hydrochloric acid in 25 ml. of ethanol and refluxed 3.5 hours. The product solution then showed $\lambda_{\max}^{\text{alc}}$ 288 mμ, α 14.87. The product was watered out of solution and recovered by filtration. The crude IV could not be crystallized from many common solvents, such as ethanol, benzene and acetonitrile. It crystallized readily from carbon tetrachloride as a molecular complex which, after formation, could not be dissolved in carbon tetrachloride: yield 7.80 g. or 61%.

Treatment of 1.0 g. of the carbon tetrachloride complex containing 0.79 g. of IV (on the basis of the neut. equiv. 417) with ethereal diazomethane and subsequent removal of the ether by evaporation, gave the methyl ester which readily crystallized. One recrystallization from methanol–water gave 0.71 g. (90%) of the ester, m.p. 151–154°. Three additional recrystallizations gave 0.42 g. of the pure methyl ester of IV, m.p. 162–162.5, $[\alpha]_D$ +71° (1.0% in ethanol), $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 9.72.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.39; H, 9.23.

The carbon tetrachloride complex of IV gave a new molecular compound with acetic acid. Three recrystallizations of the crude carbon tetrachloride complex from glacial acetic acid gave a crystalline equimolecular compound of IV and acetic acid, which decomposed slowly above about 150° and had $[\alpha]_D$ +62° (2.0% in ethanol), $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 8.37.

Anal. Calcd. for $C_{22}H_{34}O_5$: neut. equiv., 188; C, 70.74; H, 8.78. Found: neut. equiv., 188; C, 70.76; H, 8.60.

Dehydration of II.—Three grams of the crude hydroxyenone II, $[\alpha]_D$ +43° (1% in acetic acid), was dehydrated by refluxing in 30 ml. of glacial acetic acid for 10 min. During this time the rotation decreased to $[\alpha]_D$ −12° (1% in acetic acid). No further change occurred on refluxing for an additional 20 minutes. The dehydrated product (III) was precipitated as a white powder from the acetic acid solution by the careful addition of water. The white powder melted over a wide range and little improvement was effected in attempts to crystallize it from several solvents. The crude product showed $\lambda_{\max}^{\text{alc}}$ 293 mμ, α 26.3; calculated(10) for 6-ketoabietic acid $\lambda_{\max}^{\text{alc}}$ 296 mμ.

Rearrangement of III to 6-Hydroxydehydroabietic Acid IV.—One gram of III was refluxed for 15 hours in 20 ml. of glacial acetic acid containing 3 drops of concd. H_2SO_4. During this time the rotation changed from $[\alpha]_D$ −12° to $[\alpha]_D$ +75° (5% in acetic acid) and the ultraviolet absorption changed from $\lambda_{\max}^{\text{alc}}$ 293 mμ, α 26, to $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 8.7. The crude product was precipitated from the acetic acid by careful addition of water, thoroughly washed with water, suspended in boiling water and dried; yield 0.84 g. of crude IV. On recrystallization from CCl_4 the expected molecular compound was obtained, m.p. 155–160°. This melting point was not lowered by mixing with the CCl_4 molecular compound from pure IV.

6-Hydroxydehydroabietinol (V).—A slurry of 1.31 g. of lithium aluminum hydride powder was prepared in 25 ml. of dry ether in a 100-ml. flask equipped with a stirrer, reflux condenser, heating mantle and addition funnel. A solution containing 2.00 g. of the acetic acid complex of IV described above was added to the stirred slurry over a period of 20 minutes. After the slurry had been heated at reflux for an additional 20 minutes, the excess lithium aluminum hydride was destroyed by addition of wet ether. Following the acidification of the mixture with 40 ml. of 3 *N* aqueous sulfuric acid, the ether layer was separated and washed successively with water, dilute sodium bicarbonate, and water. The ether was evaporated to leave a residue of 1.48 g. (92%) of crude V, m.p. 166–174°. The residue was taken up in methanol–water, treated with a little activated carbon and recrystallized to constant m.p. 181–182°. $[\alpha]_D$ +63° (1.0% in ethanol), $\lambda_{\max}^{\text{alc}}$ 283 mμ, α 10.93, yield 0.83 g.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.63; H, 9.79.

Acknowledgment.—We wish to express our appreciation to Mr. L. E. Brown, of the Southern Utilization Research and Development Division, New Orleans, La., for the determination of the elemental analyses.

Olustee, Fla.

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(10) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949 pp. 192–193.

[Contribution from the Chemistry Division of Oak Ridge National Laboratory]

Molecular Rearrangements. XIV. The Hydrogen–Deuterium Isotope Effect in the Pinacol Rearrangement of Triarylethylene Glycols[1]

By Clair J. Collins, William T. Rainey, William B. Smith and Irving A. Kaye

Received June 19, 1958

The hydrogen–deuterium isotope effects in the acid-catalyzed rearrangement of 1,1,2-triphenylethylene glycol (Iac) and 1,1,2-triphenylethylene-$^2H_1$ glycol (Iefg) have been determined in the presence of several different catalysts to be approximately 3. The first-order rates of rearrangement of the foregoing glycols at 43.3° in aqueous ethanolic 3.13 *N* H_2SO_4 have been determined, as have the rearrangement rates of 1,1-diphenyl-2-*p*-tolylethylene glycol (IVa), 1,1-diphenyl-2-*p*-tolylethylene-$^2H_1$ glycol (IVd), and *threo*- and *erythro*-1,2-diphenyl-1-*p*-tolylethylene glycol (VIII). Each reactant produces an aldehyde and one or two ketones. From (1) a comparison of the rates of appearance of these products, (2) the constancy of the hydrogen–deuterium isotope effect with varying catalyst and (3) the observation that *threo*- and *erythro*-VIII are interconverted in 3.13 *N* aqueous ethanolic H_2SO_4 more rapidly than they rearrange, the mechanism of the rearrangement is believed to consist of a reversible formation of open carbonium ion in which no participation by neighboring substituents is required, followed by irreversible migration of hydrogen or aryl. The previous[2a] observation that the k_ϕ/k_H ratio in the rearrangement of I varies from 7.3 to 0.04, depending on catalyst, is explained on the basis of control of these phenyl/hydrogen migration ratios by the relative populations of particular ionic conformations. The intramolecularity of deuterium migration has been established.

In four earlier papers[2] we discussed the mechanisms of the rearrangements of several triaryl substituted glycols. Although the behavior of these glycols in cold concentrated sulfuric acid is now relatively well understood,[2] it is not clear why the ratio of phenyl to hydrogen migration (k_ϕ/k_H) in the rearrangement of triphenylethylene glycol (I) to II and III is not constant, but varies from 7.3 to 0.04, depending upon the catalyst used.[2a] This phenomenon undoubtedly is related to the

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[1] This paper is based upon work performed at Oak Ridge National Laboratory which is operated by Union Carbide Corporation for the Atomic Energy Commission.

[2] (a) C. J. Collins, This Journal, **77**, 5517 (1955); (b) B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4329 (1956); (c) V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958); (d) L. W. Kendrick, Jr., B. M. Benjamin and C. J. Collins, *ibid.*, **80**, 4057 (1958).

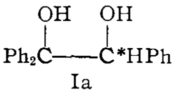
TABLE I

THE HYDROGEN–DEUTERIUM ISOTOPE EFFECT IN THE REARRANGEMENT OF TRIPHENYLETHYLENE GLYCOL

Reactant	Catalyst	Product II, %	Product III, %	% C^{14} in $(Ph)_2C{=}O$	k_ϕ/k_D	k_ϕ/k_H	k_H/k_D
Ie	Concd. H_2SO_4	100	0	67.5	23.9	(7.33)[2a]	3.3
If	Concd. H_2SO_4	100	0	64.0	17.0		2.3
Ig	Concd. H_2SO_4	...	..	2.8			
III[a]	Concd. H_2SO_4	100	0	<1%			
If	Boiling HCOOH	100	0	56.5	5.53	(1.70)[2a]	3.3
Ig	Boiling HCOOH	...	..	7.4			
III[a]	Boiling HCOOH	100	0	6.9			
Ie	HCOOH, 27.6°	14.5	79.7	100	5.49		3.3
Ic	HCOOH, 27.6°	37.6	62.4	100		1.66	
Ig	HCOOH, 27.6°	...	..	7.4			
If	$(COOH)_2 \cdot 2H_2O$, reflux	76.8	23.2	49.8	3.47		3.1
Ic	$(COOH)_2 \cdot 2H_2O$, reflux	87.4	12.6	83.4		1.13	
Ig	$(COOH)_2 \cdot 2H_2O$, reflux	...	..	5.3			
If	31.5% H_2SO_4, boiling	77.4	22.6	29.2	1.17	(0.435)	2.7
Ig	31.5% H_2SO_4, boiling	...	..	3.4			

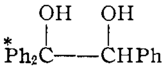
[a] Labeled in the aldehyde carbon.

steric properties of the molecules involved, to the geometry of each transition state and to the degree of participation by migrating phenyl and hydrogen. We have, therefore, studied the hydrogen–deuterium isotope effects in the rearrangement of triphenylethylene glycol (Ia and Ic) and of triphenylethylene-$^2H_1$ glycol (Ie, If and Ig)



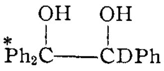
$$Ph_2\overset{OH}{C}-\overset{OH}{C}{}^{*}HPh$$

Ia



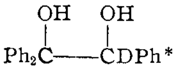
$$\overset{*}{Ph_2}\overset{OH}{C}-\overset{OH}{C}HPh$$

Ic



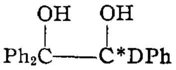
$$\overset{*}{Ph_2}\overset{OH}{C}-\overset{OH}{C}DPh$$

Ie



$$Ph_2\overset{OH}{C}-\overset{OH}{C}DPh^{*}$$

If



$$Ph_2\overset{OH}{C}-\overset{OH}{C}{}^{*}DPh$$

Ig

$Ph_2CHCOPh$
II

Ph_3CCHO
III

with the purpose of gaining some knowledge of the foregoing factors (the asterisks refer to the positions of carbon-14 labeling).

The methods for determining the contributions of each of four reaction paths to the rearrangement of Ia and Ic have been outlined in paper V.[2a] These same methods have now been applied to the rearrangement of triphenylethylene-$^2H_1$ glycol (I-efg). Given in Chart I is a scheme for the rearrangement of Ie which is similar to that given in paper V[2a] for the rearrangement of Ic. By inspection of Chart I it can be seen that a determination of the contribution of each path to the rearrangement of triphenylethylene-$^2H_1$ glycol should permit an evaluation of the ratio

$$\frac{k_\phi}{k_D} = \frac{\text{contributions of paths 3 and 4}}{\text{contribution of path 2}}$$

A comparison of the ratio k_ϕ/k_D with the values for k_ϕ/k_H previously determined[2a] for given conditions of reaction should lead to an evaluation of the isotope effect

$$\frac{k_H}{k_D} = \frac{k_\phi}{k_D} \times \frac{k_H}{k_\phi}$$

provided we make the assumption that k_ϕ is the same for the rearrangements of Iac and Iefg. The results of these determinations together with certain additional experiments upon Ia, Ic and III are given in Table I. The ratio k_H/k_D for the appropriate rearrangements for each catalyst are given in the last column of Table I. It is clear that under all reaction conditions employed the isotope effect (k_H/k_D) is about 3. Since kinetic measurements on the rearrangement of I under any of the conditions mentioned in Table I were not feasible, we searched for an appropriate system in which

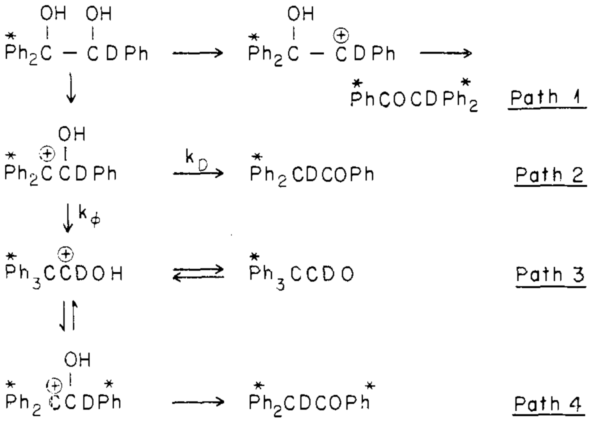
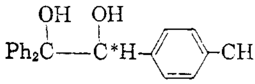
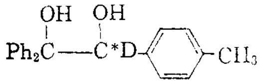


CHART I

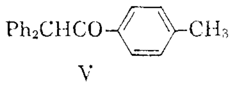
such measurements could be made. The system sulfuric acid–water–ethanol (3.13 N in sulfuric acid) proved satisfactory. Thus the first-order rates of rearrangement at 43.3° of Ia, Ie, IVa and IVd were determined with respect to each glycol. It was proved independently that under these



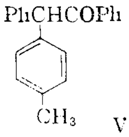
IVa



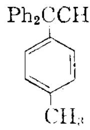
IVd



V



VI



VII

conditions (a) glycol I yields II and III quantitatively, the products being stable and (b) glycol IV yields a mixture of the ketones V and VI plus the aldehyde VII quantitatively, these products also being stable. By use of the carbon-14 dilution

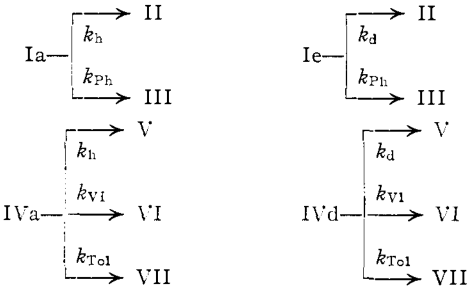
TABLE II

FIRST-ORDER RATES OF DISAPPEARANCE OF Ia, Ie, IVa AND IVc AND APPEARANCE RATES OF THE VARIOUS PRODUCTS IN 3 13 N AQUEOUS ETHANOLIC H_2SO_4 AT 43 3°

Reactant	$k_1 \times 10^5$, min.$^{-1}$	Ratio II/III or V/VII	k_H/k_D	$k_{Ph} \times 10^5$, min.$^{-1}$	$k_{Tol} \times 10^5$, min.$^{-1}$	$k_h \times 10^5$, min.$^{-1}$	$k_d \times 10^5$, min.$^{-1}$	k_h/k_d
(+)-I	11.94 ± 0.14[a,b]	..	..	....	....	....	....	..
Ia	12.04 ± .22[b,c]	2.52	..	3.4 ± 0.4[f]	....	8.6 ± 0.4	....	..
Ie	7.03 ± .25[b]	1.09	2.3	3.4 ± 0.4			3.7 ± 0.4	2.3
IVa	39.5 ± .5[b]	0.408[d]			26.3 ± 1.0	10.7 ± 1.0		
IVd	32.9 ± .003[b]	0.141[e]	3.0		27.5 ± 0.7		3.9 ± 0.7	2.7

[a] Rate of racemization. The error given in this column is standard error. [b] All first-order rate constants were calculated by the method of least squares. [c] In the rearrangements of Ia and Ie there is not more than 3% secondary hydroxyl removal. This small fraction has been neglected in the calculations of Table II, for its inclusion does not sensibly change the results. [d] The mole fractions of V, VI and VIII were 0.2718, 0.0622 and 0.6660, respectively. [e] The mole fractions of V, VI and VII were 0.1181, 0.0452 and 0.8367, respectively. [f] The error in this and other appearance rates of Table II is approximately twice the estimated standard error.

method the ratios of II and III formed from Ia and Ie were determined, and by similar means the yields of V, VI and VII from IVa and IVd were obtained. The latter three compounds also were determined independently by ultraviolet absorption methods. If we now define rate constants for the disappearance of Ia, Ie, IVa and IVd, respectively, as k_{Ia}, k_{Ie}, k_{IVa} and k_{IVd}, then each of these rate constants may be further subdivided into the rates of appearance of the appropriate products.



Thus, for the rearrangement of Ia

$$k_h = k_{Ia} \times \text{mole fraction of II in product}$$

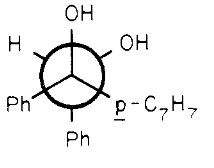
and

$$k_{Ph} = k_{Ia} \times \text{mole fraction of III in product}$$

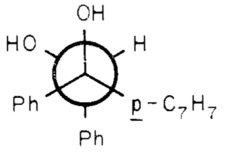
The method used for the rate studies was a modification of the method of Lane and Walters[3] in which glycol is recovered quantitatively from aldehyde and ketone products by means of chromatographic separation on alumina. A minimum of five and a maximum of eight points were taken for each kinetic run. An additional determination of the rate of racemization of (+)-1,1,2-triphenylethylene glycol was also made. The results of these kinetic determinations, the ratios of the products II/III or V/VII, and the various calculations of the rates of appearance of the products k_h, k_{Ph}, k_d and k_{Tol} are given in Table II.

The first-order rate constants for the rearrangements of *threo*-[2b] and *erythro*-VIII[2b] in 3.13 N aqueous ethanolic sulfuric acid at 43.3° were measured with respect to glycol. Further, the yields of *threo*-VIII and *erythro*-VIII after approximately 10 and 20% completion of reaction were established by the isotope dilution method. These results are given in Table III.

Next the infrared and nuclear magnetic resonance spectra of the ketonic products from the rearrangements of triphenylethylene-2-^2H_I glycol in (a) cold, concentrated sulfuric acid, (b) dilute sulfuric acid, (c) boiling formic acid and (d) boiling oxalic acid dihydrate were determined. The infrared spectra of the ketones produced in boiling formic acid, or in boiling oxalic acid dihydrate were the same as the spectrum of authentic benzhydryl phenyl ketone, indicating that no deuterium remained in these samples. The spectrum of the ketone obtained in the presence of cold, concentrated sulfuric acid, however, was dissimilar; for example, (1) strong absorption bands at 8.1 and 11.1 μ were present which were not exhibited by authentic II; and (2) not present was a strong absorption at 8.4 μ, present in the spectrum of authentic II. When the ketone from (a) above was reduced with lithium aluminum hydride, the spectrum of the carbinol produced was nearly indistinguishable from that of authentic benzhydrylphenylcarbinol; however, upon reoxidation to ketone, the spectral differences (mentioned under 1 and 2 above) reappeared. The spectrum of the ketone obtained through rearrangement of 1,1,2-triphenylethylene-2-$^2H_1$ glycol in dilute sulfuric acid indicated partial retention of deuterium.



Threo - VIII



Erythro - VIII

TABLE III

SUMMARY OF FIRST-ORDER KINETIC DATA FOR *threo*- AND *erythro*-VIII IN 3.13 N AQUEOUS ETHANOLIC H_2SO_4 AT 43.3°

Reactant	$k_1 \times 10^5$, min.$^{-1}$	After 10–11%[a] reaction, % *Erythro*	After 10–11%[a] reaction, % *Threo*	After 22%[a] reaction, % *Erythro*	After 22%[a] reaction, % *Threo*
erythro-VIII	70.4 ± 0.19[b]	60	40	47	53
threo-VIII	68.5 ± 0.09[b]	40	60	52	48

[a] The figures in these columns refer to the percentages of *threo*- and *erythro*- glycol present in reisolated VIII after 11 and 22% reaction, respectively. [b] Standard error.

From these results we infer that deuterium is not removed from the molecule when Iefg is subject to

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(3) J. F. Lane and D. R. Walters, THIS JOURNAL, **73**, 4234, 4238 (1951).

rearrangement in cold, concentrated sulfuric acid, and that deuterium is only partially lost when boiling, dilute sulfuric acid is used as the catalyst. This conclusion was supported by the n.m.r. traces, which showed that a peak in the expected region present in authentic benzhydryl phenyl ketone and in the ketones from the rearrangement of Iefg in boiling formic or oxalic acids, was absent in the ketone sample obtained upon rearrangement of Iefg in cold, concentrated sulfuric acid. The ketone produced in the presence of dilute sulfuric acid exhibited a weaker peak than that shown by authentic benzhydryl phenyl ketone.

Finally it was shown that benzhydryl phenyl-C^{14} ketone undergoes negligible isotope position isomerization in cold, concentrated sulfuric acid in 24 hours, or in boiling formic acid in 18 hours. Benzhydryl-$^2H_1$ phenyl ketone, however, suffers complete exchange of its deuterium for hydrogen upon being heated under reflux in formic acid for 23 hours.

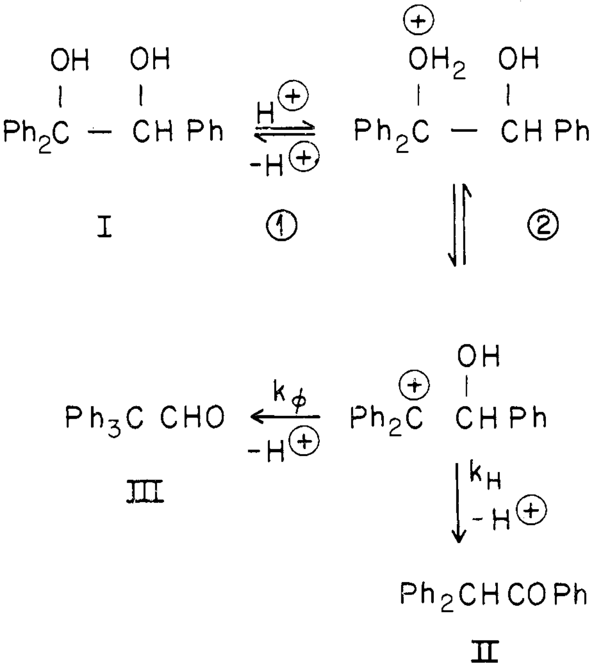
Discussion

From the foregoing data the following conclusions may be drawn: (1) From Table I, in which the k_H/k_D ratios are listed for the rearrangement of triphenylethylene glycol and triphenylethylene-$^2H_1$ glycol, it is clear that the hydrogen–deuterium isotope effect is about 3, and that the magnitude of the effect is insensitive, within the limits of experimental error, to the catalyst employed. Although primary hydrogen–deuterium isotope effects as high as 14.5 have been reported,[4c] reactions[4] in which the isotope effect lies between 4 and 14.5 have been considered to involve the removal of hydrogen or deuterium as positive ions. In reactions in which primary hydrogen–deuterium isotope effects of 3 or less have been established, the bond-breaking normally has involved extraction of H or D as a free radical,[5] or the migration of H or D through a hydride shift.[5b–5h] Thus we may conclude that the presently observed effect of about 3 is in the high range of isotope effects for those reactions proceeding through hydride shifts, and the intermediate tertiary carbonium ions probably require very little stretching of the C–H or C–D bonds.

(2) From Table II it can be seen that the rates (k_{Ph}) of formation of triphenylacetaldehyde from either triphenylethylene glycol (Ia) or from triphenylethylene-$^2H_1$ glycol (Ie) are identical within experimental error (about 10%). A comparison of the rates (k_{Tol}) of formation of diphenyl-*p*-tolylacetaldehyde also shows that these rates are the same whether the reactant is IVa or IVd. Thus the substitution of deuterium for hydrogen in either triphenylethylene glycol (I) or in 1,1-diphenyl-2-*p*-tolylethylene glycol (IV) does not greatly affect the rate of aldehyde formation. Similarly, although k_h for reactants Ia and IVa seem to differ by at least 8%, k_d for reactants Ie and IVd are the same within experimental error (10–20%). This means that the substitution of *p*-tolyl for phenyl in the 2-position of the glycol has at best a small effect upon the rates at which either hydrogen or deuterium migrate to yield the appropriate ketones. Since the rates of racemization and rearrangement of 1,1,2-triphenylethylene glycol are identical, we conclude that there is no rapid, reversible removal of secondary hydroxyl under the reaction conditions employed.

(3) From Table III two significant facts are apparent: (a) the *threo* and *erythro* forms[2b] of glycol VIII rearrange at experimentally indistinguishable rates and (b) both *threo*- and *erythro*-VIII are interconverted early in the reaction to the same 50:50 mixture, for when either is the initial reactant the glycol reisolated after 22% of the reaction consists of approximately equal amounts of *threo*- and *erythro*-VIII. From Table III we infer that under the specific conditions employed for the experiments of Table III *t*-hydroxyl removal from any of the glycols studied is reversible, and more rapid than the rates at which the glycols rearrange, although it is not necessarily true that hydroxyl removal should be reversible under all of the conditions used. We suspect, in fact, that this step is irreversible in cold, concentrated sulfuric acid.

(4) Given the conclusions of the foregoing three paragraphs, it is now possible to write a general mechanism for the acid-catalyzed rearrangements of the triaryl glycols. 1,1,2-Triphenylethylene glycol is used to demonstrate the mechanism



That step 2 must be reversible in 3.13 *N* aqueous ethanolic H_2SO_4 follows from the interconversion (Table III) of *threo*- and *erythro*-VIII. The tertiary carbonium ion formed in step 2 is considered

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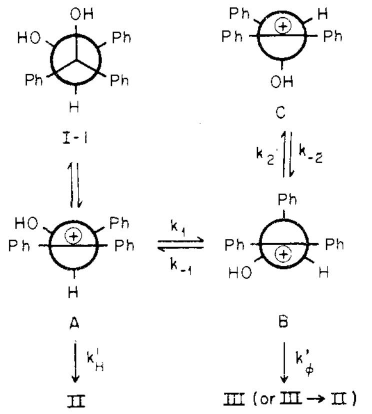
(4) (a) W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934); (b) H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, **7**, 34 (1935); (c) F. H. Westheimer, Abstracts 14th National Organic Symposium, Purdue University, June, 1955, pp. 13–20; (d) V. J. Shiner, THIS JOURNAL, **74**, 5285 (1952); (e) K. B. Wiberg and R. Stewart, *ibid.*, **78**, 1214 (1956); (*f*) K. B. Wiberg, *ibid.*, **76**, 5731 (1954); (g) F. H. Westheimer and N. Nicolaides, *ibid.*, **71**, 25 (1949).

(5) (a) P. D. Bartlett and F. A. Tate, *ibid.*, **75**, 91 (1953); (b) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); (c) **76**, 1603 (1954); (d) **78**, 2653 (1956); (e) V. J. Shiner, Jr., and S. Cross, *ibid.*, **79**, 3599 (1957); (f) E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 6307 (1952); (g) **76**, 791, 794, 4495 (1954); (h) S. Winstein, Abstracts of 15th National Organic Symposium, Rochester, N. Y., 1957, p. 38.

to be a solvated, discrete intermediate in which very little progress has been made toward migration to the carbonium center by either hydrogen or phenyl. This statement seems reasonable from the constancy of the hydrogen–deuterium isotope effect (Table I) with various catalysts and from the fact (Table II) that when the migrating aryl group is changed from phenyl to *p*-tolyl there is small rate enhancement in the migration of hydrogen or deuterium. Similarly, as hydrogen is substituted for deuterium (Table III) there cannot be more rate enhancement than about 12% in the migration of phenyl or of *p*-tolyl.[6] The equilibrium constants for steps 1 and 2 for Iac, Iefg, IVa and IVd must be nearly equal; otherwise the constants $k_{\rm H}$ in the rearrangements of Ia and IVa, $k_{\rm Ph}$ in the rearrangements of Ia and Iefg, $k_{\rm d}$ in the rearrangements of Iefg and IVd and $k_{\rm Tol}$ in the rearrangements of IVa and IVd would not be, for each pair of reactants, so nearly the same. This means again that since both I and IV go to tertiary carbonium ions stabilized by two phenyls, the specific rates of ionization and reformation of I and IV are essentially identical, and uninfluenced by the substituents on the no. 2 carbon. This could only be the case if no participation (anchimeric assistance) by the substituents on the 2-carbon takes place.[7]

(5) Reasons for the large variation in $k_{\phi}/k_{\rm H}$ with catalyst[2a] may now be sought. The most attractive hypothesis consistent with the data of the present paper appears to be one based upon conformational control. Conformation I-1 seems to be the most stable arrangement for 1,1,2-triphenylethylene glycol, for it allows the two phenyls of the tertiary carbon to flank the smallest group—namely, hydrogen—of the secondary carbon. Although there does not appear to be any steric reason for supposing that ionic conformation A should be formed more readily than ionic conformation B, we propose as one explanation of our data that in the presence of weakly ionizing solvents, A is produced preferentially, then reacts more readily through hydrogen migration to produce II than it undergoes equilibrium with B. In such a solvent, however, as cold, concentrated sulfuric acid which can impart stability, and thus a longer half-life to the carbonium ion ABC, the equilibrium $A \rightleftarrows B$ could be shifted in favor of B, thus permitting migration of phenyl. An alternate possibility is that in cold, concentrated sulfuric acid B may be preferentially formed directly from reactant. One explanation for the predominance of different conformational isomers in different acids is to be found in the relative abilities of these acid solvents to distribute the carbonium ion charge. Conceivably if the carbonium ion itself received little help from solvent in such distribution, a particular ionic conformation could be most compatible with the necessary distribution of charge, whereas if the solvent were more able to help with such charge distribution a different ionic conformation would be preferred.



(6) The infrared and nuclear magnetic resonance spectra of the ketone fractions obtained upon rearrangement of 1,1,2-triphenylethylene-2-^{2}H$_1$ glycol (Iefg) may be taken as incontrovertible evidence for intramolecular deuterium (and hydrogen) migration ($k_{\rm D}$, path 2 of Chart I) during the rearrangement catalyzed by cold, concentrated sulfuric acid. Previous evidence for such intramolecularity in a pinacol-type rearrangement has been presented by Ley and Vernon.[7a] That the ketones II produced from deuterium-containing I in the presence of boiling formic or boiling oxalic acid dihydrate contain no deuterium does not necessarily indicate an intermolecular hydrogen shift under these conditions. In these two cases, considerably higher temperatures and longer contact times were employed, and even if the initially formed products did contain deuterium, this deuterium should exchange with the hydrogen of the solvent, since we have demonstrated (see Experimental section) that benzhydryl-^{2}H$_1$ phenyl ketone loses its deuterium after 23 hours in boiling formic acid. That the reaction catalyzed by dilute sulfuric acid apparently yielded ketone still containing a significant proportion of deuterium is probably a consequence of the insolubility of ketone II in this medium, with a resulting decrease in the rate at which hydrogen exchange takes place.

Acknowledgment.—The authors wish to thank Dr. Henry Morgan for furnishing certain of the infrared traces, and Professor J. H. Goldstein of Emory University for the nuclear magnetic resonance spectra.

Experimental

Preparation of the Labeled Glycols I.—The carbon-14 isotope position isomers of 1,1,2-triphenylethylene glycol (Ia and Ic) were prepared as described in paper V.[2a] The deuterium-containing glycols Ie, If and Ig were prepared from the appropriately labeled (with carbon-14) isotope position isomers of benzhydryl phenyl ketone[8] by oxidation[9] to α-phenylbenzoin followed by reduction of the benzoin so obtained with lithium aluminum deuteride,[10] or by the reduc-

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[6] It has been shown that in 1,2-shifts involving anchimeric assistance, the substitution of a second non-migrating electron-repelling group on Cβ enhances markedly the rate of neighboring group participation: S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, This Journal, **74**, 1113 (1952). It also has been demonstrated that in the rearrangement of the 2,2-diphenylethanol system, *p*-substitution of one methyl group enhances the rate at which the unsubstituted phenyl participates in the reaction: J. G. Burr, Jr., *ibid.*, **75**, 5008 (1953); *Chemistry & Industry*, 850 (1954).

[7] The reversibility, under certain conditions, of steps 1 and 2 has been demonstrated previously: (a) J. B. Ley and C. A. Vernon, *J. Chem. Soc.*, 2987 (1957); (b) J. F. Duncan and K. R. Lynn, *Australian J. Chem.*, **10**, 1 (1957).

[8] W. A. Bonner and C. J. Collins, This Journal, **75**, 5376 (1953).

[9] H. Biltz, *Ber.*, **32**, 655 (1899).

[10] Obtained from Metal Hydrides, Inc., Beverly, Mass.

tion with lithium aluminum deuteride of the α-(phenyl-C^{14})-benzoin[11] (unrearranged) obtained by the action of phenyl-C^{14}-magnesium bromide on benzoin.

Preparation of Optically Active 1,1,2-Triphenylethylene Glycol.—Mandelic acid was resolved through the quinidine salt as reported by McKenzie[12] to yield the *l*-isomer, m.p. 133°, $[\alpha]^{24-35}_{\mathrm{D}}$ 150.5° (water), and the *d*-isomer, m.p. 134°, $[\alpha]^{24-25}_{\mathrm{D}}$ 149.8° (water). The $[\alpha]^{10-12}_{\mathrm{D}}$ of the *d*-isomer was +158°. The optically active glycols were prepared by the action of phenylmagnesium bromide upon *d*- or *l*-methyl mandelate[13] to yield, from *l*-mandelic acid, (+)-1,1,2-triphenylethylene glycol, m.p. 128–129°, $[\alpha]^{24-25}_{\mathrm{D}}$ +218.2° (chloroform), $[\alpha]^{15}_{\mathrm{D}}$ +230° (chloroform) (lit.[13] +233.6°), and from *d*-mandelic acid (−)-1,1,2-triphenylethylene glycol, m.p. 129°, $[\alpha]^{24-25}_{\mathrm{D}}$ −219° (chloroform).

1,1-Diphenyl-2-*p*-tolylethylene-2-C^{14} Glycol (IVa) and 1,1-Diphenyl-2-*p*-tolylethylene-2-C^{14}-^{2}H$_1$ Glycol (IVd).—Diphenylacetyl-1-C^{14} chloride[8] was converted to benzhydryl *p*-tolyl ketone-C^{14} through the Friedel–Crafts synthesis with aluminum chloride and toluene. Thus, 10.0 g. of labeled diphenylacetic acid and 11 g. of PCl_5 were heated under reflux in dry toluene (100–200 ml.) for 30 min., then 100 ml. of toluene and 25 g. of $AlCl_3$ were added. The mixture was heated under reflux for one hour, then poured over cracked ice, to which had been added 50 ml. of concentrated HCl. The ether extract, after being washed with water and sodium bicarbonate solution, was concentrated and the oil remaining was combined with the concentrate from a previous preparation (from 6 g. of diphenylacetic acid) and distilled at 1–2 mm. The distillate was collected until the temperature rose from 190 to 210°. The yield of crystallized ketone (from hexane) was 10 g., m.p. 99°. In a typical experiment, 5.0 g. of the foregoing ketone, 35 ml. of acetic acid and 4.5 ml. of concentrated HNO_3 were heated on a hot-plate with gentle reflux for 45 minutes.[9] The mixture then was poured into water and extracted 3 times with chloroform, and the extract was washed with aqueous sodium bicarbonate solution, then water. The concentrated, dried oily residue was dissolved in 50–100 ml. of ether and reduced with lithium aluminum hydride to yield the crude glycol IVa nearly quantitatively. The product, recrystallized from alcohol, had a m.p. of 195–196°, and a radioactivity assay of 8.684 ± 0.011 mc./mole. A different preparation yielded IVa whose radioactivity assay was 2.903 ±0.005 mc./mole. The deuterium-containing glycol IVd was prepared in an analogous fashion except that lithium aluminum deuteride was employed in the final step; radioactivity assay of IVd, 2.903 ±0.005 mc./mole, m.p. 195–196°.

Procedure for Kinetic Runs.—Glycols I, IV or VIII were dissolved in 95% ethanol (1 g. of glycol for each 667 ml. of ethanol) and warmed slightly. A volume of 9.39 *N* H_2SO_4 equal to half the volume of ethanol used was added to the ethanol solution of glycol. The heat of mixing was such that with practice it was possible to bring the solution very close to the thermostat temperature of 43.3 ±0.2°. At appropriate times after temperature equilibrium had been established, aliquots of 100–200 ml. were removed and pipetted into 3–5 times the volume of water to which had been added slightly more than the theoretical amount of sodium bicarbonate. The resulting suspension was extracted repeatedly with ether, and the ether extracts were combined and concentrated to dryness. The residues each were dissolved in small volumes of benzene and placed upon 10–20 g. of alumina (80–200 mesh) in a 0.5 in. column. The chromatograph was washed with 250 ml. of benzene to yield quantitatively the ketone and aldehyde products; this was followed with 450 ml. of a 50:50 mixture (by volume) of ether–methanol, which quantitatively removed the glycol. The solutions were evaporated, at which time the aliquots containing glycol also yielded some alumina which had been removed from the column. When the residues were redissolved in ether, however, the alumina remained behind. The residues were then transferred to tared weighing bottles, which were pumped *in vacuo* over Drierite to constant weight. Subsequent weighings of each bottle, when corrected for molecular weight of aldehyde and ketone, provided the values x (weight of glycol reacted) and $(a - x)$ (weight of glycol unreacted) in the first-order rate expression

$$k = \frac{1}{t} \ln \frac{a}{a - x}$$

in which a is the initial weight of glycol. Control experiments similar to those performed by Lane and Walters[3] demonstrated the quantitative nature of the chromatographic separation as applied to the glycols I, IV and VIII. It was sometimes necessary to discard very early or very late points when the error in weighing x or $(a - x)$ became too large. With these exceptions all calculated first-order constants were steady throughout the reactions studied.

The Racemization Rate of (+)-1,1,2-Triphenylethylene Glycol [(+)-I].—The (+)-glycol (0.32585 g., $[\alpha]^{24-25}_{\mathrm{D}}$, +218.2° (chloroform), m.p. 128–129°), was dissolved in 100 ml. of 95% ethanol. The mixture was warmed slightly and 50 ml. of 9.39 *N* H_2SO_4 (stock solution) was added. The mixture was brought to the thermostat temperature of 43.3 ±0.2°, then placed in a jacketed 2-dm. polarimeter tube through which water from the thermostat was rapidly circulated. The observed rotations together with the time, in minutes, respectively, are: 0.794, 460; 0.710, 1510; 0.677, 1900; 0.569, 3325; 0.463, 4880; 0.386, 6550; 0.352, 7175.

Determination of Ratios of Products in Kinetic Runs.—The yields of II and III produced upon rearrangement of Ia or Ie were determined exactly as reported previously.[2a] In a typical experiment 200 mg. of labeled Ic was treated in identical fashion as for the samples upon which the kinetic runs were carried out, except the resulting solutions were kept at 43.3 ± 0.2° for 1 to 8 days. The isotope dilution method then was employed to give the yields of II and III, with the results shown in Table II.

The yields of V and VII produced upon rearrangement of IVa or IVd (as described in the foregoing paragraph for glycol I) were likewise determined by the isotope dilution method[2a] to give the results shown in Table IV. It was difficult to determine the yields of ketone VI by this method, so V, VI and VII were estimated by making use of the characteristic absorptions of these compounds at 253, 320 and 234 mμ, respectively, as determined with an ultraviolet spectrometer. The mixtures were treated as three-component systems, and three simultaneous equations were solved to give the results shown in Table IV, in which the yields calculated by the ultraviolet method are compared with the yields of V and VII as determined by the isotope dilution method.

TABLE IV

SUMMARY OF YIELD DETERMINATIONS OF V, VI AND VII FROM REARRANGEMENT OF IVa AND IVd IN 3.13 *N* H_2SO_4 AT 43.3°

Reactant	Method	Product V	Product VI	Product VII
IVa	Isotope diln.	25.0		62.4
IVa	Isotope diln.	25.4		65.5
IVa	U.v. spectral	25.9	6.5	60.9
IVa	U.v. spectral	26.6	5.0	61.7
IVa	U.v. spectral			63.6
Average		25.7	5.7	62.8
Adjusted average[a]		27.3	6.0	66.7
IVd	Isotope diln.	10.5		80.1
IVd	Isotope diln.	11.0		85.3
IVd	U.v. spectral	11.6	5.7	79.4
IVd	U.v. spectral	12.9	3.0	79.6
IVd	U.v. spectral			83.1
Average		11.5	4.4	81.5
Adjusted average[a]		11.8	4.5	83.7

[a] In determination of these yields the unreacted glycol was not separated chromatographically, thus the total yields of V, VI and VII are less than 100%.

Control Experiments and Proof of Isotopic Structure.—All carbon-14 labeled starting materials were cleaved and their isotopic structures were determined as previously reported.[2a,b] In order that the effect of cold, concentrated sulfuric acid and boiling formic acid upon benzhydryl phenyl ketone could be established, the following experiments were performed: (a) Benzhydryl phenyl-C^{14} ketone (250 mg., 0.987 mc. per mole) was dissolved in concentrated sulfuric acid (96%) and the resulting solution was placed in the refrigerator overnight. The ketone, once crystallized from

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[11] J. E. Eastham, J. E. Huffaker, V. F. Raaen and C. J. Collins, THIS JOURNAL, **78**, 4324 (1956), footnote 12.

[12] A. McKenzie, *J. Chem. Soc.*, **75**, 964 (1899).

[13] A. McKenzie and H. Wren, *ibid.*, **97**, 473 (1910).

ethanol, weighed 196 mg. and had a m.p. of 136–137°. Upon oxidation[2a] with 300 mg. of $KMnO_4$ in 20 cc. of acetone, 5 cc. of water and 2 cc. of glacial acetic acid there was obtained 40 mg. of benzoic acid and a benzophenone fraction which yielded 123 mg. of 2,4-dinitrophenylhydrazone. The purified products were assayed for radioactivity: the benzoic acid (m.p. 122°) contained 0.9505 mc. per mole of carbon-14 and the benzophenone derivative (m.p. 239–40°) 0.019 ± 0.002 mc./mole, corresponding to a maximum of 1.9% rearrangement after 24 hours.

(b) Benzhydryl phenyl ketone (502 mg.) labeled in the 1-phenyl position (0.5954 mc./mole) and in the carbonyl-carbon (1.137 mc./mole) was heated under reflux with 15 cc. of formic acid (98–99%) for 18 hours. The reisolated ketone was crystallized once from ethanol to yield 372 mg. whose m.p. was 136°. It was cleaved[9,11] with nitric acid in acetic acid followed by chromic acid to yield benzophenone which was converted to 272 mg. of 2,4-dinitrophenylhydrazone; m.p. 239–40°, radioactivity assay 0.024 mc./mole. This assay corresponds to a maximum rearrangement of the total radioactivity of 1.3%.

(c) Benzhydryl-$^2H_1$ phenyl ketone (272 mg.) obtained through the rearrangement of Ie in cold, concentrated sulfuric acid was heated under reflux in 10 cc. of formic acid (98–99%) for 23 hours. The reisolated ketone was crystallized once from ethanol (m.p. 136–137°), and exhibited an infrared spectrum identical with that of authentic benzhydryl phenyl ketone, but different from that of the original ketone.

(d) In a typical experiment, 161 mg. of triphenylacetaldehyde (crude, m.p. 98–100°) was dissolved in 108 cc. of 95% ethanol, and to it was added 54 cc. of 9.39 N H_2SO_4. After 0.5 hour at room temperature and 0.5 hour at 48–50°, the temperature was raised to 80° for one hour. The reaction was quenched, and the reisolated material was converted to 231 mg. of 2,4-dinitrophenylhydrazone (86.6% of theory), m.p. 208–210° (crude). This is the same yield obtained when a sample of the triphenylacetaldehyde was converted directly to 2,4-dinitrophenylhydrazone. Finally, the experiment was repeated upon 83.5 mg. of triphenylacetaldehyde, dissolved in 50 cc. of 95% ethanol and 25 cc. of 9.39 N H_2SO_4. The solution was maintained at 46° for 4 hours, then at 70° for 17 hours. The reaction was quenched, and the reisolated aldehyde was converted to 124 mg. (89.5%) of 2,4-dinitrophenylhydrazone, m.p. (crude) 208–210°.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Molecular Rearrangements. XV. The Stereochemistry of the Solvolytic and Deamination Reactions of 1,2,2-Triphenylethyl Derivatives[1]

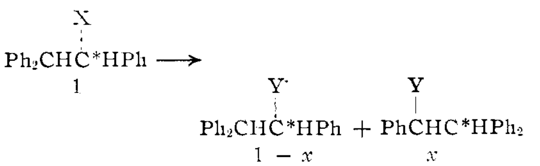
BY CLAIR J. COLLINS, WILLIAM A. BONNER AND CHARLES T. LESTER

RECEIVED JULY 3, 1958

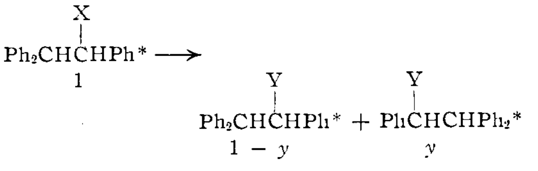
The solvolytic and deamination reactions of 1,2,2-triphenylethanol and its derivatives, previously reported with respect to radiochemistry, have now been studied stereochemically. It has been found that (1) the products of hydrolysis and acetolysis of 1,2,2-triphenylethyl tosylate and (2) the deamination product from the reaction of 1,2,2-triphenylethylamine with nitrous acid are formed with some racemization plus *retention of configuration.* The products from the deamination of labeled (−)-amine at 36.9° and of labeled (+)-amine at 25° were separated into olefin, acetate and carbinol fractions. Each carbinol fraction was further separated into retained and racemic material, then all fractions were subjected to oxidative degradation, and the carbon-14 distribution of each was determined. From these data it can be shown that there is more rearrangement of the carbon-14 label in carbinol of *inverted* configuration than in carbinol of *retained* configuration, thus completely excluding bridged ions as the cause of configuration retention. These results, however, are compatible with our previously proposed[4-6] mechanism involving equilibrating, classical carbonium ion intermediates. Retention of configuration is explained by (1) a rate of rotation (k_x, equation 4) about the central carbon–carbon bond which is not extremely rapid with respect to the rate of phenyl migration (k_y, equation 4), and (2) a preferential frontside attack by the entering group owing to steric shielding from back-side attack (Fig. 1) by an *o*-hydrogen of one of the adjacent phenyls.

Introduction

The radiochemistry of the Wagner–Meerwein rearrangement of several carbon-14 labeled 1,2,2-triphenylethyl compounds has been the subject of previous papers.[2-6] It was shown that the reactions studied could be explained most simply if it is assumed that open or classical carbonium ions, capable of phenyl migration, are the intermediates. In particular reactions of the 1,2,2-triphenylethyl system neither the chain nor the ring labels achieved their statistical values; for example, if equation 1 represents the reactions of the chain-labeled reactants, and equation 2 represents the reactions of the ring-labeled reactants, then the mole fractions x and y, respectively, of rearranged products, were less than the statistical values of 0.500 and 0.667. For a given reaction, however, y was always greater than x by an amount generally[6] predictable on the basis of the equilibrating classical carbonium ion mechanism. Certain other reactions of 1,2,2-triphenylethyl derivatives, notably



$$\underset{1}{Ph_2CH\overset{X}{C^*}HPh} \longrightarrow \underset{1-x}{Ph_2CH\overset{Y}{C^*}HPh} + \underset{x}{Ph\overset{Y}{C}HC^*HPh_2} \quad (1)$$



$$\underset{1}{Ph_2CH\overset{X}{C}HPh^*} \longrightarrow \underset{1-y}{Ph_2CH\overset{Y}{C}HPh^*} + \underset{y}{Ph\overset{Y}{C}HCHPh_2^*} \quad (2)$$

acetoxyl exchange,[5] did proceed to statistical conclusions (that is, $x = 0.500$ and $y = 0.667$), and were explained on the basis of the same general mechanism.

The idea of a bridged "bromonium" ion was invented by Roberts and Kimball[7] and was subse-

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[1] This paper is based in part upon work performed for the Atomic Energy Commission at Oak Ridge National Laboratory, operated by Union Carbide Corporation. Paper XIV, C. J. Collins, W. T. Rainey, W. B. Smith and I. A. Kaye, THIS JOURNAL, **81**, 460 (1959).

[2] W. A. Bonner and C. J. Collins, *ibid.*, **75**, 5372 (1953).

[3] C. J. Collins and W. A. Bonner, *ibid.*, **75**, 5379 (1953).

[4] C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955).

[5] W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99, 6725 (1955).

[6] W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956).

[7] I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).