TABLE I

SYNTHESIS OF CH_3F AND CD_3F

Step	Product, moles		Yield, %[a]	
	CH_3	CD_3	CH_3	CD_3
1a, 1b	0.424	0.448	84.8	89.6
2	.362	.369	85.4	82.4
3	.276	.297	76.2	80.5
Total	.276	.297	55.2	59.4

[a] The reported yields are based on 1,2-propylene carbonate. On the basis of lithium aluminum hydride and lithium aluminum deuteride the corresponding total yields are 50.2 and 54.0%.

Experimental

Preparation of Methyl-d_3 Alcohol.—Lithium aluminum deuteride (17.3 g., 0.412 mole) and 200 g. of diethyl Carbitol (refluxed over and distilled twice from sodium) were treated under nitrogen with 51 g. (0.500 mole) of 1,2-propylene carbonate (Jefferson Chemicals) which was added in 93 g. of diethyl Carbitol. The addition of the propylene carbonate solution was regulated to maintain a reaction temperature of 45–55°, and required four hours. With continued stirring the temperature of the reaction mixture was raised to 73° during four hours following the addition of the propylene carbonate. The mixture was then cooled to 4° and 389 g. (2.40 moles) of butyl Carbitol were added during a period of 30 minutes with cooling by an ice-bath. Some gas (HD) was evolved during the beginning of the butyl Carbitol addition, indicating the presence of unreacted lithium aluminum deuteride. The methyl-d_3 alcohol was then removed by passing a slow stream of dry nitrogen through the solution held at 90 to 110°, and condensed in two traps, one immersed in Dry Ice, the other in liquid nitrogen. The distillation was continued for two hours, then the crude distillates from both traps were combined and redistilled through an 18-plate column. A 0.4-g. forerun, containing heavy formaldehyde, was discarded. The fraction boiling between 58.0 and 64.4° was collected. The major portion of the methyl-d_3 alcohol had b.p. 64.4° (ref. 6 gives b.p. 64.6°) and $n^{20}D$ 1.3280. The yield was 15.7 g., 89.6% on the basis of 1,2-propylene carbonate or 81.5% on the basis of the lithium aluminum deuteride.

Preparation of Methyl-d_3 p-Toluenesulfonate.—The reaction of 15.7 g. (0.448 mole) of methyl-d_3 alcohol and 94.0 g. (0.493 mole) of tosyl chloride was carried out essentially under the conditions given by Edgell and Parts.[4] The yield of methyl-d_3 p-toluenesulfonate was 69.9 g. (82.4%), $n^{20}D$ 1.5179.

Preparation of Methyl-d_3 Fluoride.—All of the methyl-d_3 p-toluenesulfonate prepared above was treated with 64.3 g. (1.11 moles) of anhydrous KF essentially as indicated earlier[4] in the method for the absence of a solvent. The yield was 11.0 g. (80.5%). The product contained about 5% methyl-d_3 chloride, presumably due to the presence of some tosyl chloride in the methyl-d_3 tosylate. The product was purified by distillation through a Podbielniak Heli-Robot column. Assuming the boiling point of methyl fluoride as −78.414°,[19] that of methyl-d_3 fluoride was −77.9°.

Isotopic Purity.—The isotopic purity of the methyl-d_3 fluoride was determined mass spectrometrically[20]. The following distribution of isotopic species was found: CD_3F 94.4 ± 0.5%, CD_2HF 5.2 ± 0.5%, CDH_2F 0.4 ± 0.5%, corresponding to a maximum of 2 atom per cent. light hydrogen in the sample. The percentage of CD_3F and CD_2HF was obtained from the corresponding molecule–ion peaks. The absolute amount of CDH_2F could be determined with lower accuracy due to interference by ionization fragments. The mass spectroscopic data are in agreement with an approximate isotopic analysis of methyl-d_3 alcohol by means of its infrared spectra. The results also indicate that the extent of isotopic contamination in the reactions leading from methyl-d_3 alcohol to methyl-d_3 fluoride is negligible within the limits of error of the experimental measurements.

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[19] A. Michels and T. Wassenaar, *Physica*, **14**, 104 (1948).

[20] We are indebted to Dr. F. W. Lafferty of the Dow Chemical Company for this analysis.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. V. The Relative Phenyl/Hydrogen Migration Abilities in the Pinacol Rearrangement of Triphenylethylene Glycol[1,2]

BY CLAIR J. COLLINS

RECEIVED MAY 2, 1955

The pinacol rearrangement of triphenylethylene glycol (I) has been investigated. The reaction was studied by comparing the fates of the chain- and ring-labels in the glycols Ia and Ic when these glycols were subjected to the influence of five different acid catalysts. It was possible to determine with high precision: (a) the yields of benzhydryl phenyl ketone (II) and triphenylacetaldehyde (III) and (b) the extent of carbon-14 migration of each label. From the foregoing data the contribution of each of four reaction paths has been calculated under each set of conditions. It is shown that the ratio of phenyl/hydrogen migration may vary by a factor of 180 (7.33 to 0.041), depending on the catalyst used for the rearrangement. These data are explainable if it is assumed that the phenyl group can migrate more readily than hydrogen in this reaction when open, or "classical" carbonium ions are the intermediates, and less readily than hydrogen when the process is concerted.

Introduction

It has been known for some time that triphenylethylene glycol (I) may be converted to phenyl benzhydryl ketone (II). Thus Gardeur,[3] Tiffeneau[4] and Lagrave[5] all reported that this transformation occurs when I is placed under the influence of various acidic catalysts. Danilov[6] reported that the glycol I, when dehydrated with 40% sulfuric acid, yields II and triphenylacetaldehyde (III) in the ratio of 4:1. Danilov reported also that III is quantitatively converted to II in the presence of concentrated sulfuric acid.

$Ph_2COHCHOHPh$	$Ph_2CHCOPh$	Ph_3CCHO
I	II	III

Considerable knowledge concerning the pinacol rearrangement of derivatives of triphenylethylene glycol was adduced next by McKenzie and coworkers[7,8] and by Roger and McKay.[9] These

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[1] This paper is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] Papers III and IV, C. J. Collins and W. A. Bonner, THIS JOURNAL, **77**, 92 (1955); W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99 (1955).

[3] A. Gardeur, *Bull. acad. roy. Belg.*, [3] **34**, 67 (1897); *Chem. Zentr.*, **68**, II, 622 (1897).

[4] M. Tiffeneau, *Compt. rend.*, **146**, 29 (1908).

[5] R. Lagrave, *Ann. chim.*, [10] **8**, 416 (1927).

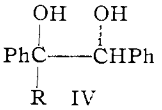
[6] (a) S. Danilov, *J. Russ. Phys. Chem. Soc.*, **49**, 282 (1917); (b) S. Danilov and E. Venus Danilova, *Ber.*, **59B**, 377 (1926).

[7] A. McKenzie, A. K. Mills and J. R. Myles, *Ber.*, **63**, 904 (1930).

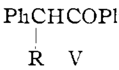
[8] A. McKenzie, R. Roger and W. B. McKay, *J. Chem. Soc.*, 2597 (1932).

[9] R. Roger and W. B. McKay, *ibid.*, 332 (1933).

investigators, on the basis of their work with α-*dl* and α-(+) forms of the general structure IV (in which the substituent R is *o*-tolyl, *m*-tolyl or *p*-tolyl), formulated a general mechanism for these re-

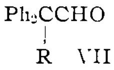


$\mathrm{Ph\overset{OH}{\underset{R}{C}}{-}\overset{OH}{C}HPh}$ IV

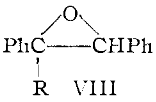


$\mathrm{Ph\underset{R}{C}HCOPh}$ V

RCOCHPh$_2$ VI



$\mathrm{Ph_2\underset{R}{C}CHO}$ VII

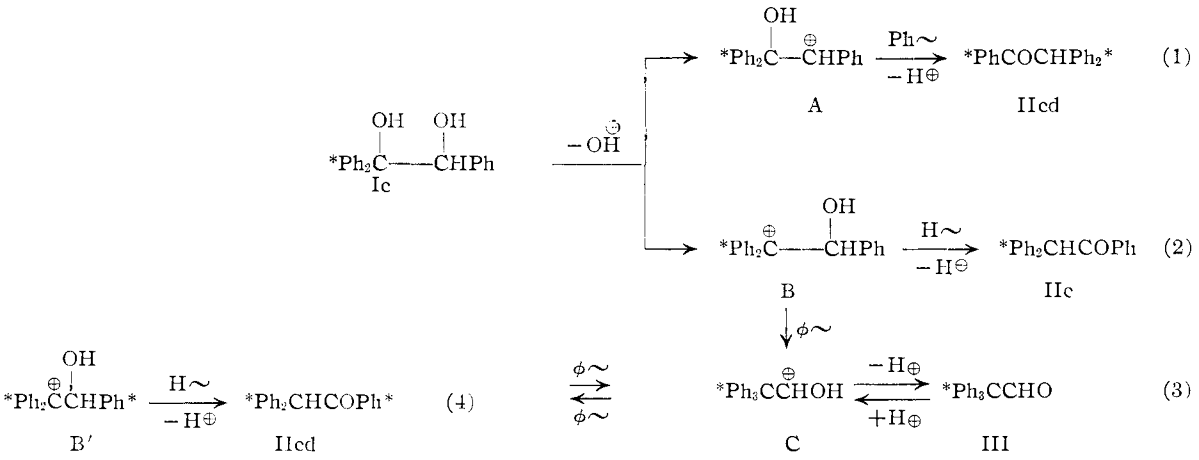


VIII

actions, involving four possible reaction paths.[10] If allowances are made for changes in mechanistic concepts since the appearance of their paper, their proposal may be written for the pinacol rearrangement of triphenylethylene glycol as outlined in Chart I. For purposes of later discussion, the consequence of ring-labeling Ic for each reaction path is included also in Chart I.

CHART I

FOUR POSSIBLE REACTION PATHS IN THE PINACOL REARRANGEMENT OF TRIPHENYLETHYLENE



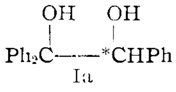
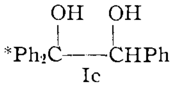
Path 1 was not considered important by Roger and McKay. The relative importances of paths 2 and 4 could not be determined by these authors, except that path 4 was excluded as a possibility in the production of the optically active α-phenyl-α-(*o*-tolyl)-acetophenone (V, R = *o*-tolyl), since asymmetry should have been destroyed during the formation of the intermediate diphenyl-(*o*-tolyl)-acetaldehyde (VII) (or its cationic counterpart). Only one other possible reaction path may be written in Chart I—namely, a path involving triphenylethylene oxide (VIII, R = Ph). It seems improbable, however, that triphenylethylene oxide should be involved as an intermediate in the pinacol rearrangement of I, in view of the observation of Lane and Walters[11] that VIII (R = Ph) is easily convertible to the glycol I under mild acidic conditions.[12]

The reaction paths of Chart I, then, offer a consistent mechanism for the acid-catalyzed rearrangement of triphenylethylene glycol (I), with two exceptions—the first being that nothing can be inferred from these schemes concerning the concerted or non-concerted nature of these processes. The second exception is that in those reaction paths (2 and 4) in which hydrogen migration is indicated, it is not necessarily true that this hydrogen transfer takes place intramolecularly—that is, the hydrogen atom α to the carbonyl group in the ketone IIc or IIcd produced through paths 2 and 4, may not always be the same hydrogen atom present in the ion B (or B′) but may have its origin outside the indicated molecules.

The present work was undertaken with the purpose of determining the relative importances of the four reaction paths of Chart I. Given in Chart II are the expected radioactivity distributions from the reaction paths through which benzhydryl phenyl ketone might be formed for each of the two reactants Ia and Ic. It can be seen from this chart that given the radiochemical consequences of the rearrangements of Ia and Ic under the same reaction conditions, the fraction of ketone II formed through each of the paths 1, 2 and 4 should be obtained easily. The contribution of path 3 to the total reaction can be obtained directly by determination of the yield of triphenylacetaldehyde (III). The results of several such studies are reported in the following sections.

CHART II

EXPECTED RADIOACTIVITY DISTRIBUTIONS FROM REACTION PATHS THROUGH WHICH BENZHYDRYL PHENYL KETONE MIGHT BE FORMED

Reactant	Path through which product is formed	Product	% C^{14} rearrangement
 $\mathrm{Ph_2\overset{OH}{C}{-}{*}\overset{OH}{C}HPh}$ Ia	1	PhCOC*HPh$_2$	100
	2	Ph$_2$CHC*OPh	0
	4	Ph$_2$CHC*OPh	0
 $\mathrm{{*}Ph_2\overset{OH}{C}{-}\overset{OH}{C}HPh}$ Ic	1	*PhCOCHPh$_2$*	50
	2	*Ph$_2$CHCOPh	0
	4	*Ph$_2$CHCOPh*	33.3

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(10) This scheme was not original with Roger and McKay, but represented[5–8] a combination of the concepts of several previous investigators.

(11) J. F. Lane and D. R. Walters, THIS JOURNAL, **73**, 4234 (1951).

(12) H. J. Gebhart and K. H. Adams, *ibid.*, **76**, 3930 (1954), support this view, and contrast the ease of conversion of VIII (R = Ph) to I with the complete failure of tetraphenylethylene oxide to undergo a similar conversion.

TABLE I

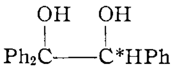
PERCENTAGE REARRANGEMENT OF CARBON-14 LABEL WHEN GLYCOLS Ia AND Ic ARE REARRANGED UNDER THE INFLUENCE OF VARIOUS ACID CATALYSTS

Expt.	Reactant	Catalyst used	Molar radioactivity of $\mathrm{Ph_2C^*{=}O}$ or $\mathrm{^*Ph_2C{=}O}$[a]	% C^{14} migration
1	Ia	Cold concd. H_2SO_4	0.036 ± 0.001[b]	
2	Ia	Cold concd. H_2SO_4	.015 ± .001	
			.025 ± .01[c]	2.5 ± 1.0[c]
3	Ic	Cold concd. H_2SO_4	.693 ± .002	
4	Ic	Cold concd. H_2SO_4	.703 ± .001	
5	Ic	Cold concd. H_2SO_4	.717 ± .002	
6	Ic	Cold concd. H_2SO_4	.696 ± .002	
			.702 ± .008[c]	29.8 ± 0.8
7	Ia	Oxalic acid dihydrate, refl.	.039 ± .0008	
			.039 ± .001[c]	3.9 ± 0.1
8	Ic	Oxalic acid dihydrate, refl.	.791 ± .001	
9	Ic	Oxalic acid dihydrate, refl.	.817 ± .001	
			.804 ± .01[c]	19.6 ± 1.0
10	Ia	Formic acid, refl.	.047 ± .001	
			.047 ± .001[c]	4.7 ± 0.1
11	Ic	Formic acid, refl.	.782 ± .001	
12	Ic	Formic acid, refl.	.797 ± .003	
			.789 ± .008[c]	21.1 ± .8
13	Ia	Dilute H_2SO_4	.045 ± .001	
14	Ia	Dilute H_2SO_4	.033 ± .001	
			.039 ± .006[c]	3.9 ± .6
15	Ic	Dilute H_2SO_4	.928 ± .005	
16	Ic	Dilute H_2SO_4	.931 ± .003	
			.930 ± .002[c]	7.0 ± .2
17	Ic	Dioxane–H_2O–HCl, refl.	.995 ± .004	
			.995 ± .004[c]	0

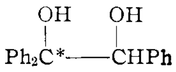
[a] Taken as the fraction of the original radioactivity of the glycols Ia or Ic. [b] Uncertainty expressed as the average deviation of the mean value of two or more determinations. [c] Uncertainty expressed as the average deviation from the averages of the mean values given above.

Methods and Results

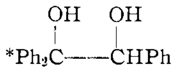
1,1,2-Triphenylethylene glycol labeled in the 2-position (Ia) was prepared from benzhydryl phenyl ketone-C^{14} (IIa)[2] by a two-step process involving oxidation of IIa in acetic acid with nitric acid by the method of Biltz,[13] followed by the reduction of the ensuing keto-alcohol to Ia with lithium aluminum hydride. Glycol Ib was prepared by the action of phenylmagnesium bromide upon the appropriately labeled methyl mandelate.[14] The phenyl-labeled glycol Ic was prepared by two methods: (a) the action of phenyl-C^{14}-magnesium bromide[2] upon benzoin[15] and (b) the action of the phenyl-C^{14}-magnesium bromide[2] upon methyl mandelate.[14] The radiochemical structures of Ia, Ib and Ic were shown to be as indicated by the oxidation of these glycols with either chromic acid or potassium permanganate to benzophenone and benzoic acid, followed by radioactivity assay of these oxidation fragments.


$\mathrm{Ph_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\text{——}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{^*HPh}$

Ia

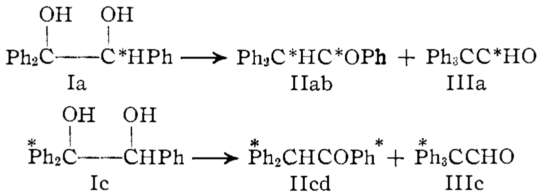

$\mathrm{Ph_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{^*}\text{——}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh}$

Ib


$\mathrm{^*Ph_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\text{——}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh}$

Ic

The glycols Ia and Ic were subjected to the pinacol rearrangement in the presence each of the following acidic catalysts: (1) cold concentrated sulfuric acid, (2) refluxing oxalic acid dihydrate, (3) refluxing formic acid, (4) refluxing dilute sulfuric acid and (5) refluxing dioxane–hydrochloric acid mixtures. These catalysts were selected because they are, in general, the ones which had been used previously to effect rearrangement of triphenylethylene glycol and its derivatives.[3–9,11]


$$\underset{\text{Ia}}{\mathrm{Ph_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\text{——}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{^*HPh}} \longrightarrow \underset{\text{IIab}}{\mathrm{Ph_2C^*HC^*OPh}} + \underset{\text{IIIa}}{\mathrm{Ph_3CC^*HO}}$$

$$\underset{\text{Ic}}{\overset{*}{\mathrm{P}}\mathrm{h_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\text{——}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh}} \longrightarrow \underset{\text{IIcd}}{\overset{*}{\mathrm{P}}\mathrm{h_2CHCOPh}^*} + \underset{\text{IIIc}}{\overset{*}{\mathrm{P}}\mathrm{h_3CCHO}}$$

For those experiments in which the extent of carbon-14 migration was to be determined, the products IIab and IIcd were purified by crystallization from ethanol and then oxidized with permanganate to benzophenone and benzoic acid.

$$\mathrm{IIab} \xrightarrow{\mathrm{KMnO_4}} \mathrm{Ph_2C^*{=}O} + \mathrm{PhC^*OOH}$$

$$\mathrm{IIcd} \xrightarrow{\mathrm{KMnO_4}} \overset{*}{\mathrm{P}}\mathrm{h_2C{=}O} + \overset{*}{\mathrm{P}}\mathrm{hCOOH}$$

The benzophenone fractions were converted quantitatively to their 2,4-dinitrophenylhydrazones, and the latter were assayed for radioactivity content. The molar radioactivities of these derivatives were taken as a direct measure of the amount of carbon-14 migration attending the particular reaction studied. The results of these experiments are

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(13) H. Biltz, *Ber.*, **32**, 650 (1899).

(14) S. F. Acree, *ibid.*, **37**, 2763 (1904).

(15) A. McKenzie and H. Wren, *J. Chem. Soc.* (*Trans.*), **97**, 473 (1910).

given in Table I. It was necessary to use glycol Ia rather than Ib in these experiments because of the rather large error introduced into the migration calculations by the oxidative isotope effect during the action of permanganate on ketone IIb (labeled in the benzhydryl portion of the molecule). Preliminary experiments in which Ib was used erroneously indicated the amount of rearrangement of the chain-label to be 8–13% of the total reaction for each acid catalyst employed. It was shown independently that ketone II is stable to the action of acid by demonstrating no carbon-14 rearrangement in a sample of benzhydryl phenyl-C^{14} ketone IId which had been dissolved in concentrated sulfuric acid for 24 hours.

For those experiments in which the yields of ketone II and aldehyde III were to be determined by the isotopic dilution method,[16] the reaction product from glycol Ib was diluted to a given volume with ether, and then divided into two equal portions. To one portion was added a weighed amount of non-radioactive ketone II. The solution was concentrated to dryness, the concentrate then was crystallized twice from ethanol, and the product was assayed for radioactivity. To the other portion, a weighed amount of non-radioactivet riphenylacetaldehyde III was added. The solution was concentrated to dryness, the concentrate was dissolved in alcohol and treated with an excess of 2,4-dinitrophenylhydrazine hydrosulfate. The derivative was twice crystallized from dioxane–ethanol solutions and then assayed for radioactivity. From the molar radioactivities of the diluted ketone IIab and of the diluted derivative of the aldehyde III the yields of II and III under each set of conditions were calculated with high accuracy. The results of these yield determinations are given in Table II. Although ideally both the yield data and the migration data should be determined for each catalyst, using the product from a single experiment, this procedure was not practical. Because of the high degree of duplicability of the ring-label rearrangements (Table I) the author has assumed that the yield data for II and III are similarly invariant.

From the foregoing data, therefore, the contribution of each path to the total reaction has been calculated when glycol I is subjected to rearrangement under the conditions employed in the present experiments. These contributions are given in Table III. Also given in Table III are the ratios for each acid catalyst, of phenyl/hydrogen migration (to the *t*-carbon atom). These were obtained simply by dividing the sum of the contributions of paths 3 and 4 by the contribution of path 2 for each reaction.[17,18]

TABLE II

YIELDS OF BENZHYDRYL PHENYL KETONE (II) AND OF TRIPHENYLACETALDEHYDE (III) AS DETERMINED BY THE ISOTOPE DILUTION METHOD WHEN TRIPHENYLETHYLENE GLYCOL (I) IS TREATED WITH VARIOUS ACID CATALYSTS

Catalyst	Yield of II, %	Yield of III, %	Total, %
Cold concd. H_2SO_4	100.1 ± 1.0	0.77 ± 0.04	100.9
Oxalic acid dihydrate	69.5 ± 0.5	29.9 ± .1	99.4
Formic acid	101.6 ± .6	0.98 ± .08	102.6
Dil. H_2SO_4	84.9 ± .4	16.5 ± .2	101.4
Dioxane–water–HCl	93.6 ± .9	3.9 ± .1	97.5

TABLE III

CONTRIBUTIONS OF PATHS 1, 2, 3 AND 4 TO THE TOTAL REACTION WHEN TRIPHENYLETHYLENE GLYCOL IS REARRANGED WITH VARIOUS ACIDIC CATALYSTS

Catalyst	Contribution of path, % 1	2	3	4	Ratio ϕ/H migration
Concd. H_2SO_4	2.5	11.7	0	85.8	7.33
Oxalic acid	2.7	29.9	29.9	37.5	2.25
Formic acid	4.7	39.0	0	56.3	1.44
Dil. H_2SO_4	3.2	67.4	16.5	12.9	0.435
Dioxane–H_2O–HCl	0	96.1	3.9	0	0.0406

For simplicity, the aldehyde yields were used in calculating the data of Table III. The aldehyde yields were taken as zero in the reactions using concentrated sulfuric and formic acids as catalysts. A sample calculation follows by which the data (Table III) for the oxalic acid-catalyzed reaction were obtained if x = fraction of II formed through path 2

$(0.961 - x)$ = fraction of II formed through path 4

$$0.804 = 0.039\ (0.5) + x + \frac{(0.961 - x)2}{3}$$

$x = 0.426;\ (0.961 - x) = 0.535$

Contrib. of path 1 = 3.9(0.701) = 2.7%
Contrib. of path 2 = 42.6(0.701) = 29.9%
Contrib. of path 3 = 29.9%
Contrib. of path 4 = 53.5(0.701) = 37.5%
Total 100.0%

Discussion

The very slight contribution of path 1 to the total reaction of triphenylethylene glycol in the presence of any of the acidic catalysts employed is completely compatible with prediction.[17,19] It would be expected that the tertiary hydroxyl of I would most certainly be removed through acid catalysis in preference to the secondary hydroxyl, owing supposedly to the greater stabilizing effects on the ion B of two phenyl groups, as compared to the single phenyl group which can stabilize ion A. There is no criterion, however, for predicting the relative tendency for migration of hydrogen *versus* phenyl. Also, the reason for the rather wide variation of this ratio from 7.33 to 0.041 is not readily apparent.[20] Owing to the facts that (a) the reactions in cold, concentrated sulfuric acid and in refluxing formic acid were homogeneous, while the others were not and (b) the temperatures of reaction varied from 0° in concentrated sulfuric acid to over 200° in

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(16) R. H. Mayor and C. J. Collins, THIS JOURNAL, **73**, 471 (1951).

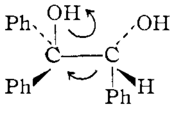
(17) For a discussion of the position of hydrogen in the "mobility sequence," see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 474–480.

(18) D. J. Cram, THIS JOURNAL, **74**, 2137 (1952), has compared the abilities of phenyl and hydrogen to participate in intramolecular rearrangements of the 3-phenyl-2-butanol system.

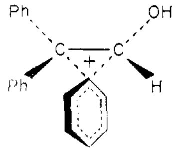
(19) For a good review of the pinacol rearrangement see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 12.

(20) It is interesting that D. J. Cram (ref. 18) estimated that the ability of phenyl to participate in an intramolecular displacement reaction is about eight times that of hydrogen in the 3-phenyl-2-butyl system. This value is close to the maximum phenyl/hydrogen migration of 7.33 observed in the present work.

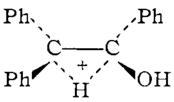
refluxing oxalic acid dihydrate, it is not possible to answer this question without further study. One can speculate, however, that the catalysts are listed in Table III in the order of decreasing ionizing power, with concentrated sulfuric acid the solvent with the greatest ability to form ion B through removal of a tertiary hydroxyl ion from glycol I. In concentrated sulfuric acid, therefore, the mechanism of this rearrangement probably approaches the limiting carbonium-ion mechanism written in Chart I. In two systems similar to triphenylethylene glycol. moreover, it is known that, in refluxing dilute sulfuric acid, hydrogen migration can take place intramolecularly and in a concerted fashion. Thus, Roger and McKay[9] isolated an optically active *o*-tolyldesoxybenzoin (V, R = *o*-tolyl) from (+)-*o*-tolylhydrobenzoin (IV, R = *o*-tolyl). Similarly, Mislow and Siegel[21] isolated an optically active phenyl-*o*-tolylacetaldehyde when (+)-1-phenyl-1-*o*-tolylethylene glycol was boiled with dilute sulfuric acid. It is then probable that triphenylethylene glycol I is converted to ketone II through path 2 *via* an intramolecular, concerted migration of hydrogen, when boiling, dilute sulfuric acid is the reaction catalyst. The observed variation in the phenyl/hydrogen migration ratios thus may be rationalized if a large inhibition to the migration of phenyl (B → C, Chart I) is assumed under conditions in which the departing (tertiary) hydroxyl needs an assist—that is, under conditions in which the phenyl migrates at approximately the same time as the hydroxyl is being removed by the solvent. For example, the conformation indicated in structure IX would lead to a transition state (or bridged ion) D in which phenyl *vs.* hydrogen and phenyl *vs.* hydroxyl are *cis* to each other, a condition which, if the *cis* effect[22] controls the reaction, should be favored over E, in which phenyl *vs.* phenyl and phenyl *vs.* hydroxyl are in eclipsed positions. Yet, in dilute sulfuric acid, under conditions in which we may assume[9,21] that hydrogen migration takes place intramolecularly and in a concerted fashion, the ratio of phenyl to hydrogen migration (D to E) is 0.435 or 1:2.3, the reverse order of what would be predicted on the basis of the *cis* effect.[22] In this instance, therefore, it seems possible that a steric resistance to phenyl migration might take place at the migration terminus[17] [the 1-carbon atom of triphenylethylene glycol I], such that the bulk of the two phenyl groups already present on the 1-carbon interferes with the concerted migration of the adjacent phenyl. The considerably smaller size of the hydrogen then would permit its migration in preference to phenyl. Under conditions, however, permitting formation of the carbonium ion B, the planar configuration of the trigonal carbon atom possessing the positive charge might reduce the steric resistance to phenyl migration to the extent that it then takes preference over migration of hydrogen. If one assumes that the catalysts are listed in Tables I, II and III in the order of their decreasing ability to ionize glycol I, the data of this paper, therefore, are consistent with this simple explanation.[23]



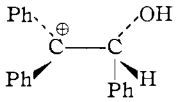
IX



D



E



B

In order to gain more information on the mechanism of the pinacol rearrangement, it is contemplated that future experiments will include (a) studies with Ia and Ic in homogeneous media in which the concentrations of a single acid catalyst are varied, (b) studies with the glycols IV (in which R = *o*-tolyl and *p*-tolyl) to determine the radiochemical and stereochemical consequences of the acid-catalyzed rearrangements and (c) studies with deuterium or tritium in which the conditions permitting concerted hydrogen migration during rearrangement of glycol I might be established.

Experimental

1,1,2-Triphenylethylene Glycol (Ia, Ib, Ic) Labeled C-1, C-2 and 1-Ph.—Benzhydryl phenyl ketone-C^{14} prepared as described previously,[2] was converted to triphenylketol by the method of Biltz.[19] The crude ketol was not purified, but was converted to Ia with lithium aluminum hydride. In this way 4.7 g. (88%) of once-crystallized Ia (alcohol-water) was obtained from 5.0 g. of ketone. The m.p. was 167–168°. The radioactivity assay was 2.198 ± 0.001 mc./mole. Glycol Ib (C-1 labeled) was prepared from methyl mandelate-*carboxy*-C^{14} according to Acree.[20] Labeled mandelic acid was prepared from benzaldehyde and sodium cyanide-C^{14} according to Vogel.[24] The product Ib had a m.p. of 167–169°, and a radioactivity assay of 2.032 ± 0.007 mc./mole. Another preparation possessed a molar radioactivity of 2.193 ± 0.005 mc. Glycol Ic was prepared in two different ways: (a) by the action of phenyl-C^{14}-magnesium bromide (0.991 mc./mole)[2] upon methyl mandelate,[20] to yield a product whose m.p. was 165–167° and whose radioactivity was 1.979 ± 0.014 mc./mole: and (b) by the action of phenyl-C^{14}-magnesium bromide (0.991 mc./mole)[2] upon benzoin,[21] to yield a product whose m.p. was 165–167°. The assay of this sample was taken to be 0.991 mc./mole.

TABLE IV

RADIOCHEMICAL STRUCTURE DETERMINATIONS OF GLYCOLS IA, IB AND IC

Glycol	Assay, mc./mole	Benzophenone 2,4-dinitrophenylhydrazone assay, mc./mole
Ia	2.198 + 0.001	0.029[a]
Ib[b]	2.193 ± .005	2.193[a]
Ib	2.193 ± .005	2.190[a]
Ic	1.982 ± .002	1.979 ± 0.014

[a] Single determination. [b] Chromic acid oxidation.

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[21] K. Mislow and M. Siegel, THIS JOURNAL, **74**, 1060 (1953).

[22] D. Y. Curtin and co-workers, *ibid.*, **72**, 961 (1950); **73**, 992 (1951); **73**, 3453 (1951); **74**, 5905 (1952); **75**, 6011 (1953).

[23] This explanation is not unique, as there are other hypotheses which will equally well accommodate the data. For example, different degrees of solvation of the hydroxyl groups of D and E might strongly affect their relative stabilities through operation of the *cis* effect (ref. 22). It is also possible that the transition states for rearrangement of phenyl or of hydrogen may be affected radically by the degree of hydrogen bonding to solvent exhibited by the potential carbonyl oxygen atom (the hydroxyl oxygen of D or E). The latter possibility was suggested by Dr. J. D. Roberts.

[24] A. I. Vogel, "Practical Organic Chemistry," 2nd Edition, Longmans, Green and Co., New York, N. Y., 1948, p. 734.

TABLE V

RADIOACTIVITY ASSAY DATA FOR CARBON-14 MIGRATIONS ATTENDING REARRANGEMENTS OF GLYCOLS Ia AND Ic

Expt.	Reactant	Molar radioactivity of reactant, mc./mole	Catalyst	Molar radioactivity of $Ph_2C^*{=}O$ or $Ph_2{}^*CO$ 24DNPH
1	Ia	2.198 ± 0.001	Concd. H_2SO_4	0.0780 ± 0.0003
2	Ia	2.198 ± .001	Concd. H_2SO_4	0.0321 ± .0007
3	Ic	1.980 ± .001	Concd. H_2SO_4	1.372 ± .002
4	Ic	0.991 ± .001	Concd. H_2SO_4	0.697 ± .001
5[a]	Ic	1.980 ± .001	Concd. H_2SO_4	1.421 ± .003
6	Ic	1.980 ± .001	Concd. H_2SO_4	1.379 ± .001
7	Ia	2.198 ± .001	Oxalic acid dihydrate	0.0847 ± .0008
8	Ic	1.980 ± .001	Oxalic acid dihydrate	1.566 ± .002
9	Ic	0.991 ± .001	Oxalic acid dihydrate	0.810 ± .001
10	Ia	2.198 ± .001	Formic acid	0.1029 ± .0005
11	Ic	1.980 ± .001	Formic acid	1.548 ± .002
12	Ic	0.991 ± .001	Formic acid	0.790 ± .003
13	Ia	2.198 ± .001	Dil. H_2SO_4	.0995 ± .0013
14[b]	Ia	2.198 ± .001	Dil. H_2SO_4	.0713 ± .0008
15	Ic	1.980 ± .001	Dil. H_2SO_4	1.837 ± .010
16	Ic	0.991 ± .001	Dil. H_2SO_4	0.923 ± .003
17	Ic	1.980 ± .001	Dioxane–HCl	1.977 ± .007

[a] Ketone IIcd was cleaved with alkali and the diphenylmethane was oxidized to benzophenone with chromic acid. [b] Ketone IIab was reduced with lithium aluminum hydride prior to oxidation.

TABLE VI

RADIOACTIVITY ASSAYS OF PERTINENT FRACTIONS FOR YIELD CALCULATIONS OF II AND III WHEN Ia IS SUBJECTED TO PINACOL REARRANGEMENT UNDER THE INFLUENCE OF VARIOUS ACID CATALYSTS:

	Assay, mc./mole, of		
Catalyst	Ia	Reisolated IIab	2,4-DNPH of reisolated IIIa
Concd. H_2SO_4	2.032 ± 0.007	0.985 ± 0.009	0.0145 ± 0.0009
Oxalic acid dihydrate	2.032 ± .007	.802 ± .006	.4455 ± .0005
Formic acid	2.032 ± .007	.982 ± .006	.018 ± .0017
Dil. H_2SO_4	2.032 ± .007	.901 ± .004	.2703 ± .0022
Dioxane–HCl	2.032 ± .007	.950 ± .009	.0717 ± .0014

Radiochemical Structure Determinations of Ia, Ib and Ic.—The structure proof of each glycol was demonstrated by oxidation of samples of Ia, Ib and Ic to benzophenone and benzoic acid as described previously.[2] The benzophenone fractions were converted to their 2,4-dinitrophenylhydrazones, thrice crystallized from dioxane, then assayed for radioactivity. These data are summarized in Table IV. All of these derivatives had m.p.'s of 237–239°. The benzoic acid samples were discarded.

Determination of Percentage Carbon-14 Rearrangement under the Influence of Various Acid Catalysts. (1) **Concentrated Sulfuric Acid.**[13]—Cold, concentrated sulfuric acid (10 cc.) was added to 500 mg. of the appropriately labeled glycol (Ia or Ic), and the mixture was stirred by means of a magnetic stirring bar for 5 minutes or until homogeneous. The solution then was placed in a refrigerator for four hours, after which time it was poured over 25–50 g. of cracked ice. The white precipitate was extracted four times with ether, the ether layer was washed with water and aqueous bicarbonate solution, and the ether extract was concentrated to dryness. The concentrate was dissolved in 30–40 cc. of ethanol, the solution was boiled with Norit, then filtered through a talc pad. The white crystals of II which separated usually weighed 300–375 mg. (64–80%) and had a m.p. of 135.5–136.5°. If the m.p. was lower than this value, one further crystallization was usually sufficient to raise it to this point. (2) **Oxalic Acid Dihydrate.**[13]—Oxalic acid dihydrate (8.0 g.) was added to 500 mg. of glycol Ia or Ic in a 50-cc. flask. The contents of the flask were then heated under reflux for eight hours, a Glas-Col mantle being used as the source of heat. The contents of the flask, on cooling, were worked up as described in part 1. (3) **Formic Acid.**—Formic acid (12.5 cc. of Eastman Kodak Co. white label, 98–100%) was added to 500 mg. of glycol Ia or Ic. The mixture was heated under reflux for 17 hours, then worked up as described in part 1 of this section. (4) **Dilute Sulfuric Acid.**[13]—To 500 mg. of glycol Ia or Ic in a 100-cc. flask was added 10 cc. of dilute sulfuric acid (2 parts water and 1 part 95–98% concentrated sulfuric acid). The mixture was heated under reflux for 6 hours, then worked up as described in part 1. (5) **Dioxane–Hydrochloric Acid.**[17]—To 500 mg. of glycol Ia or Ic was added 8.3 cc. of dioxane and 16.7 cc. of concentrated hydrochloric acid. The mixture was heated under reflux for 90 minutes, then an additional 8.3 cc. each of dioxane and concentrated hydrochloric acid was added, and heating under reflux was continued until a total of 8 hours has been completed. The mixture was worked up as described in part 1.

Permanganate Oxidations of Ketones IIab or IIcd.—The ketones IIab or IIcd were oxidized with potassium permanganate as previously reported[2] to yield benzophenone and benzoic acid. The benzophenone fractions were converted to their 2,4-dinitrophenylhydrazones, and the latter were thrice crystallized from dioxane prior to radioactivity assay. The benzoic acid fractions were discarded. All 2,4-DNPH derivatives had m.p.'s of 237–239°. In Table V are given the radioactivity assay data from which were calculated the data of Table I.

Yield of Determinations of II and III from Action of Various Acid Catalysts on Ib.—The yields of II and III during rearrangement of the glycol Ia were determined by subjecting 500-mg. samples of Ia (2.032 ± 0.007 mc./mole) to the pinacol rearrangement under the influence of the five different acid catalysts exactly as described previously in the Experimental section. The dried ether extract from the work-up of each reaction product was diluted to 100 cc. in a volumetric flask, and each solution was homogenized. To one 50-cc. portion was added 250 mg. of non-radioactive ketone II,[2] the ketone was reisolated, after ensuring homogeneity, by crystallizing the concentrate twice from ethanol (once after Norit treatment). The m.p.'s of these samples were 136–137.5°. To the other 50-cc. portion of reaction product was added 250 mg. of non-radioactive triphenylacetaldehyde (III).[25] After ensuring

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[25] The author is indebted to Mr. V. F. Raaen for supplying him with this material, which was prepared by the method of Danilov.[16]

homogeneity the solution was concentrated to dryness. The concentrate was dissolved in ethanol, and the aldehyde was converted to its 2,4-dinitrophenylhydrazone. After two crystallizations, the m.p.'s of the derivatives so prepared were 211–212°. The ketone IIab and the derivative of the aldehyde IIIa reisolated from each reaction mixture then were assayed for radioactivity. The results of these assays are given in Table VI. From these data, the yields, in mg. of II and III, may be calculated as

$$\frac{x}{x + 500}(2.032) = \text{assay of IIab}$$

$$\frac{y}{y + 500}(2.032) = \text{assay of IIIa 2,4-DNPH}$$

where x = yield of ketone II and y = yield of aldehyde III. From calculations of the foregoing type, were obtained the results given in Table II.

Anal. Calcd. for $C_{26}H_{20}N_4O_4$: C, 69.03; H, 4.42; N, 12.40. Found: C, 69.06, 68.92; H, 4.46, 4.59; N, 12.73, 12.94.

Radioactivity Determinations.—These were carried out as previously described, using the Van Slyke wet combustion method in conjunction with ion-current measurements of the evolved carbon-C^{14} dioxide using a vibrating reed electrometer.[2] The uncertainties expressed for radioactivity assays are average deviations from the mean value of two or more determinations.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Thermal Decomposition of Tri-(*p*-nitrophenyl)-methyl Nitrate. A New Example of the Wieland Rearrangement[1]

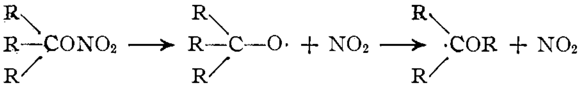
BY M. FREDERICK HAWTHORNE

RECEIVED MAY 31, 1955

Tri-(*p*-nitrophenyl)-methyl nitrate has been prepared, characterized and found to be relatively stable toward solvolytic decomposition. The thermal decomposition of tri-(*p*-nitrophenyl)-methyl nitrate, when carried out in the absence of air and in chlorobenzene solution at 130°, produces 4,4′-dinitrobenzophenone, 2,4-dinitrophenol, tri-(*p*-nitrophenyl)-carbinol and a moderate yield of 4,4′,4″,4‴-tetranitrobenzpinacol di-(*p*-nitrophenyl)-ether, the dimer resulting from the Wieland rearrangement of the tri-(*p*-nitrophenyl)-methoxy radical.

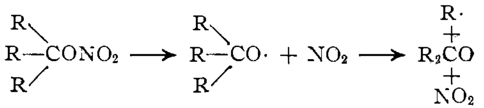
The recent preparation of triphenylmethyl nitrate[2-4] has shown this compound to be an extremely unstable entity which decomposes on attempted isolation. Baker and Heggs[5] have reported the isolation and characterization of a similarly reactive nitrate ester, benzhydryl nitrate. Both of these esters are characterized by extremely facile solvolytic reactions, as shown by the production of N-diphenylmethylacetamide from the reaction of benzhydryl nitrate with acetamide at 80–120°.

Perhaps the most interesting feature of this class of nitrate ester is their potential ability to undergo the Wieland[6] rearrangement (1) upon homolytic thermal decomposition. Cristol and Leffler[2] have



R = aryl group (1)

reported that the thermal decomposition of triphenylmethyl nitrate in such solvents as carbon tetrachloride and nitrobenzene yields triphenylcarbinol, benzophenone, picric acid and oxides of nitrogen. These products were rationalized by the authors on the basis of a *β*-cleavage process (2) followed by a series of oxidation–reduction reactions which lead eventually to picric acid. No direct evidence for the process 1 was obtained.



(2)

R = phenyl

In view of these results it was of importance to prepare a stable triarylmethyl nitrate ester which might illustrate a Wieland rearrangement. Since Bartlett and Cotman[7] have shown that diphenyl-(*p*-nitrophenyl)-methyl hydroperoxide gives nearly exclusive migration of the *p*-nitrophenyl group on thermal decomposition, one would expect tri-(*p*-nitrophenyl)-methyl nitrate (I) to be quite favorably constituted to give a similar rearrangement on thermal decomposition. Furthermore, the introduction of *p*-nitro groups into trityl nitrate should increase the solvolytic stability of the resulting nitrate ester.

Tri-(*p*-nitrophenyl)-methyl nitrate (I) was prepared in high yields by the metathetical reaction of silver nitrate with tri-(*p*-nitrophenyl)-methyl bromide in acetonitrile at room temperature. The material proved to be unusually stable toward solvolytic hydrolysis but gave oxides of nitrogen on long standing in the crystalline state or on melting (156°).

When compound I was treated with iodide ion in acetone solution, the intensely green color of the tri-(*p*-nitrophenyl)-methyl radical was observed in the presence of iodine.[8]

Solution of (I) in concentrated sulfuric acid resulted in the formation of the orange tri-(*p*-nitrophenyl)-methylcarbonium ion and not an ion similar to the light yellow oxonium ion resulting from the protonation of *p*,*p*′-dinitrobenzophenone. The nitrate ester I is apparently cleaved according to path 3 in preference to 4.[9]

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) S. J. Cristol and J. E. Leffler, THIS JOURNAL, **76**, 4468 (1954).

(3) R. T. Merrow and R. H. Boschan, *ibid.*, **76**, 4622 (1954).

(4) G. W. Cheeseman, *Chemistry and Industry*, 281 (1954).

(5) J. W. Baker and T. G. Heggs, *ibid.*, 464 (1954).

(6) H. Wieland, *Ber.*, **44**, 2550 (1911).

(7) P. D. Bartlett and J. D. Cotman, THIS JOURNAL, **72**, 3095 (1950).

(8) J. E. Leffler, *ibid.*, **75**, 3598 (1953), reported many examples of similar reactions involving tri-(*p*-nitrophenyl)-methyl bromide.

(9) Path 4 represents the acid-catalyzed decomposition of the nitrate ester by a path similar to that observed in the acid-catalyzed decomposition of certain tertiary hydroperoxides. See reference 7 for an example of this hydroperoxide rearrangement. Evidently the low ionic migratory aptitude of the *p*-nitrophenyl group makes this path quite unfavorable.