Unless the observed isotope effect results from a combination of opposing factors, they point to a concerted reaction with quite small charge accumulation.

Experimental Section

Deuterium analyses were performed by Mr. Josef Nemeth, Urbana, Ill. α -Methyl-styrene- d_3 , a gift from Dr. William Bayne,¹² was vacuum distilled prior to use. α-Methylstyrene, EKWL, was fractionated prior to use. Both samples were homogeneous upon glpc examination. Diphenylketene was prepared as described.18

Deuterium Isotope Effect Measurements.—Mixtures of Ph-CCH₃—CH₂ and PhCCD₅—CH₂ were prepared and their deu-terium content obtained. Mass spectral examination showed that over 95% of deuterium-containing species was d_8 ; subsequent calculations assumed only d_8 species. Both runs were performed simultaneously to minimize effects of temperature variation.

Run 1.—A solution of 1.384 g (11.6 mmol) of α -methylstyrene (9.30 atom percent excess deuterium, or 31.0% PhCCD₃=CH₂) and 0.348 g (1.79 mmol) of diphenylketene was stored in the dark under nitrogen at ambient temperature for 6 days. Excess olefin was distilled at 0.5 mm to afford 1.20 g (87%) of recovered α -methylstyrene. The residue was chromatographed on 42 g of silica gel 80-200 and eluted with 1.2% ether-Skellysolve B to afford 0.205 g (43%) of 3-methyl-2,2,3-triphenylcyclobutanone. A center cut was twice recrystallized from methanol to afford material of mp 77-78.14 Deuterium analysis showed 4.45 atom per cent excess deuterium, or 29.7% d3 species.

Run 2.-A solution of 1.384 g (11.5 mmol) of olefin (13.60 atom per cent excess deuterium or 45.3% PhCCD₃=CH₂) and 0.353 g (1.82 mmol) of diphenvlketene was reacted as above for 10 days. Chromatography followed by two recrystallizations from methanol and one from Skellysolve B-ether afforded the cyclobutanone, mp 96-97, 6.95 atom per cent excess deuterium or 46.3% ds product.

Istotope effect calculations were made using the relation

$$\frac{k_{\rm H}}{k_{\rm D}} = \left(\frac{{\rm P}_{\rm H}}{{\rm P}_{\rm D}}\right) / \left(\frac{{\rm S}_{\rm H}}{{\rm S}_{\rm D}}\right)$$

valid for competitive reactions run to small conversions (under 16% in our case). Ratios were obtained from deuterium analyses and relevant data are presented above. In run 1 the ratio $P_{\rm H}/P_{\rm D}$ was independently determined from nmr measurements (using undeuterated ketone as reference) as 0.70 ± 0.03 and $k_{\rm H}/k_{\rm D}$ was calculated using the ratio $S_{\rm H}/S_{\rm D}$ from deuterium analysis.

Registry No.—Diphenylketene, 525-06-4; α -methylstyrene, 98-83-9.

Acknowledgments. — This work was supported by the National Science Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund for partial support of this research. The author thanks East Tennesse State University for the gracious hospitality accorded him during 1969-1970, and Dr. William Bayne for stimulating discussions.

(12) W. F. Bayne, Ph.D. Thesis, University of Connecticut, 1970.

Notes

Acidity of Hydrocarbons. XXXIV. **Rate of Proton Abstraction from** *p*-Trifluoromethyltoluene by Lithium Cyclohexylamide in Cyclohexylamine^{1,2}

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Received April 6, 1970

A study of the significance of the concept of fluorine anionic hyperconjugation in fluoro-substituted carbanions⁴⁻⁶ requires an accurate value for the base-catalyzed proton exchange of *p*-trifluoromethyltoluene (TFMT). Our earlier study of the protodetritiation of substituted toluene- α -t's with lithium cyclohexylamide (LiCHA) in cyclohexylamine (CHA) showed that several substituents followed the Hammett relationship with $\rho =$ 4.0;⁶ however, only an approximate rate was obtained for the *p*-trifluoromethyl substituent. TFMT decomposes LiCHA and necessitates the use of a competition method. We have now remeasured this reactivity by comparisons with both fluorobenzene-2-d(t) and triphenylmethane-d(t). In this method a mixture of the three compounds in cyclohexylamine is treated with a limited amount of LiCHA. The amount of isotope lost from the standard compounds before the destruction of catalyst by TFMT provides two independent measures of the relative rates of the latter reaction.⁶ Moreover, the use of both TFMT and TFMT- α - d_3 has permitted the determination of the first directly measured hydrogen-deuterium isotope effect, $k_{\rm H}/k_{\rm D}$, in the LiCHA-CHA system.

Experimental Section

Mass spectra were determined by Miss Sherri Firth using a modified consolidated Electrodynamics 21-103C mass spectrom-eter. Deuterium analyses were performed at $\gtrsim 10$ eV. Gas chromatographic (glpc) analyses were performed using an Aero-graph 1520 instrument. Tritium activities were determined by liquid-scintillation counting in low-potassium glass vials by the external standard ratio technique⁷ using a Nuclear Chicago Mark I Series Model 6860 scintillation counter equipped with a barium-113 δ source. Activities of samples were in the range 15,000-50,000 cpm. Background was ≤ 30 cpm. Counting efficiencies were 28-44%. It is believed that the accuracy of the tritium activity determinations is $\pm 1\%$.

p-Trifluoromethyltoluene- α - d_3 .—As adapted from the method of Schlosser,⁸ a mixture of 6.0 g (25.1 mmol) of p-trifluoromethylbenzyl bromide (prepared from the commercially available benzoyl chloride by reduction with lithium aluminum hydride, and conversion to the benzyl bromide with hydrobromic acid)⁹

(1) This research was supported in part by Grant GM-12855 of the National Institutes of Health, U. S. Public Health Service.

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(3) Woodrow Wilson Fellow, 1964-1965; National Science Foundation Predoctoral Cooperative Fellow, 1965-1967; Eastman Kodak Science Award, 1966.

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⁽¹⁴⁾ The reported melting point of the cyclobutanone is $88.5-89.5^{\circ}$ (ref 11), although more recent preparations show mp 94-95° (R. Huisgen, personal communication). Comparison of our preparation with an authentic sample kindly supplied by Professor Huisgen showed identical $R_{\rm f}$ values on tlc (alumina, 2:1 Skellysolve B-benzene; one spot for both samples) and identical nmr spectra. However, our preparation showed additional weak absorptions in the ir fingerprint region. One further recrystallization of our preparation from Skellysolve B-ether afforded material of mp 95-96°, whose ir spectrum is superimposable upon that of the authentic sample.

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	χλ	<u>[a</u>	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	1 ^b
	d	t	d	t
	A. p -CF	C6H4CH3 (TFMT) Run		
Compd				
\mathbf{TFMT}	0.57 ± 0.02		(1,00)	
Fluorobenzene-2-d(t)	0.859 ± 0.006	0.940 ± 0.010	0.27 ± 0.03	0.11 ± 0.02
Triphenylmethane- α - $d(t)$	0.920 ± 0.005		0.150 ± 0.014	
	B. p-CF ₃ C	C ₆ H ₄ CD ₈ (TFMT-d ₃) Run		
\mathbf{TFMT} - d_3	0.56 ± 0.002		(1.00)	
Fluorobenzene-2-d(t)	0.274 ± 0.008	0.586 ± 0.010	2.23 ± 0.14	0.92 ± 0.06
Triphenylmethane- α - $d(t)$	0.499 ± 0.006	0.786 ± 0.020	1.20 ± 0.08	0.42 ± 0.05
TFMT- d_3 Fluorobenzene-2- $d(t)$ Triphenylmethane- α - $d(t)$	$\begin{array}{c} 0.56 \pm \\ 0.274 \pm 0.008 \\ 0.499 \pm 0.006 \end{array}$	$\begin{array}{c} 0.002 \\ 0.586 \pm 0.010 \\ 0.786 \pm 0.020 \end{array}$	(1 2.23 ± 0.14 1.20 ± 0.08	$\begin{array}{c} .00) \\ 0.92 \pm 0.06 \\ 0.42 \pm 0.05 \end{array}$

TABLE I				
Competition Experiments for Proton Abstraction with LiCHA at 22°				

 $^{a}X = 1 - y/y_{0}$ in which y_{0} is the amount of isotope at the start and y is the amount at end of experiment; X = 1 -fraction reacted. For TFMT and TFMT- d_{2} , X pertains to fraction of compound not destroyed by reaction. $^{b}k/k_{0} = \log X/\log X_{0}$.

and 7.25 g (27.6 mmol) of triphenylphosphine was refluxed in xylene for 20 hr. The resulting fine white precipitate was collected and washed twice with ether, yielding 12.18 g (31.3 mmol, 78% yield) of phosphonium salt. A portion of this material (7.24 g, 14.4 mmol) was treated with 40 ml of 1.5 M sodium deuterioxide solution (prepared by adding freshly cut and cleaned sodium to 99.85 mol % deuterium water) resulting in a precipitate and loss of solution color (20 hr). After steam distillation, the organic layer was separated, dried over phosphorus pentoxide, and distilled bulb to bulb under high vacuum to yield 1.82 g (11.1 mmol, 77% yield) of product containing <4% of impurities by glpc (20% Apiezon N). The mass spectrum indicated a mol wt of 163 with major fragments corresponding to the loss of CF3 and F (70 eV) and an isotopic composition of 95.5% d_3 and 4.35% d_2 (low voltage). The infrared spectrum contained bands at 2295, 2175, 1054, 900, and 694 cm⁻¹ not present in normal p-trifluoromethyltoluene, and bands in the C-H region, 1460, and 950 cm⁻¹ diminished or were missing relative to the unlabeled molecule. The nmr spectrum contained an AB pattern centered at τ 2.76, $\Delta \nu = 0.24$ ppm, $J_{AB} = 8.1$ Hz, with impurity peaks at τ 3.10 and 7.82. The methyl hydrogens appeared as a small broad peak at τ 7.70 integrating to less than 3% of the aromatic resonances.

p-Trifluoromethyltoluene.—In a manner identical with that described for the synthesis of p-trifluoromethyltoluene- α - d_3 , 3.50 g (7.0 mmol) of p-trifluoromethylbenzyltriphenylphosphonium bromide was treated to yield 0.93 g (5.8 mmol, 83% yield) of product containing <3% impurities by glpc (20% SE-30). The mass spectrum indicated a mol wt of 160. The infrared¹⁰ and nmr¹¹ spectra agreed with published reports.

Other Reagents.—Fluorobenzene-2-d(t) was described previously.¹² Triphenylmethane- α -d(t) was prepared by Dr. T. L. Kruger by quenching the Grignard reagent from triphenylmethyl chloride with D₂O containing tritium. The product was purified by column chromatography and recrystallization and showed 93.7% d_1 by mass spectroscopy. Lithium cyclohexylamide was prepared by reaction of butyllithium with CHA and removal of volatiles in high vacuum. The resulting white solid was redissolved in fresh CHA distilled on the vacuum line to produce a solution titrated as 0.12 \pm 0.02 M by reaction with bromobenzene.¹³

Rate Measurements.—Two 150-ml pear-shaped flasks fitted with a Teflon stopcock and, above the stopcock, a sidearm through which dry nitrogen was blown while adding reagents (to protect the reaction solution from condensing moisture), were washed with CHA and blown out with argon until dry. Into each flask was syringed 20.0 ml of CHA. A mixture consisting of 119.5 mg of TFMT, 56.3 mg of PhF2-d(t), 134.4 mg of Ph₃CD(T), and 75.5 mg of mesitylene (internal standard) dissolved in 1.50 ml of CHA was syringed into one flask (A); a mixture consisting of 119.6 mg of TFMT- α - d_3 , 61.1 mg of PhF2-d(t), 133.4 mg of Ph₃CD(T), and 68.1 mg of mesitylene dissolved in 1.50 ml of CHA was syringed into the other flask (B). A 10-ml aliquot was withdrawn from each flask as an initial kinetic point and added to a separatory funnel containing 10 ml of concen-

(11) "Nmr Spectra Catalog," Varian Associates, Vol. 1, Palo Alto, Calif., 1962, Spectrum No. 190.

(12) A. Streitwieser, Jr., and F. Mares, J. Amer. Chem. Soc., 90, 644 (1968).

(13) A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Laughton, J. Phys. Chem., 68, 2916 (1964).

trated HCl, ~ 10 g of ice, and 1.5 ml of spectral-grade pentane. After separation, the organic layer was dried over MgSO₄ and worked up by glpc as described below.

Into each flask was syringed 1.50 ml of the LiCHA solution. A transient red color appeared (Ph_3C^-) which faded to a yellowbrown color in ~1 min. Solution B took a longer time to fade than solution A consistent with the isotope effect found. After 3 hr, 10-ml aliquots were remove from each flask and worked up as described above for the initial point. No attempt was made to thermostat the reaction solutions during the "kinetic run." Ambient temperature was 22°.

The pentane extracts of two "kinetic points" were analyzed by temperature programmed glpc (20% Apiezon N) under conditions such that all peaks were well resolved. The effluents of relevant peaks were collected in melting point capillaries, sealed, and analyzed later for deuterium content by low-voltage mass spectrometry. In a second injection, the effluent of each relevant peak was bubbled into ~ 2 ml of spectral-grade iso-octane. The tritium activity of this solution was determined by liquid-scintillation counting and converted to the specific activity using the concentration determined by the uv absorbance. A third injection was made to have a further determination of relative peak areas. For all three injections the relative peak areas of TFMT (or TFMT- d_3) and mesitylene were determined by electronic integration of the millivolt recorder output of the glpc thermal conductivity detector and gave results in satisfactory agreement with stoichiometry. The relative peak areas of the other components were also determined and showed no significant change upon reaction. A summary of the results of both runs is presented in Table I.

Results

This type of competition experiment is equivalent to a two-point kinetic run and requires for accuracy compounds that have similar reactivities and a total reaction of about 50%. These requirements are best met in the "B" experiment which yields a relative rate, fluorobenzene-2: triphenylmethane- α of 1.86 \pm 0.10 for D exchange and 2.21 ± 0.23 for T exchange. Because of the small extent of T exchange for triphenylmethane, experiment "A" gives only a ratio for D exchange, 1.83 \pm 0.18, in good agreement with "B." In other work¹⁴ we have measured these ratios in kinetic runs for isotope exchange and obtained D 1.90, T 1.80, in good agreement with the present experiments. From the known ratio, $k(Ph_3CD)/k(C_6H_5CH_2D)$, 935 at 25°,¹⁵ the present results give for $k(\text{TFMT-}d_3)/k(C_6H_5CH_2D)$, 779 ± 60 . Correcting for the statistical factor (1/3), secondary deuterium isotope effects $(1.31)^{16}$ and the presence of hydrogen in the CD_3 group (0.91), the calculated ratio, $k(p-CF_3C_6H_4CH_2D)/k(C_6H_5CH_2D)$, is 310 ± 22 at 22°. Correction to 50° assuming constancy of entropy of activation gives a rate ratio of 189 ± 13 . This

(14) F. Mares, unpublished results.

(15) A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, J. Amer. Chem. Soc., 86, 3578 (1964), and results to be published.

(16) A. Streitwieser, Jr., and D. E. Van Sickle, ibid., 84, 254 (1952).

⁽¹⁰⁾ E. W. Della, J. Amer. Chem. Soc., 89, 5224 (1967).

number agrees well with the value, ~ 180 , reported previously.⁶

The conclusion that this number is a relative proton exchange rate implies that $k_{-1} \ll k_2$ in the reaction sequence

$$CH_{3}C_{6}H_{4}CF_{3} \xrightarrow{k_{1}} -CH_{2}C_{6}H_{4}CF_{3} \xrightarrow{k_{2}} CH_{2}=C_{6}H_{4}=CF_{2} \longrightarrow polymer$$

The results in Table I also yield the rate ratio, $k(\text{TF-MT})/k(\text{TFMT-}d_8)$, of 8.2 ± 0.5 . Correcting as before gives $k(p\text{-}CF_3C_6H_4CH_2\text{-}H)/k(p\text{-}CF_3C_6H_4CH_2\text{-}D)$, $k_H/k_D = 6.9 \pm 0.5$. This value is in the high normal region for primary isotope effects and confirms that C-H bond breaking is the rate-determining step for decomposition of TFMT; that is, if "return" $(k_{-1} \sim k_2)$ from the intermediate carbanion were significant, a reduced isotope effect would have been observed.

Other observations consistent with the proposed reaction sequence are that the ratio of the amount of base used to TFMT destroyed was determined experimentally to be 1.04 ± 0.01 and no significant amounts of the other components are lost; thus, LiCHA, fluorobenzene, diphenylmethane, and triphenylmethane do not react with the quinodimethane at a rate competitive with polymerization. It is also significant that fluorobenzene¹² and benzotrifluoride^{14, 17} do not decompose in LiCHA at rates competitive with the present reaction.

To evaluate the substituent effect of the CF_3 group with the present results, we first observe that the other eight substituents of Streitwieser and Koch⁶ in tritium exchange of substituted toluenes with LiCHA give a least squares Hammett slope, $\rho = 3.74 \pm 0.16$, with a correlation coefficient of 0.995. The reactivities of the CF₃ substitutents then give σ^- (m-CF₃) 0.47, $\sigma^ (p-CF_3)$ 0.60. Both values are higher than the corresponding σ values, 0.42 and 0.53, respectively, and are, therefore, more consistent with a π -inductive effect than with a fluorine no-bond resonance mechanism. This result is discussed in more detail elsewhere¹⁸ but we note here that these results are also inconsistent with the decomposition reaction being a concerted process. Any reaction scheme involving simultaneous proton removal and fluoride elimination can be dismissed on the basis that the reactivity of TFMT for proton transfer is rather normal.

Registry No.—TFMT, 6140-17-6; LiCHA, 26372-63-4.

(17) H. N. Niemeyer, unpublished results.

(18) D. Holtz, Progr. Phys. Org. Chem., in press.

A New Route to 8- and 9-Substituted Carenes

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Received June 25, 1970

The recent isolation and characterization of l-sirenin $(1a)^1$ and l-sesquicarene $(1b)^2$ have indicated a need for

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synthetic routes to 8-substituted carenes.³ During the past year, several synthesis of $dl-1a^4$ and $dl-1b^5$ have been reported which utilize intramolecular carbene addition reactions of acyclic precursors for the construction of the required bicyclo[4.1.0]heptane ring system. Consideration of the unusual biological activity of l-sirenin $(1a)^1$ suggested the desirability of preparing l-1a



and related compounds by a route which would yield optically active carenes substituted at C-8 and possibly also at C-9.⁶ Consequently, our efforts in this general area have been directed toward this goal. We report here a conversion of commercially available (-)-perillaldehyde (2a) into 8- and 9-hydroxy-2-caren-10-oic acid methyl esters.

The approach used was patterned on the reported preparation of (+)-2-caren-10-al⁷ via addition of hydrogen bromide to the isolated double bond of (-)-perillaldehyde (2a) followed by treatment of the crude bromide with potassium *tert*-butoxide. It was envisioned that the carbanion of epoxide i (R = CHO or COOCH₃) would also undergo intramolecular formation of a cyclo-



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