118.67 (=CH₂), 127.74 (=CH), 128.10 (=CH), 128.64 (=CH), 129.90 (=CH), 130.05 =(CH), 131.36 (=CH), 131.93 (=CH), 135.92 (=C), 140.62 (=C), 141.02 (=CH), 145.17 (=C), 162.01 (C1). Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10; S, 9.39. Found: C, 66.76; H, 5.69; N, 3.97; S, 9.50.

Reduction of 7a and 8a by Bu₃SnH. A solution containing 85 μ L of freshly distilled Bu₃SnH and 15 mg of AIBN in 5 mL of benzene was added over 8 h to a solution of 110 mg (0.25 mmol) of 8a in 10 mL of benzene irradiated at room temperature with a mercury lamp. After completion, the solvent was evaporated and the residue, dissolved in acetonitrile, was washed twice with pentane. Flash chromatography (CH₂Cl₂-Et₂O; 100:0 to 80:20) afforded 74 mg of a mixture of 13a and 14a in a 85:15 ratio (82% overall yield). Coversely the reduction of 20 mg of 7a under identical conditions afforded 8 mg of 12a (50%).

N-Benzyl-4-methyl-3-(tosylmethyl)-2-pyrrolidone (12a, 13a). 12a: ¹H NMR (400 MHz) 0.99 (d, J = 7.0, 3 H), 2.46 (s, 3 H), 2.74 (sext., J = 7, H4), 2.80 (d, J = 9.9, H5a), 3.07 (ddd, J = 12, 7, 1.7, H3, 3.21 (dd, J = 14.3, 12.1, H7a), 3.41 (dd, J = 14.3, H7a), 3.41 9.9, 6.0, H5b), 3.70 (dd, J = 14.3, 1.7, H7b), 4.43 (AB type spectrum, $J_{AB} = 14.7$, $\Delta \nu = 53.5$ Hz, NCH₂), 7.15–7.20 (m, 2 H), 7.28–7.39 (m, 5 H), 7.81 (d, J = 8.3, 2 H); ¹³C NMR 15.41 (CH₃, C6), 21.67 (CH₃), 29.51 (C4), 41.60 (C3), 47.08 (CH₂Ph), 52.42 $(C5^*)$, 52.51 (C7*) (these assignments may be reversed), 127.78 (=CH), 127.97 (=CH), 128.15 (=CH), 128.75 (=CH), 130.03 (=CH), 135.96 (=C), 136.39 (=C), 144.95 (=C), 171.87 (C=O); MS 357 (16), 293 (2), 202 (5), 201 (5), 188 (7), 186 (5), 174 (34), 145 (5), 110 (8), 92 (8), 91 (100), 85 (16), 71 (15), 70 (7), 69 (9), 65 (10), 57 (27), 55 (15), 43 (20), 42 (5), 41 (28), 39 (8), 29 (6), 28 (15), 27 (5), 18 (7); HRMS calcd for C₂₀H₂₃NO₃S 357.1398, found 357.1411. 13a: ¹H NMR (400 MHz), 1.28 (d, J = 6.7, 3 H), 2.46 (s, 3 H), 2.42-2.51 (superimposed m, H4), 2.64 (ddd, J = 9.7, 8.3, 2.7, H3, 2.84 (dd, J = 9.8, 7.3, H5a), 3.11 (dd, J = 14.3, 9.7, H7a), 3.35 (dd, J = 9.8, 8.1, H5b), 3.76 (dd, J = 14.3, 2.7, H7b), 4.41(AB type spectrum, $J_{AB} = 14.8$, $\Delta \nu = 18.6$ Hz, NCH₂), 7.18–7.21 $(m, 2 H), 7.26-7.40 (m, 5 H), 7.82 (d, J = 8.2, 2 H); {}^{13}C NMR (100)$

MHz) 18.71 (CH₃, C6), 21.65 (CH₃), 33.19 (C4), 44.84 (C3), 46.99 (CH₂Ph), 52.30 (C5), 57.50 (C7), 127.77 (-CH), 128.00 (-CH), 128.11 (-CH), 128.78 (-CH), 129.97 (-CH), 135.94 (-C), 136.73 (-C), 144.86 (-C), 172.96 (C-O); MS 357 (23), 293 (1), 202 (6), 188 (10), 186 (6), 175 (6), 174 (62), 145 (11), 110 (11), 92 (11), 91 (100), 85 (4), 71 (7), 69 (9), 65 (11), 57 (14), 55 (11), 43 (10), 42 (5), 41 (14), 39 (5), 28 (23), 18 (9); HRMS calcd for C₂₀H₂₃NO₃S 357.1398, found 357.1411.

Data for 14a: ¹H NMR (400 MHz) 2.03 (qd, J = 11.1, 7.5, H4), 2.74 (d, J = 14.4, H6a), 3.03 (dd, J = 14.4, 12.5, H7a), 3.08 (dd, J = 14.4, 12.5, H7a)J = 11.1, 9.5, H5a), 3.17 (td, J = 12.5, 2.5, H3), 3.30 (dd, J = 9.5, J7.5, H5b), 3.48 (dd, J = 14.4, 11.1, H6b), 3.90 (dd, J = 14.4, 2.5, H7b), 4.48 (AB type spectrum, $J_{AB} = 14.7$, $\Delta \nu = 34.5$ Hz, NCH₂), 7.05 (s, 1 H), 7.17-7.24 (m, 3 H), 7.28-7.36 (m, 3 H), 8.01 (d, J = 8, 1 H); ¹³C NMR (100 MHz) 21.34 (CH₃), 37.08 (C6), 41.43 (C4), 46.41 (C3), 46.72 (CH₂Ph), 49.58 (C5), 54.48 (C7), 127.82 (-CH), 127.85 (=CH), 128.11 (=CH), 128.85 (=CH), 129.14 (=CH), 132.24 (=CH), 135.95 (=C), 137.27 (=C), 138.87 (=C), 144.97 (=C), 171.99 (C=O); the assignments followed from COSY and HETCOR experiments. NOE experiments led to no enhancement of H3 when irradiating H4 and vice versa; MS 357 (2), 356 (8), 355 (40), 337 (11), 320 (17), 187 (5), 186 (16), 185 (6), 119 (6), 118 (5), 106 (12), 105 (6), 92 (8), 91 (100), 77 (5), 65 (12), 55 (5), 43 (5), 28 (21), 27 (5), 18 (14); HRMS calcd for C₂₀H₂₁NO₃S 357.1242, found 357.1252.

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Supplementary Material Available: NMR spectra for compounds 3a, 3b, 4, 6c, 7c, 6d, 12a, 13a, and 14a and MS data of compounds 12a, 13a, and 14a (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

The Kinetic Acidity of 1,1,1-Triphenylethane¹

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Hydrogen isotope exchange studies were carried out on the methyl group of 1,1,1-triphenylethane, 1, with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA). Mixtures of labeled compounds were used, $Ph_3C-^{14}CH_3$ (1-¹⁴C), Ph_3CCH_2T (1-t), Ph_3CCH_2D (1-d), and Ph_3CCD_3 (1-d₃). The second-order rate constant for tritium exchange, 3.6×10^{-5} M⁻¹ s⁻¹, is 9.0×10^{-5} the rate of benzene and 8.5×10^{3} times the rate of exchange of cyclohexane. The primary isotope effect, $k_D/k_T = 1.8$, and corresponds to $k_H/k_D = 3.8$, a moderate value that is comparable to that of cyclohexane and indicates an unsymmetrical transition state. The α -secondary isotope effect, $k_H/k_D = 1.2$, indicates that C-H bonds at the carbanion center have significantly lower bending frequency at the transition state.

Introduction

A substantial body of experimental data has appeared from this laboratory concerning the kinetic acidities of unconjugated hydrocarbons with cesium cyclohexylamide (CsCHA) in cyclohexylamine.² This work is significant as a measure of relative carbanion stability in solution because the low acidities of these compounds make meaningful equilibrium studies exceptionally difficult. The kinetic acidities of alkanes and other unconjugated hydrocarbons is of further recent interest because of their possible relevance in "hydrocarbon activation" by transition-metal organometallic compounds.³ Although our past studies have provided relative reactivities of some unconjugated tetrahedral C-H bonds, further details of transition-state structure, such as those obtainable from isotope effects, is made difficult by their exceptional unreactivity: half-lives for tritium exchange of alkanes and cycloalkanes even with CsCHA range from decades to centuries. For this reason, the methyl group of 1,1,1-triphenylethane, 1, was of especial interest. It is an unconjugated group but preliminary studies indicated a reactivity of about 10⁴ that

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Table I. Detritiation of the Methyl Position of 1,1,1-Triphenylethane in CHA/CsCHA at 50 °C from Run RED-1

		³ H					
	time (10 ⁻⁵ s)	14C	[CsCHA] (M)				
	0.000	7.752	0.0450				
	1.587	5.882	0.0456				
	2.912	4.785	0.0450				
	4.218	3.802	0.0451				
	5.838	2.976	0.0451				
	6.990	2.513	0.0451				
	80	0.008					

of cyclohexane.⁴ sufficiently high for use of ordinary kinetics techniques. Moreover, this reactivity lies about midway between cyclohexane and benzene where it would provide a convenient bridge in studying relative rates of other compounds. In the present study we report exchange kinetics for mixtures of isotopically substituted compounds, Ph₃C-¹⁴CH₃ (1-¹⁴C), Ph₃CCH₂T (1-t), Ph₃CCH₂D (1-d), and Ph₃CCD₃ $(1-d_3)$. The results provide not only the kinetic acidity of 1 but also primary and secondary isotope effects; the latter have never been reported before for an isolated methyl group.

Results and Discussion

Tritium exchange can be a useful method for measuring kinetic acidity but an important limitation in analysis by scintillation counting⁵ is that one must know the mass or concentration of material to be counted, either by weighing the material or by some indirect method. In early experiments with 1-t,⁶ a spectroscopic approach was used to determine the concentration of 1,1,1-triphenylethane in the scintillation cocktail but the UV spectra of the material isolated from kinetic runs was complicated by the production of small amounts of decomposition products and reproducible results could not be obtained.

A different approach, which eliminates these problems. was used for this work. The value of a double-label technique was demonstrated previously for kinetic acidity measurements leading to the aqueous pK of toluene.⁷ In this technique, the compound of interest contains both ³H, which is exchanged and lost over time, and ¹⁴C, which does not participate in the exchange. The kinetics is followed by counting ${}^{3}H$ and ${}^{14}C$ simultaneously. The ratio ${}^{3}H/{}^{14}C$ will decrease over time, and is not concentration dependent. That is, the ¹⁴C content provides a measure of the amount of substrate being counted. In the case of 1,1,1triphenylethane, this technique was applied by including 1^{-14} C in the kinetic mixture. It has been shown⁸ that for minimum error in the simultaneous counting of ³H and ¹⁴C. the ratio ${}^{3}\text{H}/{}^{14}\text{C}$ should lie between 2 and 10. The mixture was prepared such that this condition held throughout the runs. 1-d and $1-d_3$ were added to obtain the deuterium loss rate constants needed to calculate the primary and secondary isotope effects.

Detritiation Kinetics of 1,1,1-Triphenylethane. Four runs were completed that contained 1-t and $1-{}^{14}C$. In all cases, the reaction mixture prepared in a glovebox was distributed into tubes, which were sealed and placed in a constant temperature bath at 50 °C. At convenient times, the triphenylethane mixture was extracted from the contents of each tube, dissolved in a scintillation cocktail,



Figure 1. Detritiation of the mixture of 1,1,1-triphenylethanes in CsCHA/CHA at 50 °C for run RED-1.

Table II. Protiodetritiation Rate Constants for 1.1.1-Triphenylethane

-,-,						
[CsCHA] M	$10^6 k_1 \ s^{-1}$	$10^5 k_2 \ \mathrm{M}^{-1} \ \mathrm{s}^{-1}$				
0.045	1.61	3.57				
0.025	0.93	3.72				
0.170	6.17	3.63				
0.090	3.07	3.41				
		3.58 单 0.09				
	[CsCHA] M 0.045 0.025 0.170 0.090	[CsCHA] M 10^6k_1 s^{-1} 0.045 1.61 0.025 0.93 0.170 6.17 0.090 3.07				

Table III. Percentage of Mono-, Di-, and Trideuterated and All-Protic 1,1,1-Triphenylethane for Run RED-3

	· · -	•			
 time (10 ⁶ s)	%D ₃	$\%D_2$	%D ₁	%D ₀	
0.000	42.78	1.37	19.79	35.74	
0.556	3.98	14.88	24.59	54.31	
1.087	0.91	6.48	18.09	74.67	
1.767	0.0	3.11	10.38	87.07	
2.225	0.0	2.35	6.97	91.10	
2.373	0.0	0.0	7.02	91.06	

and counted simultaneously for ³H and ¹⁴C. The concentration of CsCHA was also determined for each point in the run. By this method, a reproducible second order rate constant of 3.58×10^{-5} M⁻¹ s⁻¹ was obtained. As an example, the data for the first run is shown in Table I.

A plot of the values in Table I is shown in Figure 1. The resulting pseudo-first-order rate constant, $k_{\rm T}$, is 1.62×10^{-7} s⁻¹. Division of $k_{\rm T}$ by the average concentration of CsCHA, 0.045 M, gives the second-order rate constant for protiodetritiation of 1,1,1-triphenylethane, $k_2 = 3.57 \times 10^{-5}$ M^{-1} s⁻¹. The results for all of the runs are summarized in Table II.

Previous determinations of detritiation rates of benzene and cyclohexane have resulted in absolute rate constants for these compounds of 0.4 $M^{-1} s^{-1}$ and $4.2 \times 10^{-9} M^{-1} s^{-1}$, respectively, at 50 °C.^{2b} Using these values, we compute the relative kinetic acidity of 1,1,1-triphenylethane as 9.0 \times 10⁻⁵ times benzene and 8.5 \times 10³ times cyclohexane. Thus, 1,1,1-triphenylethane exchanges about 4 orders of magnitude slower than benzene and about 4 orders of magnitude faster than cyclohexane. The rate increase compared to cyclohexane undoubtedly reflects the significant electron-attracting inductive effect of the three phenyl groups in 1.

Protiodedeuteration of 1,1,1-Triphenylethane. The procedure used in the first run (RED-1) for the determination of the deuterium loss rate constants for 1,1,1-triphenylethane was not satisfactory. For that run, aliquots resulting from the points taken at specific times were submitted for mass spectrometry analysis and samples were treated as a whole, evaporating solvent and scanning for all ions. For subsequent runs, a capillary column GC/MS instrument was used for the deuterium analyses

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Table IV. Summary of Protiodedeuteration Second-Order Rate Constants for 1,1,1-Triphenylethane

run	$10^5 k_{\rm D} \ ({ m M}^{-1} \ { m s}^{-1})$	$10^4 k_{D_2} (M^{-1} s^{-1})$	$(\mathbf{M}^{-1} \mathbf{s}^{-1})$	[CsCHA] (M)	$\frac{3k_{\rm D}}{k_{\rm D_3}}$	$\frac{2k_{\rm D}}{k_{\rm D_2}}$	$\frac{3k_{\mathrm{D}_2}}{2k_{\mathrm{D}_3}}$	
RED-3	6.76	1.03	1.42	0.025	1.43	1.31	1.09	
RED-4	6.19	1.02	1.28	0.170	1.45	1.21	1.20	
avg	6.48	1.03	1.35					

and gave much improved results, with clean and reproducible mass spectra. The heights of the peaks were corrected for ¹³C and ²H, and the relative heights were used to compute the percentages of mono-, di-, trideuterated, and all-protic triphenylethane present in the sample. Results for one run are summarized in Table III.

As can be seen in Table III, D_3 falls off in a familiar first-order fashion, D_2 initially increases then falls off, D_1 behaves in a manner similar to D_2 , and D_0 steadily increases. For the calculation of the isotope effects, we treat the data to obtain all of the deuterium rate constants. The model used is shown in eqs 1-4. These equations are

$$D_3 \xrightarrow{k_3} D_2 \xrightarrow{k_2} D_1 \xrightarrow{k_1} D_0$$
(1)

$$\frac{\mathrm{d}\mathrm{D}_3}{\mathrm{d}t} = -k_3\mathrm{D}_3 \tag{2}$$

$$\frac{\mathrm{d}\mathrm{D}_2}{\mathrm{d}\mathrm{t}} = k_3\mathrm{D}_3 - k_2\mathrm{D}_2 \tag{3}$$

$$\frac{\mathrm{d}\mathrm{D}_1}{\mathrm{d}t} = k_2\mathrm{D}_2 - k_1\mathrm{D}_1 \tag{4}$$

straightforward to solve by matrix algebra.⁹ Fitting of the integrated equations to the experimental data was performed by means of the routine SYSNLIN (especially designed for nonlinear systems) in the SAS statistical analysis package.¹⁰ The results of this procedure are summarized for two runs in Table IV. For comparison, two previous workers in our group obtained preliminary protiodedeuteration rate constants for 1,1,1-triphenylethane using material containing only one deuterium in the methyl group. Their values of $\sim 6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ and 8.4×10^{-5} M⁻¹ s⁻¹, respectively, in reasonable agreement with the value obtained here of $6.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

With all of the deuterium rate constants available, we can calculate the primary and secondary isotope effects for the system. The primary isotope effect, $k_{\rm D}/k_{\rm T} = 1.81$. The secondary isotope, as summarized in Table IV, averages 1.20 per deuterium; that is, a deuterium atom vicinal to the deuteron lost in the exchange makes the exchange slower by 20%, which indicates that the C–H bonds of the methyl group have significantly lower bending frequencies in the transition state than in the hydrocarbon. We can convert the deuterium to tritium isotope effect to the more familiar deuterium to protium isotope effect, $k_{\rm H}/k_{\rm D}$, by application of the Swain–Schaad equation, eq $5.^{11}$ With

$$\frac{k_1}{k_2} = \left(\frac{k_3}{k_4}\right)^x \quad \text{where } x = \frac{\frac{1}{(m_1)^{1/2}} - \frac{1}{(m_2)^{1/2}}}{\frac{1}{(m_3)^{1/2}} - \frac{1}{(m_4)^{1/2}}} \quad (5)$$

the masses for deuterium, tritium, and protium we obtain:

$$\left(\frac{k_{\rm D}}{k_{\rm T}}\right)^{2.263} = \frac{k_{\rm H}}{k_{\rm D}} \tag{6}$$

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It has been proposed¹² that reduced masses should be used for the calculation of the exponent in the Swain-Schaad relation because a carbon-protium vibration is involved. The exponent resulting from the use of reduced masses is 2.344. The value of 1.81 for $k_{\rm D}/k_{\rm T}$ translates to $k_{\rm H}/k_{\rm D}$ = 3.83 from eq 6 or 4.03 using 2.344 as the exponent. This value of the primary isotope effect is in an intermediate range indicative either of an unsymmetrical transition state¹³ or that some internal return is occurring in the system.¹⁴ Primary isotope effects of more acidic hydrocarbons with CsCHA are in a more normal higher range^{24,15} and internal return is negligible. If the more modest primary isotope effect in the present case is the result of some internal return, the fraction of internal return should be higher for a more basic carbanion and a less acidic hydrocarbon should give a still smaller primary isotope effect. The test has already been done. Some years ago we determined the total isotope effect per position of cyclohexane relative to perdeuterocyclohexane:^{2b} $k_{C_0H_{12}}/k_{C_0D_{12}}$ = 6.5 \pm 0.6. This rate ratio contains α and β secondary deuterium isotope effects as well as a primary isotope effect. For a given position in cyclohexane, there is a geminal position and four vicinal positions. The geminal of α -deuterium should contribute an isotope effect of 1.2 as found above for triphenylethane. Vicinal or β secondary deuterium isotope effects are commonly in the range of 5-15%.¹⁶ A β -D effect of 1.11 ± 0.03 was found for the exchange of $C_6H_5CHDCH_3$ relative to $C_6H_5CHDCD_3$ with LiCHA;17 thus, a value of about 4% for deuterium should not be far off for use in cyclohexane. Therefore, for C_6H_{12} relative to C_6D_{12} , the calculated total secondary isotope effect is $(1.2)(1.04)^4 = 1.4$, leaving the primary isotope effect as 6.5/1.4 = 4.6, a value in the same range as that found for 1,1,1-triphenylethane, 3.8-4.0. This agreement suggests that for these weakly acidic hydrocarbons the transition state is not symmetrical and is probably displaced to the product side. It is interesting to note in this connection that ab initio calculations of the proton-transfer reactions of lithium and sodium amide and of amide ion with methane give transition states in which the C-H bond to the transferred hydrogen has been stretched about 0.05 Å more than the N-H bond.¹⁸

Conclusion

The present results confirm the expected mechanism of the reaction: CsCHA abstracts a proton from the methyl group of 1 via a transition state involving extensive C-H bond breaking. The α -secondary isotope effect shows that the remaining C-H bonds have a looser vibration con-

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sistent with the reduction in coordination around the carbon. The reactivity of 1 indicates that the transition state has substantial carbanion character. No phenyl rearrangement was observed; thus, the intermediate organocesium compound undergoes proton transfer with solvent much faster than rearrangement.

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Cyclohexylamine (CHA) was dried over sodium hydroxide pellets, fractionally distilled (bp 134 °C), dried over lithium cyclohexylamide (LiCHA), vacuum transferred to a dry flask, and stored in a glovebox. ¹H NMR spectra were acquired in deuteriochloroform on the UCB-200, a 200-MHz superconducting FT spectrometer. Chemical shifts are reported in δ values, the standard being the residual proton absorption of deuteriochloroform (δ 7.24). ¹H NMR data are given in the following format: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). Mass spectra were determined at the UC Mass Spectrometry Laboratory, and the deuterium content of compounds was calculated using the ISOCOR program¹⁹ which corrects line heights for natural abundances of ¹³C, ¹⁵N, ¹⁷O, and ¹⁸O. Activities of labeled compounds were determined on a Searle Model Mark III liquid scintillation counter, using a scintillation cocktail containing 0.4% 2,5-diphenyloxazole (PPO) and 0.01% p-bis(2-(5-phenyloxazolyl))benzene (POPOP) in toluene. All air-sensitive compounds were handled under an argon atmosphere. Glovebox manipulations were carried out under an argon atmosphere in a Vacuum Atmospheres Model HE 43-2 Dri-Lab with attached HE 493 Dri-Train. Constant temperature baths were monitored with a Hewlett-Packard Model 2801A quartz thermometer calibrated against the triple point of water.

1,1.1-Triphenylethane, 1. To a stirred solution of 1.70 g (7.0 mmol) of triphenylmethane in 40 mL of dry dimethyl sulfoxide (distilled from calcium hydride) in a three-necked 150-mL flask was added 4.0 mL of a 2 M solution of butyllithium in hexane (7.7 mmol). After being stirred for 25 min, the red solution was quenched with 1.3 mL (20 mmol) of methyl iodide. Water (20 mL) was added with cooling and stirring, and an oil separated that solidified on cooling overnight. The solid was filtered, washed with water, dried, and recrystallized from ethanol to afford 1.3 g (72%) of 1,1,1-triphenylethane, mp 95–96 °C [lit.²⁰ mp 94.8–95.0 °C]; ¹H NMR δ 7.17 (m, 15 H), δ 2.20 (s, 3 H) [lit.²¹ δ 7.2 (m, 15 H), δ 2.2 (s, 3 H)]; MS (m/e, % RIC) 258, 4.84; 243, 30.04; 181, 5.72; 165, 17.27.

1-14C was prepared similarly from 0.1 mCi of [14C]-iodomethane; specific activity 45 000 dpm/mg.

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 $1-d_3$ was prepared similarly except that CD_3I was used.

[2-3H]-1,1,1-Triphenylethane, 1-t. To 40 mL of dry diethyl ether under an argon atmosphere in a three-necked 150-mL flask provided with a reflux condenser were added 1.4 g of magnesium turnings (57.6 mmol) and 5.00 g of 2-chloro-1,1,1-triphenylethane²² (17 mmol). The mixture was heated at reflux for 12 h after which there was a yellow solution and a white precipitate present in the flask. The mixture was cooled to 0 °C with an ice bath and quenched with 1.0 mL of tritiated water (5 mCi/mmol). After 20 m, 1.0 mL of concentrated hydrochloric acid was added and the mixture was filtered to remove unreacted magnesium, which was washed with ethyl ether. The combined ether extracts were washed with sodium bicarbonate and brine and dried over magnesium sulfate. Removal of the solvent in a rotary evaporator left an oily residue that crystallized from ethanol. Recrystallization from ethanol gave 3.16 g (72%) of 1-t, specific activity 67000 dpm/mg.

1-d. The same procedure was used with D_2O .

Triphenylethane Kinetic Runs. In a glovebox under an argon atmosphere was prepared a mixture from 50 mL of stock CsCHA solution and ca. 200 mg of the mixture of 1, 1-t, 1-14C, 1-d, and 1-d₃ in 5 mL of CHA. About 11 mL of this solution was added as fast as possible to each of five identical reactors consisting of an $8^1/_2$ -in. o.d. Pyrex tube sealed on one end and provided with a 14/30 male joint and a crimp on the other end. The joints were greased, and the reactors were fitted with vacuum stopcocks having two 14/30 female joints. The reactor tubes were then taken out of the box, frozen in liquid nitrogen, and evacuated. While under vacuum, the reactors were sealed at the crimp with a gas/oxygen torch. The contents were thawed by immersion in water at room temperature, and the reactors were then placed in a constant temperature bath at 50.00 ± 0.02 °C. At appropriate intervals, a reactor tube was removed from the bath and cracked open inside a glovebag containing argon. Approximately 2 mL of the solution was removed by means of a syringe provided with a long needle and placed in a preweighed vial containing ca. 2 mL of bromobenzene. The rest of the solution was then quenched with water. The vial was weighed and then stored under argon for ca. 24 h for later determination of CsCHA concentration.²³ The solution remaining in the tube was transferred to a separatory funnel and treated with 10 g of ice was added, 5 mL of pentane, and 25 mL of 3 N hydrochloric acid. The organic layer was treated three times with ice and acid and then washed with brine until neutral. The dried organic phase was divided into two equal parts. One part was used for mass spectral analysis. The solvent was removed from the other part using a rotary evaporator and the residue was counted simultaneously for ³H and ¹⁴C.

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⁽¹⁹⁾ Written in house by Julian E. Schafer and William R. Young.

⁽²²⁾ Prepared by W. R. Young (ref 4).