The assignment of the band near 1590 cm.$^{-1}$ was based on its presence in "rhodo-type" chlorins and its absence in hindered chlorins, chlorins that have no COOH or $COOCH_3$ on C-6, and derivatives with an intact ring between C-γ and C-6, *i.e.*, phorbins and purpurin 18*a*. These marked differences in the infrared spectra between hindered and unhindered chlorins stand in distinct contrast to the similarity of their spectra in the visible region.

Bellamy[19] has cited a paper by Brown and Todd,[20] and has mentioned that the two carbonyl absorption bands associated with the anhydride structure are separated by only 34 cm.$^{-1}$ in the cyclic six-membered ring anhydride studied by these workers. This is in contrast to the bands in other types of anhydrides, which are about 60 cm.$^{-1}$ apart. We have studied one six-membered anhydride, purpurin 18*a* methyl ester, and find a difference of 31 cm.$^{-1}$, which is in satisfactory agreement with the work of these authors.

In each spectrum in Fig. 1 the bands near 3000 cm.$^{-1}$ result from C–H stretching. Although not shown, each compound had but one peak assignable to N–H stretching, and this was found near 3350 cm.$^{-1}$.

Acknowledgment.—H. R. W. is indebted to Dr. N. H. Cromwell of the University of Nebraska, Lincoln, Nebr., and to Dr. H. E. Zimmerman of Northwestern University, Evanston, Ill., for helpful discussions of portions of this work.

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[19] Reference 15, p. 128.

[20] B. R. Brown and A. R. Todd, *J. Chem. Soc.*, 1280 (1954).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF BOSTON UNIVERSITY AND THE RICE INSTITUTE]

Ionization Equilibria of Mono-*p*-methyl and Mono-*p*-trideuteriomethyl Trityl Chloride in Liquid Sulfur Dioxide[1]

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The secondary isotope effect on the equilibrium of ionization of mono-*p*-methyl trityl chloride to the ion pair, $p\text{-}CH_3\text{-}C_6H_5C(Cl)(C_6H_5)_2 \overset{K_1}{\rightleftarrows} \overbrace{p\text{-}CH_3C_6H_5C^+(C_6H_5)_2Cl^-}$, due to replacing methyl protium with deuterium has been estimated at 0.16° by a method which employs conductance data at relatively low dilution (600 l. mole^{-1}). This method is 5 to 10 times as precise as comparison of equilibrium constants calculated from conductance data for higher dilutions. The value of $(K_1)_H/(K_1)_D$ per deuterium atom is estimated to be 1.003 ± 0.005.

Studies of reactions proceeding *via* transition states in which positive charge is delocalized from the reaction site into an aromatic ring have provided significant insight into the nature and scope of the secondary deuterium isotope effect. These have included investigation of the solvolysis in acetic acid and/or aqueous acetone of *m*- and *p*-methyl substituted α-phenylethyl chlorides, variously substituted with deuterium,[2] the solvolysis in aqueous ethanol and acetone[3] of several mono-*p*-alkylbenzhydryl chlorides substituted with deuterium at the α-carbon of the *p*-alkyl group and the nitration, mercuration and bromination of toluene substituted in the methyl group with deuterium or tritium.[4] In these reactions the replacement of α-hydrogen of a *p*-alkyl group by deuterium is associated with a kinetic isotope effect, k_H/k_D, which is quite small, ranging from a maximum of about 1.05 per deuterium atom[2] down to values indistinguishable from unity. This isotope effect appears to be dependent on the nature of the solvent.

This report presents the results of a study of the isotope effect on an equilibrium which is closely related to the assumed equilibria between reactants and transition states in the above cases. Earlier studies of the ion-forming equilibria of trityl chloride and many of its *o*-, *m*- and *p*-substituted derivatives together with data on the dissociation equilibria of many ionophores have provided a convenient means of evaluating substituent effects on the ionization equilibrium: $Ar_3CCl \overset{SO_2}{\rightleftarrows} \overbrace{Ar_3C^+Cl^-}$.[5] The similarity of substituent effects in this system to those observed in reactions like the solvolyses and electrophilic substitution reactions cited above has recently been elegantly demonstrated.[6] Studies of these equilibria provide a measure of substituent effects where full carbonium ion character is unequivocally developed.[7]

Equilibrium Constants.—Initially, it was hoped that thermodynamic equilibrium constants, K_{exp}, evaluated from conductance data collected by our usual methods[5] by means of Shedlovsky's procedure[8] could be determined with sufficient precision to provide a useful measure of the secondary deuterium isotope effect. In order to maximize the accuracy of the comparison, an unusually large number of conductance runs were carried out;

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[1] Paper VII in the series "Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide." Paper IV in the series "Isotope Effects in Carbonium Ion Reactions."

[2] (a) E. S. Lewis and G. M. Coppinger, THIS JOURNAL, **76**, 4495 (1954); (b) E. S. Lewis, R. R. Johnson and G. M. Coppinger, *ibid.*, **81**, 3140 (1959).

[3] V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 373 (1957).

[4] C. G. Swain, T. E. C. Knee and A. J. Kresge, *ibid.*, **79**, 505 (1957).

[5] *Cf.* N. N. Lichtin and M. J. Vignale, *ibid.*, **79**, 579 (1957), and earlier papers.

[6] Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4986 (1958).

[7] The absorption spectrum of the ionophore triphenylcarbonium perchlorate dissolved in liquid sulfur dioxide has been shown by P. D. Bartlett and R. E. Weston, Jr., to be identical with the spectrum of triphenylcarbinol dissolved in concentrated sulfuric acid (*cf.* ONR Technical Report No. 6 under Project No. NR-056-095, Contract No. N5 ori-76, Task xx, April 10, 1952).

[8] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

TABLE I

CONDUCTANCE DATA OF THREE TYPICAL RUNS[a]

p-CH_3-Trityl Cl I V^b	Λ^c	*p*-CH_3-Trityl Cl II V^b	Λ^c	*p*-CD_3-Trityl Cl[d] V^b	Λ^c
534.6	105.0	531.6	105.4	563.3	106.1
1455	132.0	1439.5	131.8	1548	133.8
3965	157.8	3899	157.3	4251	159.2
10768	177.5	10564	175.5	11680	178.6
29240	189.8	28632	185.8	32090	190.6

[a] Chloride I was prepared by standard procedures beginning with Matheson methyl *p*-toluate and phenylmagnesium bromide. Chloride II was prepared by a synthetic route that paralleled that employed in the synthesis of the deuterium compound; *cf*. Experimental for details. [b] Liters mole^{-1}. [c] Mhos cm.^{2} mole^{-1}, corrected for solvent conductivity. [d] 2.43 atoms D per molecule.

TABLE II

QUANTITIES DERIVED FROM THE SHEDLOVSKY ANALYSIS[a]

Solute	10^4-Kexp, mole l.$^{-1}$	S_K 50% conf. limit	S_K 95% conf. limit	Λ_0 mhos cm.^{2} mole^{-1}	S_Λ 50% conf. limit	S_Λ 95% conf. limit	n
Mono-*p*-CH_3-trityl Cl(I)	6.4_7	0.18	0.54	$204._0$	0.7	2.0	39
Mono-*p*-CH_3-trityl Cl(II)	6.2_5	.21	.68	$204._1$	1.0	3.3	10
Mono-*p*-CD_3 trityl Cl[b]	6.6_5	.12	.37	$202._8$	5.0	1.8	18

[a] Variances are adjusted for the number of individual data, n, with the aid of statistic "t" values. [b] 2.43 atoms D per molecule.

fifteen useful runs with the protium compound, mono-*p*-methyl trityl chloride, and five with the trideuteriomethyl compound. The data of three typical conductance runs are presented in Table I.

K_{exp} and Λ_0 were calculated from the data by least square solution of Shedlovsky's equation.[5,8] Values of Λ at dilutions less than 2×10^3 l. mole^{-1} were not employed in the calculation and the upper limit of dilution (about 5×10^4 l. mole^{-1}) was chosen so that the conductivity of the solvent (0.5 to 1.4×10^{-7} mho cm.$^{-1}$) was never greater than 3% of the total. Values of K_{exp} and Λ_0 and the square roots of their variances, S_K and S_Λ, respectively, calculated for 95 and 50% confidence limits[9] are presented in Table II.

These results permit no conclusion to be drawn concerning the existence or sign of the isotope effect. The magnitudes of S_K calculated with 95% confidence limits provide a warning against treating the apparent difference between the values of K_{exp} for the protium and deuterium compounds as real.[10] Furthermore, since the statistical uncertainties are of the order of magnitude of the maximum anticipated isotope effect it would seem that these measurements cannot provide useful information on the secondary deuterium isotope effect.

Estimation of the Isotope Effect.—The above discouraging conclusion is, however, not final. It can be demonstrated that, although the uncertainty in K_{exp} as determined by these methods is of the order of several per cent., *the isotope effect on* K_{exp} *can be estimated much more precisely*. In order to do this, it first must be recognized that the equivalent conductances, λ^+ (at any specified values of V), of *p*-CH_3-trityl cation and *p*-CD_3-trityl cation are identical. This follows from the fact that although they differ by about 1% in mass, these cations cannot differ significantly in geometry. Both the limiting conductance of an ion of given charge type and the dependence of conductance on dilution are functions of ionic size but not of ionic mass.[11] Therefore, Λ_c, the equivalent conductance of each solute at a fixed stoichiometric concentration, C, is related to the concentration of free ions by the same proportionality constant. Although $(\Lambda/\Lambda_0)_c$ is not equal to α_c, the degree of dissociation at stoichiometric concentration C for either solute, it differs from α_c for these solutes by the same factor.[12] Since Λ_0 is identical for both, Λ_c is an exact measure of α_c. The relationship between α_c and K_{exp} is given by eq. 1. In the concentration range of the measurements described below, $\alpha f_\pm$ cannot be taken as equal to $(C^{-1}K_{exp})^{1/2}$, however, and it is necessary to calculate the effect on α of a small change in K_{exp}.

$$K_{exp} = \frac{\alpha^2 C f_\pm^2}{1 - \alpha} \quad (1)$$

This can be done with the aid of the Debye–Hückel equation, which takes the form of equation 2 for this system.[13] It is thereby found that,

$$-\log f_\pm = \frac{6.687[C\alpha_c]^{1/2}}{1 + 15.48[C\alpha_c]^{1/2}} \quad (2)$$

with $C = 1.8 \times 10^{-3}$ M, a 1% change in K_{exp} (taken as 6.5×10^{-4}) will produce an 0.32% change in α_c and therefore in Λ_c.

K_{exp} is, however, not itself a direct measure of the isotope effect since it is related to both an ionization constant, K_1, which is subject to any isotope effect that may be present, and a dissociation constant, K_2, which is not. From equation 3 and an estimate of K_2 which has been made previously[5] it can be shown that K_{exp} will reflect about 80% of the isotope effect on K_1. Thus an isotope effect of 1% will produce a change of about 0.25% in Λ_c.

$$K_{exp} = \frac{K_1 K_2}{K_1 + 1} \quad (3)$$

Figure 1 represents data which serve, on the basis of the above analysis, to evaluate the isotope

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[9] S_Λ^2 is based on S_a^2, the variance in the intercept, a, of the Shedlovsky line. Since K_{exp} is determined from the slope, b, of this line *via* the relationship slope = $1/K_{exp}\Lambda_0^2$, the variance in K_{exp} is calculated from S_a^2 and S_b^2 (the variance in the slope) *via* the relationship $S_K^2 = (a/b)^2[4S_a^2 + (a/b)^2 S_b^2]$. *Cf.* O. L. Davies "Statistical Methods in Research and Production," Oliver and Boyd, London, 1949, p. 37.

[10] The difficulty in precise evaluation of K_{exp} for electrolytes as strong as these is illustrated by comparing the data of Table II with earlier values[5] of K_{exp} and Λ_0, namely, 7.7×10^{-4} and 196. The latter were calculated from earlier measurements with the inclusion of 3 points (of 13) for which the solvent conductivity was 6.5 to 10% of the total. Upon elimination of these points to meet the standards of the present work, K_{exp} and Λ_0 become $6.8 \pm 0.83 \times 10^{-4}$ and 199 ± 4, respectively (95% confidence limits, $n = 10$). It is also noteworthy that the degree of uncertainty in K_{exp} is largely indicated by S_b^2, the variance in the slope of the Shedlovsky line. This uncertainty is not immediately obvious from the scatter of experimental $1/\Lambda S(z)$ values about the Shedlovsky line although it is calculated from them.

[11] *Cf.* H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," third edition, Reinhold Publishing Corp., New York, N. Y., 1958, pp. 156 and 284.

[12] This is not rigorously true since Λ_0 varies with ionic strength and therefore with α_c. This effect can be shown to be more than an order of magnitude smaller than the dependence of Λ_c on K_{exp} and can be safely neglected.

[13] The Debye–Hückel a parameter is herein identified with Bjerrum's q, which for this medium is equal to 19.92 Å.

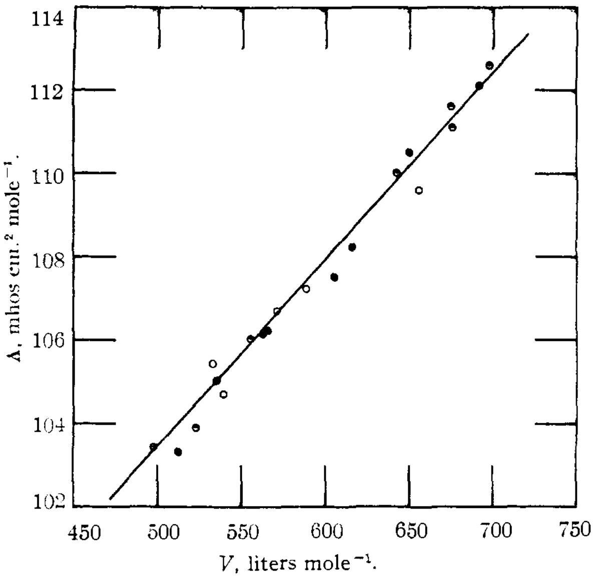

Fig. 1.—Conductance data for weighed points: *p*-methyltriphenylchloromethane (I), ◒; *p*-methyltriphenylchloromethane (II), ○; *p*-methyl-d_3-triphenylchloromethane, ●. The line corresponds to eq. 4 and is based on data for protium compounds only.

effect in this system. Each point represents a measurement obtained with a solution prepared on the vacuum line by dissolving a known weight of solute (18–30 mg. weighed to ±0.02 mg.) in a known volume (50–52 ml.) of dried, degassed solvent; *i.e.*, none of these measurements involved dilution of the initially prepared solution. In this concentration range solvent conductivity makes up only about 0.05% of the solution conductivity and the usual small fluctuations in its magnitude are negligible; its value was therefore taken as 1×10^{-7} mho cm.$^{-1}$ in calculating the indicated values of Λ_c. Table III summarizes these values. The data can be evaluated conveniently by comparing the points for the deuterium compound with the best straight line, determined by the method of least squares, corresponding to the data for the protium compound, *i.e.*, with equation 4.

$$\Lambda = 80.86 + 0.04502V \qquad (4)$$

The mean deviation of Λ_c for the protium compound from this line is 0.27%. The mean deviation from this line of the points for the deuterium compound is 0.31%, but the scatter is one sided. Summing these deviations, $(\Lambda_D - \Lambda_H)_c$, algebraically rather than summing their absolute values yields a "mean deviation" of −0.19%. The isotope effect may be estimated from the mean value of the ratio $(\Lambda_H/\Lambda_D)_c$, where Λ_H is calculated from the interpolation formula, eq. 4, and Λ_D values are experimental. Since this mean value is 1.0020 with a standard deviation of 0.0029, the isotope effect $(K_1)_H/(K_1)_D$ may be taken as 1.008 ± 0.012 for 2.43 deuterium atoms or 1.003 ± 0.005 per deuterium atom.

Discussion

The development of full carbonium ion character is not associated in the present case with a significant secondary isotope effect. It may be tempting to assume that this result is due to a relatively low sensitivity of the reaction equilibrium to substituent effects: K_1 is increased only sixteenfold by introduction of a *p*-methyl group into trityl chloride. The introduction of a *p*-methyl group into α-phenylethyl chloride or benzhydryl chloride does not, however, increase the rates of their solvolytic reactions by greatly different factors. In acetolysis of α-phenylethyl chloride at 50° the factor is about 25[2,14] and in solvolysis of this compound at 70° in "80% acetone" it is about 37.[2,15] The factor for benzhydryl chloride at 0° lies in the vicinity of 32 for solvolysis in "90% alcohol" and aqueous acetone of several compositions.[16] Finally, Swain, *et al.*,[4] have demonstrated that a substantial secondary isotope effect is not observed in aromatic bromination which is characterized by a very much larger substituent effect.[17] No correlation is apparent between the sensitivity of these reactions to substituent effects and the magnitude of the secondary deuterium isotope effect.[18]

TABLE III

DATA FOR "WEIGHED" POINTS

Protium compound		Deuterium compound	
V, liters mole^{-1}	Λ, mhos cm.^{2} mole^{-1}	V, liters mole^{-1}	Λ, mhos cm.^{2} mole^{-1}
499.0	103.4		
520.9	103.9	513.6	103.3
531.6[a]	105.4[a]		
534.6	105.0		
538.7[a]	104.7[a]		
554.5	106.0	563.3	106.1
571.2[a]	106.7[a]	565.7	106.2
587.4[a]	107.2[a]	604.6	107.5
642.8	110.0	615.7	108.2
654.5[a]	109.6[a]	649.8	110.5
675.3	111.6		
676.3	111.1		
699.2	112.6	693.3	112.1

[a] Sample II, all other data in these columns with sample I.

It must also be recognized that the procedure for estimating the isotope effect presented here is sensitive to the presence of very small amounts of non-conducting impurities in the solutes. That such an error, if present, is not large is indicated by the Λ_0 values of Table II.

Experimental

The equipment and procedures employed in the conductivity measurements are described elsewhere.[19] The tem-

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[14] J. Steigman and L. P. Hammett, THIS JOURNAL, **59**, 2541 (1937). The medium employed by these workers was 0.1 *M* in LiCl and also in LiOAc whereas Lewis, *et al.*, employed a medium 0.1 *M* only in LiOAc.

[15] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1207 (1937). Comparison is based on extrapolation of the data of Lewis, *et al.*, which were obtained in a medium 0.1 *M* in NaCl. This solute was absent in the older work.

[16] V. J. Shiner, Jr., and C. J. Verbanic, THIS JOURNAL, **79**, 369 (1957).

[17] The Hammett ρ-value is about 11 for this reaction[6] whereas it is about 4 for the ionization of substituted trityl chlorides in SO_2 and for the solvolysis of substituted benzhydryl chlorides in a variety of media; *cf.* H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

[18] Some of the factors which may influence the magnitude and sign of the secondary isotope effect are discussed in ref. 2b.

[19] (a) N. N. Lichtin and H. Glazer, THIS JOURNAL, **73**, 5587 (1951); (b) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160 (1956).

perature was maintained at 0.16 ± 0.01° in a large refrigerated oil-filled thermostat. All solutions were measured in the same conductivity cell. This was similar to that previously described[19a] except that mercury junctions were eliminated. Usually only four and, at most, five dilutions were carried out before achieving the highest dilution employed in the Shedlovsky calculation so as to minimize the error inherent in the internal dilution procedure. Sample weights were determined with a precision of ±0.1%. The usual procedures were employed in preparing solutions for measurement of only the initial solution as well as in runs involving several dilutions. At dilutions around 600 l. mole^{-1} resistance measurements were made with a precision of ±0.01%.

Mono-*p*-methyltriphenylchloromethane I.—Mono-*p*-methyltriphenylcarbinol was prepared by reaction of phenylmagnesium bromide with methyl toluate in dry ether. The residue isolated after hydrolysis and steam distillation of the reaction mixture was recrystallized to constant m.p. from benzene to yield a product melting at 72.5–73°. This material was converted to the chloride by refluxing its solution in acetyl chloride (4 moles per mole of carbinol) under a nitrogen atmosphere for 15 minutes in apparatus which had been dried in an oven. The crystals which formed on cooling were recrystallized from 1.7 ml./g. of solute of a 2:3 mixture of 30–60° petr. ether and ether which had been dried over sodium. The product was collected under nitrogen, washed with cold sodium-dried 30–60° petr. ether and dried in an Abderhalden apparatus over NaOH and paraffin by pumping at 4 mm. for 15 hours at 56°. This procedure provided a 70% yield of chloride (based on the carbinol) melting at 98–99°. This material contained a negligible amount of deuterium in excess of normal isotopic composition.[20]

Mono-*p*-methyl-d_3-triphenylchloromethane.—The synthesis of this material started with trideuteriomethylbenzene, the preparation of which has been described.[2b] Analysis by mass spectrometry showed 2.92 atoms of deuterium per molecule and nuclear magnetic resonance spectra indicated roughly 0.5 atom of methyl group protium per molecule.[2b] Methyl-d_3-benzene was converted to mono-*p*-methyl-d_3-benzophenone, thence to mono-*p*-methyl-d_3-triphenylcarbinol and finally to the chloride as follows.

Mono-*p*-methyl-d_3-benzophenone.—A 7.5-g. sample of methyl-d_3-benzene was dissolved in 60 ml. of carbon disulfide and placed in a 500-ml. three-necked flask fitted with stirrer, reflux condenser and dropping funnel, together with 27 g. of anhydrous aluminum chloride. The mixture was heated to boiling and 11 g. of benzoyl chloride was added over a period of half an hour. Heating was continued for one hour more, then the carbon disulfide was removed by distillation and the residue was poured into 600 ml. of 10% sulfuric acid. The mixture was extracted with ether, and the ether extract was washed with water, 5% sodium bicarbonate solution and finally saturated sodium chloride. It then was dried over magnesium sulfate. The ether was removed by distillation, the residue was dissolved in petr. ether (30–60°) and, on cooling, 11 g. (70%) of the ketone crystallized in three crops, m.p. 55.5–57°.

Mono-*p*-methyl-d_3-triphenylcarbinol.—*p*-Methyl-d_3-benzophenone (8 g.) was added in ether solution over a period of half an hour to a solution of phenylmagnesium bromide, prepared in the usual way from 13 g. of bromobenzene. An additional half-hour was allowed, then 30 ml. of 4 *N* hydrochloric acid was added. The ether layer was washed with water and with saturated sodium chloride and dried over magnesium sulfate. The ether was distilled and the residue recrystallized from 30–60° petr. ether in the presence of charcoal, yielding 5.01 g. of carbinol (45%), m.p. 77–79°. Recrystallization from 80% ethanol yielded crystals of m.p. 77.4–77.8°.

Mono-*p*-methyl-d_3-triphenylchloromethane.—The recrystallized carbinol (3.25 g.) was treated with 7.5 g. of acetyl chloride by heating under reflux, for about 20 minutes, with exclusion of atmospheric moisture. After addition of 4.6 ml. of 35–60° petr. ether, crystals formed slowly. The crystals were washed with a total of 4.5 ml. of 35–60° petr. ether in small portions, all under N_2, recrystallized from 8 ml. of 3:1 petr. ether–benzene (both predried), collected and washed with 6.5 ml. of petr. ether under nitrogen. Shortly before being used, this product was again recrystallized from 2.5 ml. of a solvent made up of acetyl chloride, petr. ether and ether in a volume ratio of 1:2:2. The product was dried in an Abderhalden apparatus by pumping for 6 hr. at 1 mm. and 41° over NaOH and paraffin to provide 1.1 g. of material melted at 97.5–98.1°. A mixture of this compound with chloride I melted at 98–99°.

Mono-*p*-methyltriphenylchloromethane (II) was prepared from toluene by a sequence that closely paralleled the preparation of the deuterium compound. The apparent discrepancy between the melting points of the carbinol precursors of chloride I and the labeled chloride was resolved by observing that the carbinol precursor of chloride II, recrystallized from 80% aqueous ethanol, melted at 78.4–79.2° but that recrystallization to constant m.p. from benzene reduced the m.p. to 72–73°. Chloride II was prepared from the carbinol subsequent to recrystallization from benzene by a procedure much like that used in preparation of chloride I. The product (1.2 g.) was recrystallized twice from 2-ml. portions of 3:1 acetyl chloride–petr. ether. The crystals were collected and washed with cold dried petr. ether under N_2 and dried in an Abderhalden apparatus by pumping at 0.025 mm. and 80° for 23 hours in the presence of NaOH and paraffin. The product melted at 98–99°. Deuterium content in excess of normal isotopic distribution was found to be negligible.[20]

Analysis for Hydrolyzable Chloride and Deuterium.—An 80–120-mg. sample of triarylmethyl chloride was weighed into a glass-stoppered Erlenmeyer flask and dissolved in 2 ml. of benzene. Ten ml. of absolute alcohol was added, the solution was mixed and 10.00 ml. of 0.1 *N* aq. NaOH added. The stoppered flask was swirled periodically during about an hour and the excess base then was titrated with 0.1 *N* aq. HCl to a methyl red end-point. The reagents were standardized using procedures and conditions analogous to those employed in the analysis.

Compound	Chlorine, %	
	Calcd.	Found
$C_{20}H_{17}Cl$ I	12.11	12.11, 12.13
$C_{20}H_{17}Cl$ II	12.11	12.10, 12.10
$C_{20}H_{14.57}D_{2.43}Cl$	12.01	12.06, 12.12

The deuterium content of *p*-trideuteriomethyl trityl chloride was assayed by a procedure that involves combustion, reduction of the resulting water to molecular hydrogen and mass spectrometric determination of the hydrogen content of the gas.[20] It was found to correspond to 2.43 atoms of deuterium per molecule. This corresponds to a negligible change in the deuterium content over the whole synthetic path from $C_6H_5CD_3$.

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[20] We are indebted to Dr. David R. Christman of the Brookhaven National Laboratory for this analysis.