been determined for several aryl- and polyarylmethanes. Relative rates at 25° are *p*-biphenylyldiphenylmethane (BDM), 2.3; di-*p*-biphenylylmethane (DBM), 1.39; triphenylmethane (TPM), 1; diphenylmethane (DPM), 0.28; *p*-methylbiphenyl (pMB), 0.0048; *m*-methylbiphenyl (mMB), 0.0021; toluene (Tol), 0.00104. Comparison with known p*K* values for some of these hydrocarbons gives a linear Brønsted correlation with $\alpha = 0.314$ and permits extrapolation to a p*K* value for toluene of 40.9. These results indicate that delocalization effects are only partially developed at the transition state and that the central carbon is still highly pyramidal at the transition state.

As part of our continuing study of equilibrium and kinetic acidities of hydrocarbons and their simple derivatives, we report in this paper a study of hydrogen isotope exchange reactivities toward lithium cyclohexylamide (LiCHA) in cyclohexylamine (CHA) of triphenylmethane (TPM), *p*-biphenylyldiphenylmethane (BDM), diphenylmethane (DPM), bis(*p*-biphenylyl)methane (BBM), and *p*-methylbiphenyl (MB). Equilibrium acidities of these hydrocarbons toward cesium cyclohexylamide (CsCHA) in CHA have been reported previously.[3,4] The combined results lead to a Brønsted comparison of the LiCHA kinetic acidities with the CsCHA equilibrium acidities and yield several important conclusions.

Experimental Section

Materials. The hydrocarbons are all well-known materials and were prepared by standard methods or purchased. Three general methods were used to introduce deuterium and/or tritium into the α positions: (a) reaction with *n*-butyllithium and quenching with the appropriate water, (b) preparation of the Grignard reagent from the chloride and quenching, and (c) preparation of the Grignard reagent by treatment of the lithium derivative with anhydrous magnesium bromide in ether followed by quenching.

Materials prepared by method a generally gave high infinity values in the kinetic runs suggesting the presence of substantial nonexchangeable isotope. This was confirmed by oxidation of some samples. Ring protonation was almost but not completely absent with the Grignard reagents. Related findings were reported earlier by Russell[5] in reactions of α-cumylpotassium and have also been discussed previously by us.[6]

Kinetic measurements were carried out with our usual procedures in which solutions of hydrocarbon and LiCHA in CHA were prepared in separate parts of a bifurcated reactor under inert atmo-

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