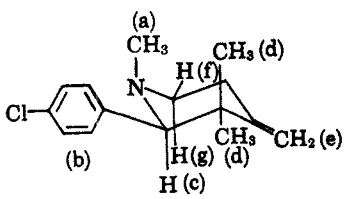
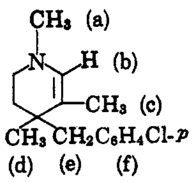
Chart V[a]



[a] Pmr (δ) of IV (free base): a = 2.18 (singlet); b = 7.23 (singlet); c = 2.98 (singlet); d = 1.25 (singlet); e = 4.71 (broad singlet); f = 3.26 (mult plet); g = 2.44 (multiplet).

IV·hydrochloride: a = 2.9 (doublet, $J$ = 5 cps); b = 7.52 (multiplet); d = 1.16 (singlet) and 1.48 (singlet); e = 5.17 (doublet, $J$ = 5 cps, one line of which appeared to be further split into a doublet, $J$ = 1 cps).

Chart VI[a]



[a] Pmr (δ) of III: a = 2.48 (s nglet); b = 5.58 (quartet, $J$ = 1 cps); c = 1.6 (doublet, $J$ = 1 cps); d = 1.0 (singlet); e = 2.68 (singlet); f = 7.17 (multiplet).

**1,3,4-Trimethyl-2-*p*-chlorobenzyl-1,2,5,6-tetrahydropyridine (II).**—A picrate was prepared from the second fraction of the distillation, and it was recrystallized several times from acetone–ethanol. This was converted to the free base by a lithium hydroxide solution. A hydrochloride was prepared and washed with acetone, which removed the more soluble IV hydrochloride. The free base was liberated once again and distilled. A picrate was prepared from this oil, mp 158–159° (lit.[2] mp 157–158°). The free base which was liberated from this picrate was converted to a hydrochloride salt and recrystallized from acetone–methanol–ether; mp 180–181°; pmr (δ) (free base): 1.58 (singlet) for the methyls on the double bond, 2.3 (singlet) for N–$CH_3$, 7.12 (singlet) for aromatic protons.

*Anal.* Calcd for $C_{15}H_{21}Cl_2N$: C, 62.94; H, 7.40; Cl, 24.77. Found: C, 63.20; H, 7.21; Cl, 24.52.

The pmr of the picrate of II was obtained in dimethyl sulfoxide, with tetramethylsilane as the internal standard: 1.48 and 1.68 (singlets) for the methyls on the double bond; 2.8 (singlet) for $N^+$-$CH_3$; and 7.44 for the aromatic protons.

**1,3,4-Trimethyl-4-*p*-chlorobenzyl-1,4,5,6-tetrahydropyridine (III).**—A picrate was prepared from the third fraction of the distillation and it was recrystallized three times from ethanol–acetone, mp 133–135°.

*Anal.* Calcd for $C_{21}H_{23}ClN_4O_7$: C, 52.67; H, 4.84; N, 11.70. Found: C, 52.95; H, 4.99; N, 11.94.

The free base was liberated from the picrate and distilled, and a hydrochloride salt was made and recrystallized from acetone–methanol–ether. This salt was converted back to a free base and a methiodide was prepared and crystallized in acetone; mp 271–273° dec; infrared[14] (free base): 3040 (w–m), 1650 (s), 860 and 810 $cm^{-1}$ (m–s) for the trisubstituted double bond; 3045 (w–m), 1890, 1770, 1725 (w), 1590 (w), 1480 (s), and 830 (m–s) $cm^{-1}$ for the *para*-substituted aromatic ring; 2810 (s) or 2780 (m), 1200 and 1150 (m) or 1150 (m), and 1090 (s) $cm^{-1}$ for the N–$CH_3$ (Chart VI).

*Anal.* Calcd for $C_{16}H_{23}ClIN$: C, 49.06; H, 5.92. Found: C, 48.88; H, 6.09.

**1,3,3-Trimethyl-2-*p*-chlorophenylpiperidin-4-one (VII).**—The 4-methylenepiperidine compound (IV, 0.1 g) was ozonized in chloroform (15 ml) at room temperature according to the method of Boekelheide and Agnello.[15] A water trap placed between the ozonolysis vessel and a potassium iodide solution collected sufficient formaldehyde to give the formaldehyde–dimedone derivative after long standing and refrigeration (*ca.* 3 mg, mp 186–189°).[16] The ozonized product was treated with zinc (1 g) and acetic acid (25 ml, 50%). Most of the chloroform was distilled from the stirred mixture, which was then filtered and made basic with concentrated ammonium hydroxide. Extraction with ether gave a yellow oil, VII. The infrared and pmr spectra of the oil are commented upon in the discussion.

A similar procedure was followed in the ozonolysis of 1,3,4-trimethyl-4-*p*-chlorobenzyl-1,4,5,6-tetrahydropyridine (III), to give VI. The infrared and pmr spectra of VI are discussed in the text.

**Acknowledgment.**—The mass spectra were determined by Drs. J. Daly and H. Fales of these Institutes. I especially wish to thank Dr. Daly for the many discussions on the interpretation of the mass spectral data, and Drs. E. L. May, E. M. Fry, R. Parfitt, L. Cohen, K. Kirk, and G. W. Milne of this Institute, for their advice during the preparation of this manuscript.

(15) V. Boekelheide and E. Agnello, *J. Am. Chem. Soc.*, **73**, 2289 (1951).

(16) "The Merck Index," P. G. Stecher, M. J. Finkel, and O. H. Siegmund, Ed., 7th ed, Merck and Co., Inc., Rahway, N. J., 1960, p 371. The formaldehyde–dimedone derivative is listed having mp 189°.

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# Kinetics and Substituent Effects in Electrophilic Aromatic Substitution. I. Tritylation of Phenol and Its Alkyl Ethers[1]

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*Received September 8, 1965*

The kinetics of the reaction of phenol, anisole, phenetole, and isopropoxybenzene with trityl perchlorate were followed dilatometrically in nitromethane. Substitution was exclusively at the *para* position by the bimolecular mechanism. The order of activation found for the substituents was $OCH_3 < OH < OC_2H_5 < OCH(CH_3)_2$. This is interpreted as the result of a progressive enhancement of the inductive effect of the alkoxy groups along the series, whereas the higher reactivity of phenol compared with that of anisole is attributed to the ability of the former to establish hydrogen bonds with the solvent. Attempts to carry out the reaction with *t*-butoxybenzene yielded 4-hydroxytetraphenylmethane, that is the substitution product of phenol. The possibility of the process taking place through the rearrangement of an oxygen-tritylated intermediate is deemed improbable.

During the past few years we have been interested in the problem of activation and orientation in the benzene ring toward electrophilic substitution when two groups are present in the ring.[2,3] These studies were carried out qualitatively, or semiquantitatively, by yield determination and product analysis. For a more basic approach to the problem it was decided to follow the

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[1] Presented in part at the Third Caribbean Chemical Symposium, Caracas, Jan 1965, and abstracted in N. Barroeta, H. Díaz, G. Chuchani, and J. Zabicky, *Acta Cient. Venezolana*, **15**, 248 (1964).

[2] G. Chuchani, *J. Chem. Soc.*, 1753 (1959); 3025 (1960); 575 (1961).

[3] M. L. Cortés and G. Chuchani, *J. Org. Chem.*, **27**, 125 (1962); G. Chuchani and J. Zabicky, *Acta Cient. Venezolana*, **15**, 253 (1964); *J. Chem. Soc.*, 297 (1966).

kinetics of substitution in disubstituted benzenes. In order to have a standard of comparison it was necessary to study also the behavior of monosubstituted benzenes carrying the same groups and under the same conditions.

Ever since Baeyer and Villiger tritylated phenol and anisole with trityl alcohol, dissolved in acetic acid in the presence of substantial amounts of sulfuric acid,[4] this process has been widely used for the synthesis of substituted tetraphenylmethanes. The elucidation of the mechanism of aromatic tritylation was the undertaking of several authors. First it was shown that sulfuric acid acts as a catalyst[5] by promoting the appearance of trityl carbonium ions. The fact that these carbonium ions are the substituting agent was confirmed by the tritylation of phenol and anisole with trityl perchlorate prepared *in situ* in nitromethane solvent.[6] The kinetics of the reaction of trityl chloride with phenol with no catalyst added was found to be of second order and autocatalyzed by the hydrogen chloride produced,[7] and a bimolecular mechanism was thus proposed. As for the bimolecular intermediates of the reaction, especially in the case of phenols, the main problem is whether tritylation takes place *via* ether formation as was an early contention,[8] or by direct attack of the trityl ion on the aromatic ring.[7,9] Recent findings[10] on the rearrangement of aryl trityl ethers support the latter contention.

We were able to find in the literature only a few works in which a series of compounds of the type $ROC_6H_5$ (R = H, alkyl) was studied kinetically when subject to aromatic substitution, namely, bromination.[11-13] In some cases the inductive order of activation of the alkyl groups (R) was observed,[11,12] but a drop in the rate of isopropyl and *t*-butyl ethers was also reported.[13] Phenol[12] was shown to react faster than anisole and to change its position in this sequence on changing temperature. The inductive sequence was also observed for the halogenation of alkyl aryl ethers when the benzene ring had a second substituent (mainly a deactivating one which is introduced in order to slow the reaction).[14]

The choice of tritylation with trityl perchlorate as the reaction in which phenol and its various alkyl ethers were to be compared kinetically presented several advantages. The trityl ion can be attained in a high yield on dissolving its perchlorate in a suitable solvent such as nitromethane, without the aid of an acid (Brønsted or Lewis), which might interfere with the reaction by complexing extensively with phenol or its ethers. Substitution takes place at the *para* position exclusively. The mechanism could be expected to be SE2 owing to the high stability of the ion in solution and to the relatively slow rate of reaction. On the other hand, some of the disadvantages of this choice were the following. There is no relatively simple method to assess the purity of trityl perchlorate[15] (this was overcome by standardizing the method of preparation of the reagent). It is difficult to trace the appearance of the product directly or spectrophotometrically (dilatometry was used). Owing to the nature of the reagent, salt effect could occur (none were appreciated in this work). The reagent undergoes a slow decomposition in solution, especially at the higher temperatures. The tetraphenylmethanes produced in the reaction are only slightly soluble in nitromethane (the last two difficulties were overcome by following initial rates only).

## Results and Discussion

In Table I the rate constants *k* of the tritylation of phenol and its ethers with trityl perchlorate in nitromethane solvent are summarized. It should be pointed out that the values found from the experimental runs were dilatometric second-order initial rate constants $k_{\text{dil}}$, in units of milliliters liters mole$^{-2}$ hour$^{-1}$, and these had to be divided by 23.72 ml mole$^{-1}$ in order to obtain the *k* values in usual units. Eight to sixteen kinetic runs were carried out for every temperature and aromatic substrate, when both the reagent and the substrate were in concentrations ranging from 0.02 to 0.08 *M*, and the $k_{\text{dil}}$ values were averaged.

TABLE I

SECOND-ORDER INITIAL RATE CONSTANTS[a] OF THE REACTION OF TRITYL PERCHLORATE AND AROMATIC SUBSTRATES OF THE TYPE $C_6H_5OR$ IN NITROMETHANE SOLVENT

| | $10^2k$ | | | |
|---|---|---|---|---|
| R | 30° | 40° | 50° | 60° |
| H | 4.18 | 9.65 | 18.05 | 39.49 |
| $CH_3$ | 2.21 | 5.12 | 9.29 | 18.45 |
| $C_2H_5$ | 5.51 | 13.75 | 26.16 | ...[b] |
| $CH(CH_3)_2$ | 6.16 | 14.11 | ...[b] | ...[b] |
| $C(CH_3)_3$ | ...[b] | ...[b] | ...[b] | ...[b] |

[a] Units of *k*: l. mole$^{-1}$ hr$^{-1}$. [b] Could not be determined owing to decomposition.

The $k_{\text{dil}}$ values determined from the runs had a standard deviation of about 6% and were sufficiently good to appreciate the substituent effects. This can be seen more clearly in Table II, where the rates relative to those of anisole are listed. On the other hand, the Arrhenius activation energies had large standard deviations which made the results indistinguishable from one another, as shown in Table II.

The relative rates in Table II can be separated in two groups for their comparison, one consisting of the results belonging to the alkoxybenzenes, and the second of those of phenol. The series of ethers studied follows the same inductive release sequence mentioned above, namely $CH_3 < C_2H_5 < CH(CH_3)_2$. This could be explained by appealing to the mesomeric mechanism of

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(14) Leading references: L. J. Goldsworthy, *ibid.*, 1148 (1936); S. J. Branch and B. Jones, *ibid.*, 2921 (1955).

(15) Direct titration with base is unreliable because perchloric acid can be one of the decomposition products present in the sample. Colorimetry or spectrophotometry would be uncertain unless the extreme dryness of the solvent is ensured.

Table II

Relative Rates and Arrhenius Activation Energies[a] for the Reaction of Trityl Perchlorate and Aromatic Substrates of the Type $C_6H_5OR$ in Nitromethane Solvent

| R | Relative rate 30° | 40° | 50° | 60° | $E_a$ |
|---|---|---|---|---|---|
| H | 189 | 189 | 194 | 214 | 14.4 ± 2.8 |
| $CH_3$ | 100 | 100 | 100 | 100 | 13.5 ± 3.5 |
| $C_2H_5$ | 249 | 267 | 282 | . . . | 14.4 ± 3.2 |
| $CH(CH_3)_2$ | 278 | 276 | . . . | . . . | 15.7 ± 2.5 |

[a] In units of kcal mole$^{-1}$. Standard deviations calculated according to L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press Inc., London, 1963, p 8.

electron release typical of substituents with unshared electron pairs.[16]

The main problem remains in the interpretation of the results found for phenol: its rates of tritylation were between those of anisole and phenetole (Table II) thus departing from the inductive sequence in which $H < CH_3$.

In the case of bromination of phenols compared with that of the corresponding anisoles, de la Mare and his co-workers[17,18] explained the larger reactivity of the former by a factor of two orders of magnitude by appealing to the hyperconjugation hypothesis, as phenols have an OH group which on hyperconjugation could enhance its electron release toward the substitution site on the aromatic ring.

An explanation based exclusively on hyperconjugation leaves without consideration important properties of the systems studied. It is an established fact that phenols can hydrogen bond extensively both among themselves and with certain solvents.[19] For extensive phenol–phenol association high concentrations of the compound, seldom encountered in kinetic work, are required.[20] On the other hand, if a suitable proton acceptor is used as solvent, extensive hydrogen bonding to it can be attained even at low concentrations of phenol. This last should be the case in acetic acid, glacial or aqueous,[21] and nitromethane,[22] used as solvents for the studies in bromination and in the present work. We believe, therefore, that hydrogen bonding should be taken into account in any attempt to rationalize the results obtained in these studies, and that it may account, at least qualitatively, for the acceleration observed in phenol.

An interesting question arises when the relative rates in this work are compared with other results. The rates of tritylation of phenol and its ethers (Table II) have a spread over a factor of 3. Although on bromination of the ethers Baddeley, *et al.*,[13] also found a relatively narrow spread, the series has to be completed with the value of phenol, which is about ninety times as large as that of anisole.[18] These differences in spread are in accordance with the classical electrophilic substitution theory[16] inasmuch as the strongest electrophile (bromine compared with the trityl ion) should produce the largest electromeric effect on the one hand, and on the other this effect will be more pronounced in aromatic substrates where the *para*-directing group is capable of enhancing its electron release by the electromeric mechanism (as in phenols, possibly by forming a stronger hydrogen bond in the transition state compared with that of the alkoxybenzenes).

Regarding the question of the process taking place by the direct attack of the trityl ion on the aromatic ring or by the rearrangement of an oxonium intermediate, there is evidence pointing at the first one as the more probable. The acid-catalyzed rearrangement of aryl trityl ethers to tritylphenols was found mainly to be an intermolecular process,[10] and therefore it is improbable that the transition state of the O-trityl bond scission (or formation) should be a part of the aromatic tritylation process.

## Experimental Section

**Materials.**—Nitromethane (Eastman Organic "practical") was purified and dried by repeated distillations over anhydrous magnesium sulfate, then over Drierite, and finally it was treated with trityl perchlorate until a deep yellow color developed and distilled again; the solvent was kept in delivery flasks adequately protected against the moisture of air. Phenol (Merck, analytical), anisole, and phenetole (B. D. H.) were purified by distillation. Isopropoxybenzene was prepared by condensing isopropyl iodide with sodium phenolate.[23] *t*-Butoxybenzene was prepared by the reaction of phenylmagnesium bromide with *t*-butyl perbenzoate (Wallace and Tiernan.)[24] 4-Hydroxy-, 4-methoxy-, and 4-ethoxytetraphenylmethane were prepared by the condensation of trityl alcohol with phenol, anisole, and phenetole, respectively.[9c]

**4-Isopropoxytetraphenylmethane.**—Triphenylcarbinol (20 g), isopropoxybenzene (11 g), and concentrated sulfuric acid (10 ml) were mixed and allowed to stand at room temperature for 2 days. The product was isolated in 75% yield, and after recrystallization had mp 173°.

*Anal.* Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.9. Found: C, 87.85; H, 6.5.

The acid hydrolysis of this product yielded 4-hydroxytetraphenylmethane.

From the tritylation of isopropoxybenzene thus described a hydrocarbon (mp 260°) was isolated as by-product, which has properties similar to those of a compound isolated on the tritylation of other isopropoxy derivatives and will be described elsewhere.[25]

**Trityl Perchlorate.**—Trityl chloride (Matheson Coleman and Bell) was hydrolyzed in boiling aqueous acetic acid to triphenylcarbinol, which was purified by recrystallization from glacial acetic acid. The carbinol was used for the preparation of the perchlorate by treatment with perchloric acid according to Dauben, *et al.*[26] A slight modification was introduced in the method for the isolation of the salt followed by these authors, consisting of fitting the reaction flask with an inverted U-tube, one of its ends dipped in the reaction mixture and the other connected to a container with sintered-glass bottom fitted for suction filtration. At the end of the reaction the mixture was

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(25) N. Barroeta, G. Chuchani, and J. Zabicky, *J. Org. Chem.*, submitted for publication.

(26) H. J. Dauben, L. R. Honnen, and K. M. Harmon, *ibid.*, **25**, 1442 (1960).

passed by suction and under dry nitrogen atmosphere to that container, washed by suction several times by adding anhydrous ether to the reaction flask, and finally dried under the same atmosphere. The bright yellow compound could be kept unchanged when protected from moisture at low temperatures in the same filtration container.

Trityl ($^{14}$C, uniformly labeled in one ring) **Perchlorate.**—Benzoic acid ($^{14}$*C, uniformly labeled in the ring*) (0.1 mcurie, Radiochemical Centre, Amersham) was dissolved in ethyl benzoate (20 g) and anhydrous ethanol (10 g), and after adding concentrated sulfuric acid (*ca.* 0.5 ml) the mixture was refluxed for 6 hr. The labeled ethyl benzoate recovered by distillation (16 g) was used to prepare triphenylcarbinol by Grignard synthesis,[27] and from this the perchlorate was prepared as described above.

Attempts to prepare 4-*t*-butoxytetraphenylmethane from *t*-butoxybenzene under various sets of conditions previously described[3,9c] or under the kinetic conditions described below yielded 4-hydroxytetraphenylmethane.

**Product Analysis.**—Solutions of phenol or its ethers and trityl perchlorate in nitromethane yielded after 1 or 2 days of standing in a water bath, at temperatures from 30 to 60°, precipitates which were identified as the corresponding tetraphenylmethane derivatives. The tritylation products gave exclusively *para* positions and they showed no depression on admixture with authentic samples[9c] obtained by the widely used method of the Baeyer–Villiger reaction.[4] The latter process was also used to prepare 4-isopropoxytetraphenylmethane which is described above and is not reported in the literature. The infrared spectra of the products obtained by both methods were identical.

**Reaction Kinetics. A. The Tracing Method.**—Ultraviolet spectroscopy could not be used to follow the appearance of the tetraphenylmethanes owing to the relatively high cutoff of nitromethane (380 m$\mu$),[28] and the following disappearance of the absorption of the trityl ion in the visible region was undesirable for several reasons: first, since the reaction is slow and one of the reagents relatively unstable, large errors could be expected when following the reaction only at its inception or until after long periods; and, second, the samples would have to be diluted in certain cases and this would have had to be done with extremely dry solvents, which is impractical. Two other methods remained at our disposal: the radiometric and the dilatometric methods. The first has the advantage of being direct but presents the practical disadvantage of being extremely laborious, as the product needs to be isolated and purified several times for each kinetic run. Dilatometry on the other hand allows one to follow the reaction in a practically continuous fashion without altering or interfering with the reaction mixture, but has the disadvantage of requiring additional information in order to convert dilatometric data into the usual kinetic dimensions of time and concentration. Being barred from carrying out the reaction for long periods of time (to obtain dilatometric data at $t_\infty$), and, since density measurements are inaccurate at high dilution, it was decided to combine the dilatometric and the radiometric methods in order to obtain the conversion factor from dilatometric kinetic data to the usual ones. Thus, several kinetic runs were carried out on the same reaction mixtures by both methods simultaneously (see below) and from the combined results of all the runs so performed the factor 23.72 ± 2.95 ml mole$^{-1}$ was obtained.

**B. Dilatometric Kinetic Measurements.**—Concentrated solutions of trityl perchlorate and of the aromatic substrate in nitromethane were prepared on the same day of the kinetic measurement. Adequate amounts of these solutions were mixed in a 100-ml measuring flask, filled to the mark with solvent, and placed in a water bath. The dilatometers, consisting of a bulb of calibrated uniform diameter (*ca.* 0.6 mm) according to a model of Benford and Ingold,[29] were carefully filled by suction with the reaction mixture and placed in a water bath controlled to ±0.01° with the bulbs completely submerged. After the temperature was allowed to equilibrate, the heights of the meniscus in both branches of the dilatometer were read at definite time intervals, with a cathetometer (Pye) in which fractions down to 0.05 mm could be determined. Simultaneously a reading in a dilatometer filled with pure solvent was taken, and sometimes slight corrections of the kinetic reading had to be made to account for expansions or contractions of the emergent capillary tubes, owing to room temperature fluctuations. Time zero was taken at the moment of mixing the reagents. The corrected readings were plotted against time and the height changes per unit time were transformed into $k_{\mathrm{dil}}$ values (Table I) on dividing by the product of the initial concentrations of reagents and further multiplying by a factor $f$ which was determined for each dilatometer as follows.

$$f = \frac{\text{capillary section in cm}^2}{\text{dilatometer capacity in l.}}$$

**C. Radiometric Kinetic Measurements.**[30]—Reaction mixtures using $^{14}$C-labeled trityl perchlorate were prepared in 200-ml measuring flasks as described above. Samples of 10 ml were withdrawn at definite time intervals and poured into 80 ml of acetone containing 400 mg of the corresponding (unlabeled) tetraphenylmethane derivative and a small amount of water, sufficient to quench the reaction but not to precipitate immediately the organic solutes. Water was added to precipitate the products and these were filtered off. The solid consisting mainly of the tetraphenylmethane was purified by repeated recrystallizations from acetic acid, adding each time but the last about 50 mg of triphenyl carbinol as a carrier,[31] until a constant melting point was attained. A sample of the purified product was weighed to about 20 mg and dissolved in 15 ml of a solution of 2,5-diphenyloxazole and 1,4-bis(4-methyl-5-phenyl-2-oxalyl)benzene in toluene and counted in a liquid scintillation counter (Packard 314 EX). No quenching of scintillation by triphenylcarbinol or the tetraphenylmethanes was observed. In order to calculate the rate constants the following formulas were used

$$s_i = \frac{c_i}{w_i}(400 + 10^3 M m_i)$$

$$m_i = \frac{t_i}{T} \cdot \frac{\Sigma_i s_i}{\Sigma_i t_i}$$

where $s_i$ is the number of counts per minute calculated for the 10-ml sample taken at time $t_i$ and arising from the tetraphenylmethane produced, $c_i$ is the number of counts per minute in the sample of weight $w_i$ in milligrams measured in the scintillation counter, $M$ is the molecular weight of the tetraphenylmethane, $m_i$ is the number of moles of the tetraphenylmethane in the 10-ml sample, and $T$ is the number of counts per minute per mole of the labeled trityl perchlorate. First the values of $s_i$ are calculated by assuming that $m_i = 0$ and then substituted in the second formula. The $m_i$ values thus found are used for the calculation of new $s_i$ values. This is repeated until stable values of $m_i$ are attained (two to three cycles were sufficient). Now the initial rate constant $k$ can be calculated with the formula

$$k = \frac{100}{[\mathrm{A}]_0[\mathrm{B}]_0} \cdot \frac{\Sigma_i m_i}{\Sigma_i t_i}$$

where A and B are the reagents.

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[27] Reference 23, p 813.

[28] "Eastman Organic Chemicals," List No. 43, Distillation Products Industries, Rochester, N. Y., 1962, p 229.

[29] G. A. Benford and C. K. Ingold, *J. Chem. Soc.*, 929 (1938).

[30] We thank Dr. M. A. Tamers and Mr. A. Carstens for counting our radioactive samples.

[31] The use of a carrier was necessary as triphenylcarbinol coprecipitates with the tetraphenylmethanes. Even after three or four recrystallizations without carrier and attaining the correct melting point, the presence of the carbinol could be detected by means of tlc and development in an atmosphere saturated with hydrochloric acid vapors: a yellow spot appeared, which vanished on being breathed over, and reappeared in the acid atmosphere.