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

Molecular Rearrangements. VIII. A Mechanistic Correlation of the Aldehyde–Ketone and Pinacol Rearrangements[1]

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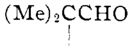
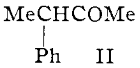
Diphenyl-*p*-tolylacetaldehyde-1-C^{14} (IV), chain- and ring-labeled 1,2-diphenyl-1-*p*-tolylethylene glycol (Va, Vb and Vc) and 1,1-diphenyl-2-*p*-tolylethylene-2-C^{14} glycol (VIa) have been prepared and subjected to rearrangement (a) in cold, concentrated sulfuric acid and (b) in boiling formic acid. Under both sets of conditions two ketones, *p*-tolyldesoxybenzoin (VII) and benzhydryl *p*-tolyl ketone (VIII), are produced from IV, V or VI. By using double-labeling techniques and by generating the same intermediate ion (X_1, Charts I, II and III) under identical conditions from the three different sources (IV, V and VI), it has been possible to relate the pinacol and aldehyde–ketone rearrangements mechanistically. For the rearrangement of the aldehyde IV, the simple ratios of the products VII/VIII (4.7 in sulfuric acid and 3.5 in formic acid) would appear to indicate phenyl/*p*-tolyl migration ratios of 2.35 and 1.75, respectively, which are inverted with respect to the usual migratory abilities of the two groups. It has been shown that the migration ratio of the one *p*-tolyl and the two phenyl groups of aldehyde IV is not reversed and is not given by the ratio of the ketonic products. The true *p*-tolyl/phenyl migration abilities in the rearrangement of IV in either sulfuric or formic acid have been estimated by the use of equation 8 to be greater than one as normally expected. It has been shown that secondary hydroxyl removal from 1,1-diphenyl-2-*p*-tolylethylene-2-C^{14} glycol (VIa) is relatively more important, with respect to tertiary hydroxyl removal, in concentrated sulfuric acid at 0°, than in formic acid at 27.6°.

Introduction

The acid-catalyzed rearrangements of di- and trisubstituted acetaldehydes to produce ketones have long been regarded as intimately related to the pinacol rearrangement,[2-5] since under relatively mild conditions aldehydes are often products of the pinacol transformation, whereas under more strongly acidic conditions, the appropriate aldehyde is capable of conversion to the same ketone or ketones obtained from the parent pinacol. Neither the pinacol nor the aldehyde–ketone rearrangement is well understood. The difficulties involved in understanding the former have been most adequately presented by Wheland.[4] The anomalies relative to the aldehyde–ketone reaction have been mentioned both by Wheland[4] and by Ingold[5] and have to do with the fact that in this rearrangement there is an apparent reversal of the usual migratory abilities of the groups involved.[4,5] Thus, di-


$(Me)_2\underset{Ph}{C}CHO$

I

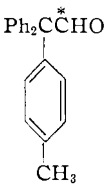

$Me\underset{Ph}{C}HCOMe$

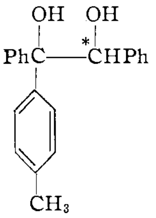
II

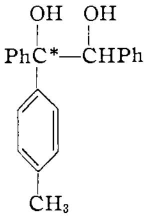
$Me_2CHCOPh$

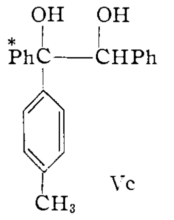
III

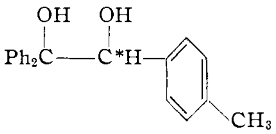
methylphenylacetaldehyde (I) in concentrated sulfuric acid yields 3-phenyl-2-butanone (II) rather than phenyl isopropyl ketone (III)[6] despite the well-known[7] fact that phenyl ordinarily possesses a migratory ability much greater than methyl. Nor is this seeming reversal of the migratory abilities confined to aldehyde I, for the phenomenon is apparently quite general.[8] In a recent paper[9] the importance of the conjugate acid of triphenylacetaldehyde as an intermediate in the pinacol rearrangement of triphenylethylene glycol was evaluated for several different acid catalysts. It appeared to us that these results[9] foreshadowed a general mechanism which would allow a correlation between the pinacol and aldehyde–ketone rearrangements and which would further clear up some of the mystery[4,5] which has been associated with these two reactions. Accordingly, we have applied the same type of radiochemical investigation[9] to the acid-catalyzed rearrangements of diphenyl-*p*-tolylacetaldehyde-1-C^{14} (IV) and the closely related glycols V[3,10] and VI.[1,11] These compounds were selected as models for this study, since the migratory abilities of *p*-


IV


Va


Vb


Vc


VIa

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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. Paper VII, J. F. Eastham, J. F. Huffaker, V. F. Raaen and C. J. Collins, THIS JOURNAL, **78**, 4323 (1956).

[2] (a) S. Danilov, *J. Russ. Phys. Chem. Soc.*, **49**, 282 (1917); **51**, 97 (1919); (b) S. Danilov and E. Venus-Danilova, *Ber.*, **59B**, 377–387 (1926).

[3] R. Roger and W. B. McKay, *J. Chem. Soc.*, 332 (1933).

[4] G. W. Wheland, "Advanced Organic Chemistry," 2d Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 494–534.

[5] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 479.

[6] A. Orékhov and M. Tiffeneau, *Compt. rend.*, **182**, 67 (1926).

[7] See, for example, M. Tiffeneau and H. Cahmann, *Bull. soc. chim.*, 1876 (1935), and the discussion of D. Y. Curtin and S. Schmukler, THIS JOURNAL, **77**, 1107 (1955), who state "that 10 is a conservative estimate for the phenyl/alkyl migration ratio . . ." in the deamination of 1-amino-2-phenylpropanol-2.

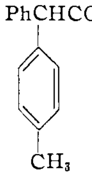
[8] For other examples of the aldehyde–ketone rearrangement in which the usual migratory abilities[4,5] of the groups are reversed, see: S. N. Danilov, *J. Russ. Phys. Chem. Soc.*, **51**, 109 (1919); **57**, 347 (1925); **58**, 129 (1926); **59**, 196, 210 (1927); **61**, 723 (1929); *J. Gen. Chem.*, **18**, 200 (1948); R. Lucas and J. Guerlain, *Bull. soc. chim.*, **49**, 1860 (1931); and K. Isimura, *Bull. chem. soc. Japan*, **16**, 196, 252 (1941); M. Tiffeneau and A. Orékhoff, *Compt. rend.*, **182**, 67 (1926).

[9] Paper V, C. J. Collins, THIS JOURNAL, **77**, 5517 (1955).

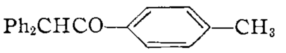
[10] (a) S. F. Acree, *Ber.*, **37**, 2753 (1904); (b) A. McKenzie, A. K. Mills and J. R. Myles, *ibid.*, **63**, 904 (1930); (c) C. F. Koelsch, THIS JOURNAL, **54**, 2049 (1932); (d) A. McKenzie, R. Roger and W. B. McKay, *J. Chem. Soc.*, 2597 (1932).

[11] The asterisks denote the positions of carbon-14 labeling. The lower-case letters after the Roman numerals indicate specific isotope-position isomers. In the case of compound V, Va was the β-diastereomer, whereas Vb and Vc were the α-diastereomers.

tolyl and phenyl do not differ so greatly[12] as those of the substituents of aldehyde I, thus permitting an accurate experimental determination of the yields of ketone VII, formed from IV by phenyl migration, and ketone VIII, formed by *p*-tolyl migration.

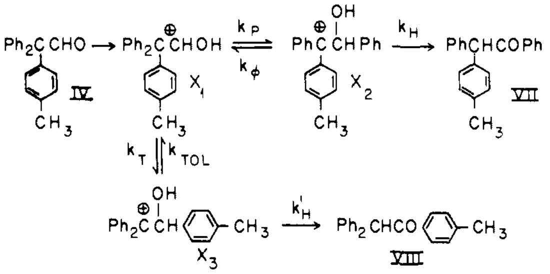


VII



VIII

When diphenyl-*p*-tolylacetaldehyde (IV), labeled with the carbon-14 in the carbonyl group, was treated with cold, concentrated sulfuric acid, the mixture of ketones VII and VIII, as determined by the radioactivity dilution method,[13] was obtained in the ratio VII/VIII = 4.7. When the aldehyde IV was treated with boiling formic acid, the same two ketones were obtained quantitatively in the ratio VII/VIII = 3.5. In each case that ketone (VII) which was formed by phenyl migration predominated over the ketone (VIII) which was formed with *p*-tolyl migration. Allowing for the statistical factor of two phenyls and only one *p*-tolyl group in aldehyde IV, in the sulfuric acid experiment the apparent phenyl/*p*-tolyl migration ratio is 2.35, whereas in the formic acid experiment this ratio is 1.75. It is difficult to believe that these two ratios represent the true *p*-tolyl/phenyl migratory abilities when the mass of data previously cited[12] is considered. Results obtained[9] for the rearrangement of triphenylethylene glycol seemed to indicate that the rearrangement of aldehyde IV to ketones VII and VIII could best be explained by the following mechanism, in which X_1, X_2 and X_3 represent three ionic species in a dynamic equilibrium:



It is apparent that if this scheme is correct, the specific rate-constant ratio k_T/k_P, rather than the product ratio VIII/VII, represents the relative migratory abilities of the one *p*-tolyl and the two phenyl groups of aldehyde IV when this aldehyde is subjected to acid catalysis. It is further apparent, even though the ratio $2k_T/k_P$ might be expected to be *greater than one*, that this ratio alone is not sufficient to control the relative yields of the ketones VII and VIII, since the additional rate constants k_ϕ, k_{Tol}, k_H and k'_H would also be expected to affect the final yields of products. The validity of the foregoing mechanism, together with its relation to the pinacol rearrangement, is established in the following sections.

Methods and Results

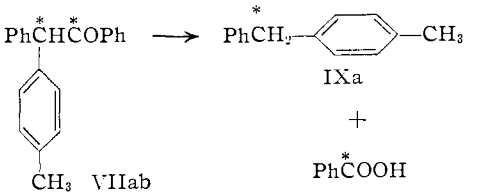
The aldehyde IV and glycols Va, Vb and VIa were subjected to rearrangement (a) in cold, concentrated sulfuric acid and (b) in boiling formic acid. The yields of ketones VII and VIII were determined by the radioactivity dilution method.[13] The results of these experiments are given in Table I. Compounds IV, Va and VIa were subjected to the same conditions in different experiments, and in each experiment the mixed ketones were cleaved with alkali

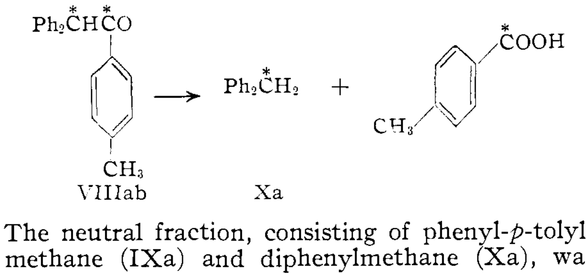
TABLE I

YIELDS OF KETONES VII AND VIII PRODUCED BY THE ACTION OF FORMIC OR SULFURIC ACID UPON IV, V AND VI

No.	Reactant	Reagent	Yield of ketone,[a] % VII	VIII	Ratio VII/VIII
1	IV	96% H_2SO_4 at 0°	82.5	17.5	4.7
2	IV	Boiling 98% formic	77.7	22.3	3.48
3	Va, β-form	96% H_2SO_4 at 0°	86	14	6.15
4	Va, β-form	96% H_2SO_4 at 0°	83.6	16.4	5.11
5	Vb, α-form	96% H_2SO_4 at 0°	85.1	14.9	5.82
		Av.	84.9	15.1	
6	Va, β-form	Boiling 98% formic	87.7	12.3	7.13
7	Vb, α-form	Boiling 98% formic	88.3	11.7	7.57
		Av.	88.0	12.0	
8	VIa	96% H_2SO_4 at 0°	83.0	17.0	4.9
9	VIa	Boiling 98% formic	71.7	28.3	2.54
10	VIa	Boiling 98% formic	71.0	29.0	2.45
		Av.	71.4	28.6	

[a] The values given in these two columns represent the yields of ketones in the products, and thus for each experiment the yields of VII and VIII will total 100. In the sulfuric acid-catalyzed reactions the combined yields of products were 94–99%. The combined yields in the formic acid-catalyzed reactions were quantitative.





The neutral fraction, consisting of phenyl-*p*-tolylmethane (IXa) and diphenylmethane (Xa), was then oxidized with chromic acid

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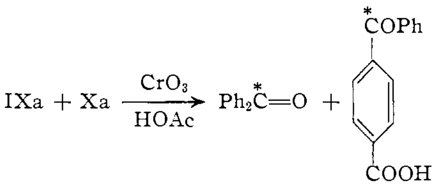
[12] J. G. Burr, THIS JOURNAL, **75**, 5008 (1953), has shown the *p*-tolyl/phenyl migration ratio to be 2.5 in the acetolysis of 2-phenyl-2-*p*-tolylethyl-1-C^{14} tosylate. J. G. Burr and L. S. Ciereszko, *ibid.*, **74**, 5426 (1952), have determined a ratio of 2.0 in the dehydration of 2-phenyl-2-*p*-tolylethanol-1-C^{14}. For the Schmidt reaction the *p*-tolyl/phenyl migration ratios have been variously reported as 3.44 [R. F. Tietz and W. F. McEwen, *ibid.*, 4011 (1955)]; 5.0 [W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950)] and 4.0 [S. N. Ege and K. W. Sherk, *ibid.*, **75**, 354 (1953)]. In the deamination of 2-amino-1-phenyl-1-*p*-tolylethanol, D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954), have reported a *p*-tolyl/phenyl migration ratio of 1.3. Thus, a good average value for this migration ratio would seem to be 3.0.

[13] R. H. Mayor and C. J. Collins, *ibid.*, **73**, 471 (1951).



The benzophenone, separated as the neutral fraction, was assayed for its radioactivity content whenever possible as the 2,4-dinitrophenylhydrazone. This fraction was always difficult to isolate, since it was the minor constituent of the reaction product. The *p*-benzoylbenzoic acid was carefully purified by repeated crystallizations and then assayed for its radioactivity content. The results of these experiments are given in Table II.

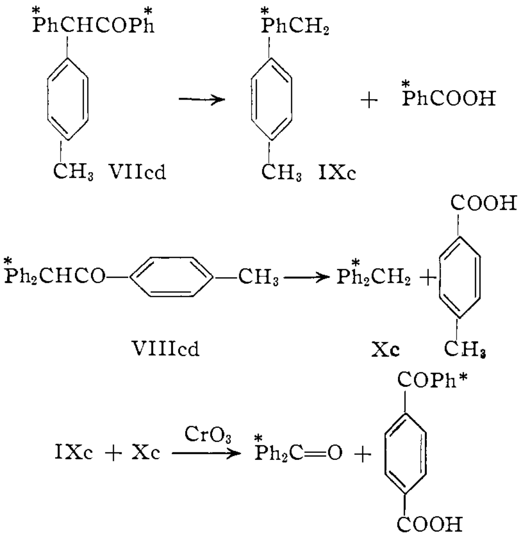
TABLE II

MOLAR RADIOACTIVITIES OF THE OXIDATION FRAGMENTS OF KETONES VII AND VIII OBTAINED BY THE ACTION OF H_2SO_4 OR HCOOH UPON IV, V, VI OR VII

No.	Reactant[a]	Acid reagent	Activity of benzoylbenzoic acid from VII	Activity of benzophenone from VIII
1	IV	96% H_2SO_4 at 0°	0.013	. . .
2	IV	Boiling formic	.115	. . .
3	Va, β-form	96% H_2SO_4 at 0°	.018	0.015
4	Vb, α-form	Boiling formic	.955	.960
5	Va, β-form	Boiling formic	.040	.038
6	VIa	96% H_2SO_4 at 0°	.278	. . .
7	VIa	Boiling formic	.174	. . .
8	VIa	Boiling formic	.165	. . .
9	VIa	Boiling formic	.165	. . .
10	Vc, β-form	96% H_2SO_4 at 0°	.563	. . .
11	Vc, β-form	Boiling formic	.765	. . .
12	VIId[b]	96% H_2SO_4 at 0°	0	. . .

[a] The molar radioactivities of the reactants are taken as 1.000 mc. per mole; the molar radioactivities of the degradation products from each reaction are taken as fractions thereof. [b] *p*-Tolyldesoxybenzoin labeled solely in the phenyl group adjacent to the carbonyl.

Glycol Vc was next accorded the same treatment just described for the chain-labeled glycol, and the ketonic products were subjected to the identical degradative scheme.



In the latter instance the neutral (benzophenone) fractions were discarded, and only the ring-labeled *p*-benzoylbenzoic acid fractions were purified and assayed. The results of these experiments are given also in Table II. Several additional experiments were then performed upon the glycols V and VI using as a solvent 98% formic acid at 27.6 ± 0.1°. Under these conditions the aldehyde IV is a product from each glycol and is quite stable. The aldehyde IV produced in each experiment could be determined by conversion nearly quantitatively to its 2,4-dinitrophenylhydrazone under conditions which did not favor the formation of the derivatives of VII and VIII. The yields of VII and VIII were determined by means of the radioactivity dilution techniques.[13] The results of these experiments are given in Table III.

TABLE III

PER CENT. YIELDS OF ALDEHYDE IV OR KETONES VII AND VIII FROM ACTION OF FORMIC ACID AT 27.6° UPON V OR VI

Compound	Reagent	Yield of 2,4-DNPH deriv. of IV, %	Corrected yield, % of aldehyde	Yield, % VII	VIII
Va	Formic acid, 27.6°			51.0	
Va	Formic acid, 27.6°	44.4			
Vb	Formic acid, 27.6°	44.9			
Vb	Formic acid, 27.6°	43.6			
Va	Formic acid, 27.6°	44.9	49[a,b]		
	Av.	44.5			
Va	Formic acid, 27.6° for 24 hr., then boiled 6 hours			88.3	11.7
VIa	Formic acid, 27.6°			5.05[d]	
VIa	Formic acid, 27.6°	83.4			
VIa	Formic acid, 27.6°	83.7			
VIa	Formic acid, 27.6°	84.7	87[a,c]		
	Av.	83.9			

[a] Although the pure aldehyde could be converted quantitatively to its 2,4-dinitrophenylhydrazone, mixtures of IV, VII and VIII did not give this derivative quantitatively, and the smaller the proportion of IV, the lower the yield. [b] The yield of aldehyde has been taken as 100 − 51 = 49%. [c] The yield of 2,4-dinitrophenylhydrazone has been divided by the correction factor 0.975. [d] Oxidation of this sample followed by radioactivity assay of the *p*-benzoylbenzoic acid obtained demonstrated that 100% of the molar radioactivity of the ketone VIIb was present in the 4-methylbenzhydryl portion of the molecule.

Discussion

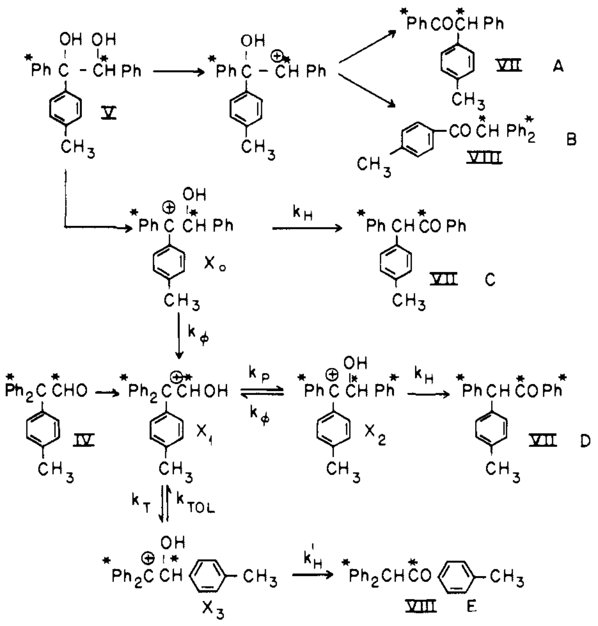
A. The Sulfuric Acid-catalyzed Reaction.—Following are the implications of the pertinent data of the preceding section: 1. Inspection of Tables I and II reveals the yield of each ketone from the different reactants, as well as the fates of the various carbon-14 labels. Given in Chart I is a mechanism for the rearrangements of IV and V which accounts for these facts and which is similar to that proposed[9] for the reaction of triphenylethylene glycol itself in cold, concentrated sulfuric acid. The consequences both of phenyl and of chain labeling are indicated.

2. The contribution of each reaction path of Chart I can now be calculated (see Experimental section). If m_a, m_b, m_c, m_d and m_e are the moles of glycol V which proceed to VII or VIII through

paths A, B, C, D and E, then $m_a = 0.017$, $m_b = 0.003$; $m_c = 0.124$, $m_d = 0.708$, $m_e = 0.148$. If our mechanism is correct, the ratio m_d/m_e should be the same, within experimental error, as the ratio of VII/VIII obtained from the aldehyde IV under the same conditions. From the foregoing results we see that m_d/m_e is 4.8, in excellent agreement with the value 4.7 (Table I, line 1) for the ketonic ratio obtained from aldehyde IV.

3. From Chart I it seems likely that ion X_2, stabilized by phenyl and *p*-tolyl groups, should have a higher stability than ion X_3, stabilized by two phenyl groups. Further, one would expect that k_{To} would be greater than k_ϕ, particularly since the tolyl group of X_3 is migrating to a less stable carbonium center than the phenyl of X_2. Provided, therefore, that k_{H} and k'_{H} are not greatly different in magnitude, it does not seem unreasonable that the ratio m_d/m_e is greater than one, even in the event the *p*-tolyl and phenyl groups exert their normal migrational tendencies[12] of about 3 to 1 in favor of *p*-tolyl (this would correspond to a $k_{\mathrm{T}}/k_{\mathrm{P}}$ ratio of about 1.5, since aldehyde IV contains two phenyls). Now if x_1, x_2 and x_3 are the instantaneous, time-variable concentrations of the ions X_1, X_2 and X_3, respectively, then from Chart I

CHART I



$$dx_2(t)/dt = k_{\mathrm{P}}x_1(t) - k_\phi x_2(t) - k_{\mathrm{H}}x_2(t) \qquad (1)$$

$$dx_3(t)/dt = k_{\mathrm{T}}x_1(t) - k_{\mathrm{Tol}}x_3(t) - k'_{\mathrm{H}}x_3(t) \qquad (2)$$

Since the reactions of Chart I were, in our experiments, allowed to go to completion, equations 1 and 2 are now integrated between the limits zero and infinity. If we replace the values $\int_0^\infty x_1(t)dt$, $\int_0^\infty x_2(t)dt$ and $\int_0^\infty x_3(t)dt$ with the "integration areas" s_1, s_2 and s_3, then, since at $t = 0$ and at $t = \infty$, the concentrations of all intermediates are zero

$$k_{\mathrm{P}}s_1 - k_\phi s_2 - k_{\mathrm{H}}s_2 = 0 \qquad (3)$$

$$k_{\mathrm{T}}s_1 - k_{\mathrm{Tol}}s_3 - k'_{\mathrm{H}}s_3 = 0 \qquad (4)$$

Thus

$$s_2 = \frac{k_{\mathrm{P}}s_1}{k_\phi + k_{\mathrm{H}}} \qquad (5)$$

$$s_3 = \frac{k_{\mathrm{T}}s_1}{k_{\mathrm{Tol}} + k'_{\mathrm{H}}} \qquad (6)$$

At complete reaction the ratio m_d/m_e is given by

$$\frac{m_d}{m_e} = \frac{k_{\mathrm{H}}s_2}{k'_{\mathrm{H}}s_3} \qquad (7)$$

It then readily follows[14] that

$$\frac{k_{\mathrm{T}}}{k_{\mathrm{P}}} = \frac{k_{\mathrm{H}}}{k_\phi} \times \frac{k_{\mathrm{Tol}}}{k'_{\mathrm{H}}} \times \frac{m_e}{m_d} \times \left[\frac{1 + \frac{k'_{\mathrm{H}}}{k_{\mathrm{Tol}}}}{1 + \frac{k_{\mathrm{H}}}{k_\phi}}\right] \qquad (8)$$

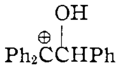
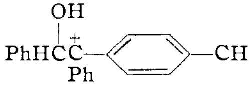
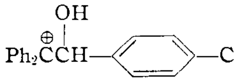
4. The ratio $k_{\mathrm{T}}/k_{\mathrm{P}}$, the true value of the migratory abilities of the one *p*-tolyl and the two phenyl groups of aldehyde IV, should be capable of calculation if the additional ratios k_{H}/k_ϕ and $k_{\mathrm{Tol}}/k'_{\mathrm{H}}$ can be determined experimentally. The ratio k_{H}/k_ϕ may be obtained directly from the contributions of paths A to E which are given in paragraph two of this section

$$\frac{k_{\mathrm{H}}}{k_\phi} = \frac{m_c}{m_d + m_e} = \frac{0.124}{0.708 + 0.148} = 0.145$$

The ratio $k_{\mathrm{Tol}}/k'_{\mathrm{H}}$ may be evaluated in principle by considering the rearrangement of glycol VIa in cold, concentrated sulfuric acid, in a manner which will be discussed later in this section for the formic acid-catalyzed reactions. The ratio $k_{\mathrm{Tol}}/k'_{\mathrm{H}}$ for the sulfuric acid-catalyzed reaction, however, is so large that the error inherent in the calculation precludes an accurate experimental determination. It is possible, despite this fact, to estimate probable values for $k_{\mathrm{Tol}}/k'_{\mathrm{H}}$ from available data. Given in Table IV are $k_{\mathrm{Ar}}/k_{\mathrm{H}}$ ratios for three different carbonium ions. We assume that in the sulfuric acid-catalyzed reaction $k_{\mathrm{Tol}}/k'_{\mathrm{H}}$ can be approximated by either of the proportions

TABLE IV

RATIOS OF ARYL TO HYDROGEN MIGRATION FOR VARIOUS CARBONIUM IONS

	Carbonium ion	$k_{\mathrm{Ar}}/k_{\mathrm{H}}$ in H_2SO_4	$k_{\mathrm{Ar}}/k_{\mathrm{H}}$ in HCOOH	Reference
1.	 $Ph_2\overset{\oplus}{C}\overset{OH}{\overset{\mid}{C}}HPh$	7.33	1.44	9
2.	 $PhH\overset{OH}{\overset{\mid}{C}}\overset{+}{\underset{Ph}{C}}-C_6H_4-CH_3$	6.9[a]	1.15	This paper
3.	 $Ph_2\overset{\oplus}{C}\overset{OH}{\overset{\mid}{C}}H-C_6H_4-CH_3$	47–56 (calcd., see text)	9.3	This paper

[a] This value is the reciprocal of k_{H}/k_ϕ = (0.145) calculated as indicated in the text.

$$k_{\mathrm{Tol}}/k'_{\mathrm{H}}\colon 9.3 = 7.33:1.44$$

$$k_{\mathrm{Tol}}/k'_{\mathrm{H}}\colon 9.3 = 6.9:1.15$$

from which values of 47 and 56 are obtained. Thus

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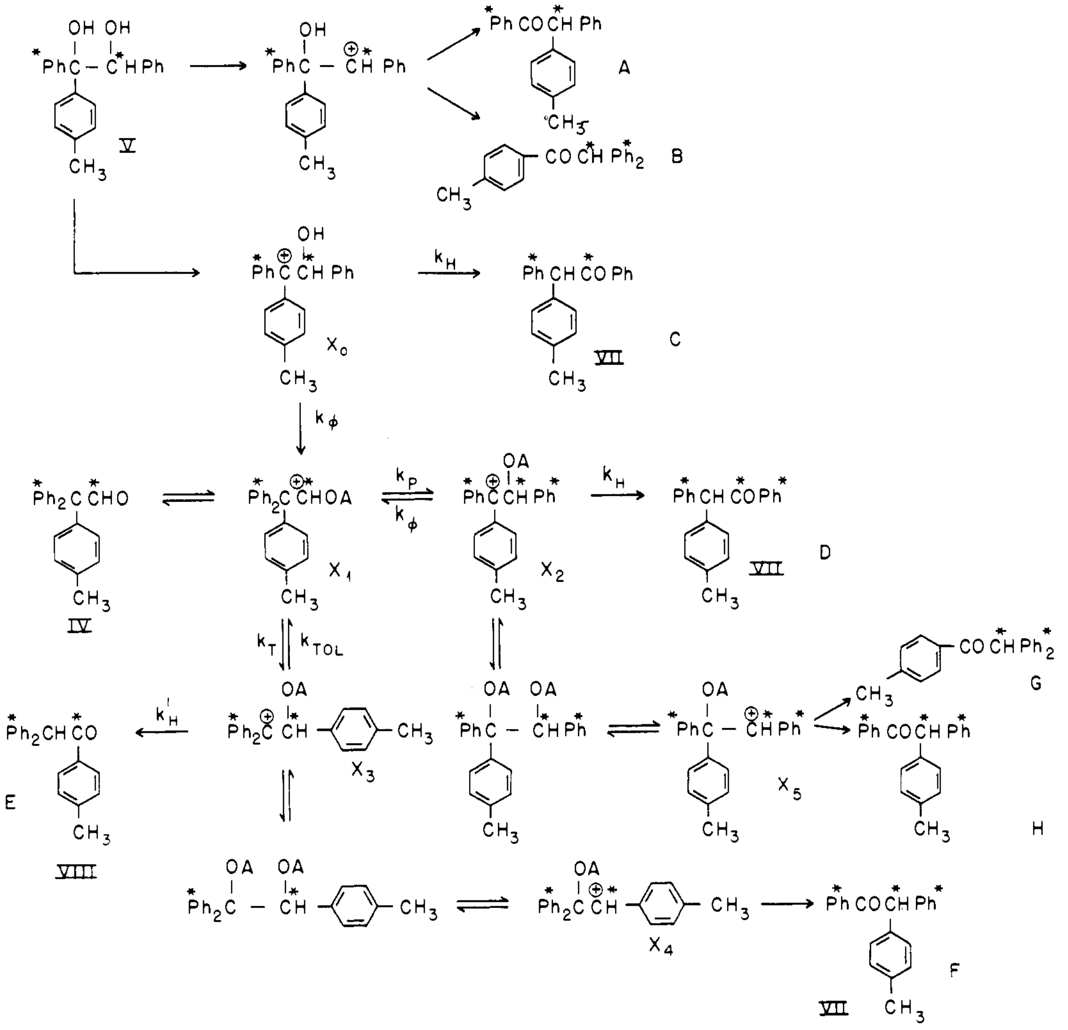
[14] Equation 8 was obtained by use of the "area theorem" of John Z. Hearon, which is evident in the derivation of equation 3 from equation 2. The authors are indebted to Dr. Hearon for pointing out the utility of this theorem in chemical kinetics and for the derivation of equation 8. It should be noted that no "steady-state" assumptions have been necessary in arriving at equation 8.

CHART II



k_T/k_P (equation 8) is calculated to be either 1.3 or 1.6, corresponding to p-tolyl/phenyl migration ratios of 2.6 and 3.2, respectively. These latter values are normal[11] and quite in agreement with the qualitative discussion given earlier in this section concerning the mechanism (Chart I) of the aldehyde–ketone rearrangement.

B. The Formic Acid-catalyzed Reactions.—Following are the implications of the data of Tables I, II and III for the formic acid-catalyzed rearrangements of IV, V and VI.

1. The reactions of IV, V and VI in boiling formic acid must be extremely more complicated than the reactions of these same compounds in sulfuric acid. The most significant difference in the radiochemical results for the two cases lies in the fact that the chain-label of aldehyde IV undergoes scrambling in boiling formic acid. This must mean, therefore, that the majority of the scrambling of the chain label of Va takes place after conversion of Va to the conjugate acid of aldehyde IV (that is, to ion X_1). This conclusion follows from lines 2, 4 and 5 of Table II. To accommodate this conclusion the mechanism outlined in Chart II—in which the group A may be either formyl or hydrogen[15]—is proposed.

2. The contributions of the reaction paths of Chart II can now be calculated. If m_a to m_f represent the moles of glycol V which proceed to product through paths A to F, and neglecting the unim-

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[15] Glycol Va, in formic acid, can probably either esterify its secondary hydroxyl group to give a formate or lose its tertiary hydroxyl to form ion X_0. The direct loss of secondary hydroxyl to form the corresponding carbonium ion is undoubtedly of insignificant importance. If the esterification reaction is slow compared to the formation of ion X_0, then paths A and B (Chart II) will likewise be of no importance. Ion X_0 can rearrange as shown (Chart II) to X_1 and the latter can esterify by the process $X_1\,[A = H] \rightarrow IV \rightarrow X_1\,[A = HCO-]$. Internal return [S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165, 2171 (1952); S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952)] can then occur as shown in Chart II, thus favoring reformation of the secondary carbonium ions with attendant aryl migration to a greater extent than is possible from the unesterified glycol itself. This hypothesis is strengthened by the observation, to be presented later, that a monoformate of triphenylethylene glycol can be isolated from a formic acid solution of that compound. From a formic acid solution of glycol V itself, a mixture of compounds, probably formates, has also been obtained. If the esterification reaction competes favorably with tertiary hydroxyl removal, then internal return can occur before formation of ion X_0, and some scrambling could take place through paths A and B.

portant contributions of paths A, B and G,[16] then it can be shown (see Experimental section for calculations) that: $m_c = 0.466$, $m_d = 0.366$, $m_e = 0.120$, $m_f = 0.040$. If the mechanism of Chart II is correct, then $(m_d + m_f)/m_e$ (which equals 3.45) should be the same, within experimental error, as the ratio of ketones VII and VIII obtained from aldehyde IV itself under these same conditions. That the latter value (3.48, from Table I, line 2) is in such close agreement with our calculated ratio, is thus excellent evidence for the validity of the mechanism.

3. It is now important to determine whether the *p*-tolyl/phenyl migration ratio, given by $2k_T/k_P$ (from equation 8), can be shown to be greater than one. The ratio k_H/k_ϕ may be evaluated directly

$$\left[\frac{k_H}{k_\phi}\right]_{100^\circ} = \frac{m_c}{m_d + m_e + m_f} = \frac{0.466}{0.366 + 0.120 + 0.048} = \frac{0.466}{0.534} = 0.87$$

It is interesting that from Table III, representing the formic acid-catalyzed reaction at 27.6°, the ratio k_H/k_ϕ at that temperature may be determined as

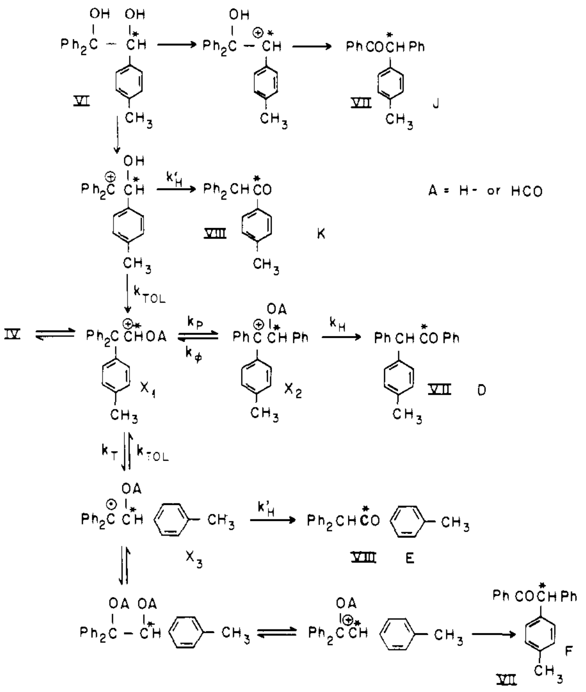
$$\left[\frac{k_H}{k_\phi}\right]_{27.6^\circ} = \frac{49}{51} = 0.96$$

It thus appears that k_H/k_ϕ is reasonably constant between these two temperatures. We may calculate also from Table III

$$\left[\frac{k_{Tol}}{k'_H}\right]_{27.6^\circ} = \frac{87}{13–5} = 11$$

It is possible to determine $[k_{Tol}/k'_H]_{100^\circ}$ from the data relative to the rearrangement of VIa of Tables I and II and from the calculated values of the contributions of the paths of Chart II. Given in Chart III is an over-all mechanism for the rearrangement of glycol VI, based upon the scheme of Chart II. Those paths whose contributions are less than a very small percentage of the total reaction (see footnote 15) have been omitted. We have already shown that once ion X_1 is formed, whether from the aldehyde IV or from the glycol V, it rearranges to VII and VIII in the same ratio when the conditions of the reaction are maintained constant. It is possible, therefore, to distinguish the contribution of path K from that of path E (Chart III), since we know the ratio $(m_d + m_f)/m_e$ from IV or V under these same conditions. Thus, if m_j, m_d and m_f are the mole fractions of the total reaction product proceeding to ketone VII through paths J, D and F, and m_k and m_e are the mole fractions of total reaction product proceeding to ketone VIII through paths K and E, then (see Experimental section for calculations): $m_j = 0.040$, $m_k = 0.093$, $m_d = 0.596$, $m_e = 0.193$, $m_f = 0.078$ and $[k_{Tol}/k'_H]_{100^\circ} = (m_d + m_e + m_f)/m_k = 9.3$, in good agreement with the value $[k_{Tol}/k'_H]_{27.6^\circ} = 11$.

Chart III



4. Equation 8, the exact solution for the mechanism of Chart I, obviously requires modification before it can be applied to the formic acid-catalyzed reaction, the mechanism for which is given in Chart II. This is true because path F has been recognized as an important contributor to the over-all reaction. It might be anticipated that path F should affect the final ratio k_T/k_P in equation 8 by only 9%, the extent to which this path contributes to the reaction. Since the products both from paths E and F proceed through ion X_3, however, the error involved is much greater than 9% because $m_f/(m_e + m_f) \times 100 = 29\%$. A further difficulty in applying equation 8 to the present data is that the ratio k_H/k_ϕ (Chart II) might not be the same in ions X_0 and X_2 when A = H and A = HCO. A rough estimate of k_T/k_P from equation 8 is 2.2, however, using $k_H/k_\phi = 0.87$, $k_{Tol}/k'_H = 9.3$ and the product ratio $(m_e + m_f)/m_d = 0.46$ This corresponds to a *p*-tolyl/phenyl migration ratio of 4.4. It seems likely, despite the uncertainties involved, that the true *p*-tolyl/phenyl migration ratio is thus greater than one.

C. General Conclusions.—From the discussion in Parts A and B of this section it has been shown that whether the conjugate acid of aldehyde IV (ion X_1) is generated from IV itself or from glycol V, it yields the same ratio of ketones VII/VIII. These ratios observed from IV, and calculated from the radiochemical data for the reactions of Va and Vc are, respectively, 4.7 *vs.* 4.8 (sulfuric acid) and 3.5 *vs.* 3.5 (formic acid). The agreement in each case is excellent and offers compelling evidence for the reliability of the mechanisms given in Charts I and II.

The *p*-tolyl/phenyl migration ratios in the aldehyde–ketone rearrangement of IV have been estimated from equation 8 as greater than one when either sulfuric acid or formic acid is the catalyst. A

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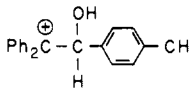
[16] Although paths A and B undoubtedly contribute to the over-all mechanism, their total participation is probably less than 1%. Similarly, although there is definite evidence that path G contributes to the mechanism (since 4% of the ketone VIII which is formed from Va contains its carbon-14 in the benzhydryl portion of the molecule), the extent of participation of path G must be only (0.04) × (0.12) or less than 0.5% of the total reaction. If one assumes that the ratio m_h/m_g is about 3 (the normal ratio of tolyl/phenyl migratory abilities[12]), then path H must participate to the extent of less than 1.5% of the total reaction. For these reasons, we neglect the contributions of paths A, B, G and H in order to simplify the calculation.

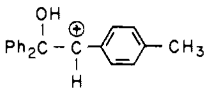
ratio of greater than one is normal[12] for *p*-tolyl *versus* phenyl migration and indicates that the aldehyde–ketone rearrangement—which has previously been considered anomalous because of an apparent reversal[4,5,8] of the usual mobility sequence—can be explained as another example of an acid-catalyzed rearrangement in which the normal order of migratory abilities is maintained. This fact is taken as additional strong evidence for the validity of the mechanisms of Charts I and II.

The values of k_{Ar}/k_H (see Table IV) vary with the catalyst employed and are greater for the sulfuric acid than for the formic acid-catalyzed reactions. This observation is consistent with those reported in a previous paper[9] and tentatively rationalized on the basis of a steric repulsion to aryl migration during the concerted migration of aryl to form a triarylmethyl group.

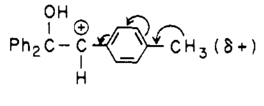
From the data of Table II it can be seen that the glycol VIa has undergone 28% scrambling of its label on conversion, in sulfuric acid, to VII. This corresponds to 23% secondary hydroxyl removal, since the yield of VII in this experiment was 83%. We have concluded (see Part A of the Discussion) that both secondary and tertiary hydroxyl removal from V and VI are irreversible processes in cold, concentrated sulfuric acid; thus the ratio 77/23 = 3.35/1 is a measure of the relative ease of formation, in this solvent, of ions Y and Z. From the data of Table III it is clear that in formic acid at 27.6° there can be a maximum of 5% secondary hydroxyl removal from VIa (Y/Z = 19/1), since this is the yield under these conditions of VIIb labeled only in 4-methylbenzhydryl portion of the chain. It is clear, therefore, that a tolyl group is much more able to stabilize ion Z relative to Y in concentrated sulfuric than in formic acid. It may be that formic acid, with a weaker ionizing ability than sulfuric, is capable of removing chiefly only the less firmly bound tertiary hydroxyl group of VI. Sulfuric acid, with a high ionizing power, is able to effect removal of both hydroxyls, being assisted in this by the tolyl group, as symbolized by either of the following;

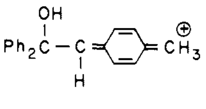


Y



Z





The tolyl group, being a better electron donor than phenyl, might be expected, in sulfuric acid, to have those electrons proportionately more available than those of phenyl to distribute the charge of the positive carbonium center. This hypothesis is supported by the observation[9] that the action of cold, concentrated sulfuric acid upon triphenylethylene glycol causes a negligible proportion of secondary hydroxyl removal.

Implicit in our calculations of the contributions of the various reaction paths of Charts I, II and III has been the assumption that the two diastereomers of ring-labeled 1,2-diphenyl-1-*p*-tolylethylene glycol (Vc) proceed to products VII and VIII with identical consequences. This assumption is not inconsistent with the work of Curtin (*cf.* references 7 and 12 and previous papers) on the *cis*-effect, since even if the reaction $X_0 \rightarrow X_1$ (Charts I, II and III) were a concerted process, the transition states for this reaction (corresponding to the two diastereomers of Vc) would be expected to be sterically equivalent, owing supposedly to the equivalent effective bulk of the phenyl and *p*-tolyl groups. To the extent also that rearrangement of the glycol V approaches the limiting carbonium ion mechanism illustrated in Charts I, II and III, the *cis*-effect would be expected to approach zero. This assumption that the diastereomeric glycols Vc rearrange identically finds further support (a) in the experimental observations (Table I) that the α- and β-forms (Vb and Va) of the chain-labeled glycol rearrange to VII and VIII with experimentally indistinguishable consequences and (b) in the agreement between the observed ratios of VII to VIII (4.7 in sulfuric acid and 3.5 in formic acid) upon rearrangement of aldehyde IV and the calculated ratios (4.8 in sulfuric acid and 3.5 in formic acid) obtained from the double-labeling experiments upon glycol V.

Current research upon the pinacol rearrangement problem is devoted to testing the generality of the mechanism outlined in this paper.

Experimental

1,2-Diphenyl-1-*p*-tolylethylene-1-C^{17} Glycol (Vb) α-Form.[17]—Carbonyl-labeled desoxybenzoin was converted to desyl bromide by the general method of Staedel and Kleinschmidt.[18] The carbon disulfide solvent was removed by distillation in an atmosphere of CO_2, and without purification the crude desyl bromide was converted to benzoin-C^{14} by the method of Ward[19]; the yield of material of m.p. 125–130° was 79%. Benzoin-C^{14}, 0.12 mole, was added to the Grignard reagent prepared from 0.37 mole of *p*-bromotoluene and 0.37 mole of magnesium. After being heated at reflux temperature for 1 hr., the reaction mixture was treated with ice and ammonium chloride solution. The glycol Va was isolated, dissolved in ethanol and the solution was decolorized with Norite. After four crystallizations the glycol had a m.p. of 167–169.5°[20] and a radioactivity assay of 0.8630 ± 0.0006 mc./mole.

1,2-Diphenyl-1-*p*-tolylethylene-2-C^{14} Glycol (Va) β-Form.—Benzyl *p*-tolyl ketone labeled in the methylene group was prepared by the Friedel–Crafts synthesis from phenylacetyl-2-C^{14} chloride and toluene. It was converted to 4-methyldesyl bromide and thence to 4-methylbenzoin-C^{14} by the methods described in the preceding section. The 4-methylbenzoin (0.033 mole) was added to the Grignard reagent prepared from 0.15 mole of bromobenzene and 0.15 mole of magnesium. When the vigorous reaction had stopped, 200 ml. of tetrahydrofuran was added and the ether was removed by distillation. The reaction mixture was heated at 50° for 18 hr. and the Grignard complex was hydrolyzed with ammonium chloride solution. The crude glycol Va was extracted from the aqueous layer with ether, the ether was removed in a current of air and the glycol was dissolved in ethanol. After clarification with Norite and four crystallizations from alcohol, the product had a m.p. of 187–188°[21] and a radioactivity assay of 2.286 ± 0.008 mc./mole.

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[17] We are indebted to Dr. H. J. Schaeffer for preparing this compound.

[18] W. Staedel and F. Kleinschmidt, *Ber.*, **13**, 837 (1880).

[19] A. M. Ward, *J. Chem. Soc.*, 1549 (1929).

[20] Reference 10a gives a m.p. 168°; reference 10b gives m.p. 161–162°.

[21] A. McKenzie and A. L. Kelman, *J. Chem. Soc.*, 412 (1934), gives a m.p. 181–182°.

1,2-Diphenyl-1-*p*-tolylethylene Glycol β-Form (Vc), 1-Phenyl-labeled.—4-Methylbenzoin (0.018 mole) was added to the Grignard reagent made from 0.028 mole of carbon-14 labeled bromobenzene and 0.03 mole of magnesium. The reaction was completed as described for the chain-labeled glycols Va and Vb. The phenyl-labeled glycol Vc had a m.p. of 187–188° and a radioactivity assay of 1.209 ± 0.001 mc./mole.

1,1-Diphenyl-2-*p*-tolylethylene-2-C^{14} Glycol (VI).[22]—*p*-Methylacetophenone (0.56 mole) labeled in the carbonyl position was oxidized to *p*-methylphenylglyoxal with SeO_2 by an adaptation of the method of Riley and Gray.[23] After removing the selenium by filtration, the *p*-methylphenylglyoxal was not isolated but was rearranged to *p*-methylmandelic acid by adding to its ethanol solution 0.56 mole of NaOH in 110 ml. of ethanol. The reaction mixture was stirred for 1 hr., then concentrated to 100 ml. by evaporating the ethanol in a current of air. Pure *p*-methylmandelic acid, m.p. 148°, was recovered in 24% yield. The methyl ester (0.132 mole) of *p*-methylmandelic acid, prepared from the acid and diazomethane, was added to 0.53 mole of phenylmagnesium bromide. The reaction was forced to completion in the tetrahydrofuran solution as described in previous sections. The glycol VI was purified by five crystallizations from ethanol, m.p. 195–196°. The radioactivity assay was 3.812 ± 0.010 mc./mole.

Diphenyl-*p*-tolylacetaldehyde-1-C^{14} (IV).—1,1-Diphenyl-2-*p*-tolylethylene-2-C^{14} glycol (VIa), 2 g., was mixed with 300 ml. of 98% formic acid. The mixture was stirred at room temperature for 24 hr. During this time the solution became yellow and the glycol slowly dissolved. Water was added until the volume was 800 ml. and the precipitate was extracted twice with ether. The ether solution was extracted with water followed by sodium bicarbonate solution. The oily material remaining after evaporation of the ether was dissolved in aqueous alcohol. Crystallization was accomplished by allowing this alcoholic solution to stand and slowly evaporate for one week. Several batches of aldehyde prepared in this way were combined and recrystallized twice from aqueous alcohol. The aldehyde had a m.p. of 60–61° and a radioactivity assay of 3.798 mc./mole.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.33. Found: C, 88.05; H, 5.92.

The 2,4-dinitrophenylhydrazone of aldehyde IV had a m.p. of 181–183°.

Anal. Calcd. for $C_{27}H_{22}N_4O$: C, 69.51; H, 4.75. Found: C, 69.40; H, 5.11.

Radiochemical Structure Determination of IV, Va, Vb, Vc and VI.—Glycol Vb was oxidized with excess $KMnO_4$ in acetone. The benzoic acid fraction was discarded and the neutral fraction containing 4-methylbenzophenone was treated with 2,4-dinitrophenylhydrazine reagent. After two crystallizations of the 2,4-dinitrophenylhydrazone, the assay was 0.7558 ± 0.0001 mc./mole. Thus the tertiary carbon position contained 87.5% of the radioactivity. This distribution of radioactivity was taken into consideration in the rearrangement experiments. Glycol Va was oxidized to benzoylbenzoic acid with chromic acid. After purification the benzoylbenzoic acid was assayed and found to be non-radioactive. All the radioactivity was in the 2-position. Glycol Vc was oxidized in the same fashion. The assay of the purified benzoylbenzoic acid was found to be 1.204 ± 0.001 mc./mole. Glycol VI was oxidized to benzophenone and terephthalic acid with chromic acid. The 2,4-dinitrophenylhydrazone derivative of the benzophenone was found to be non-radioactive. The assay of the dimethyl ester of the terephthalic acid was 3.787 ± 0.012 mc./mole. Thus the 2-position contained all the radioactivity in glycol VI. The radiochemical structure of aldehyde IV follows from the sulfuric acid-catalyzed rearrangement to VII and VIII and the ensuing degradation of these ketones (Table II).

Rearrangement of Compounds IV, Va, Vb, Vc and VI with Acid Catalysts. (1) **Concentrated Sulfuric Acid.**—In a typical experiment 3.116 g. of glycol Va was added to concentrated sulfuric acid, which had been cooled previously to 0°. The mixture was stirred by means of a magnetic stirring bar for 2 hr., during which time the reaction flask was immersed in an ice-bath. The contents of the flask were poured over 100 g. of cracked ice, and the resulting slurry was extracted with six 50-ml. portions of ether. The ether solution was washed with aqueous bicarbonate and then was evaporated to dryness. The concentrate was taken up in ethanol and diluted to 250 ml. in a volumetric flask. After the solution was mixed completely, it was divided into three aliquots to be used for determining the yields of VII and VIII and for determining the carbon-14 distribution in these products.

(2) **Boiling Formic Acid.**—Glycol Va (1.040 g.) was mixed with 10 ml. of 98–100% formic acid and the mixture was heated at reflux temperature for 20 hr. The products were not separated from the acid. The solution was diluted to 250 ml. in a volumetric flask.

(3) **Formic Acid at 27.6°.**—Glycol Va (2.000 g.) was added to a flask containing 300 ml. of 98–100% formic acid which had been in a constant temperature bath at 27.6° for 1 hr. The reaction mixture was stirred at 27.6° with a magnetic bar for 24 hr. At the end of this time the clear yellow solution was diluted with twice its volume of water, and the precipitated material was removed by six extractions with ether. The ether solution was washed with sodium carbonate solution and the ether was removed by evaporation in a current of air. There remained an oily material which was either dissolved in a small quantity of alcohol for determining the yield of aldehyde IV or it was dissolved in a measured volume of alcohol as required for isotopic dilution technique.

Yield Determinations. (1) **Ketones VII and VIII.**—An aliquot of the ethanol solution of products from the various acid-catalyzed reactions was added to a carefully weighed portion of the appropriate non-radioactive ketone. After ensuring complete solution, the solvent was evaporated and the ketone was reisolated and crystallized from ethanol (five times, once after Norite treatment) until the melting point and radioactivity assays were constant. The yields of VII and VIII were calculated from the assay data as described previously[9] and the results are given in Table I. The experiments are summarized in Table V.

(2) **Aldehyde IV.**—To the alcohol solution of the products of a reaction of glycol in formic acid at 27.6° was added an excess of 2,4-dinitrophenylhydrazine reagent. The mixture was allowed to stand for 2 days at room temperature. The crystalline 2,4-dinitrophenylhydrazone of the aldehyde which formed was collected on a weighed sintered glass filter, washed with a small portion of fresh alcohol, dried in vacuum and weighed. The yield of aldehyde was calculated from the weight of this derivative. A sample of the pure aldehyde gave a 99% yield of its 2,4-dinitrophenylhydrazone when no ketones VII and VIII were present. These ketones do not yield 2,4-dinitrophenylhydrazone under these conditions.

Determination of Distribution of Carbon-14 in Ketones VII and VIII.—In a typical experiment, the solvent was evaporated from an aliquot of the products of a rearrangement reaction. To the residue was added 25 ml. of 25% potassium hydroxide in methanol. The solution was heated at reflux temperature for 24 hr. Water was added to the reaction mixture and the neutral organic fraction consisting of diphenylmethane and phenyl-*p*-tolylmethane was extracted with ether. After evaporation of the ether, the residue was dissolved in 10 ml. of acetic acid and to it was added a solution of chromic acid in acetic acid. The mixture was heated on a steam-bath for 1 hr., after which time it was diluted with water and the precipitated organic material was extracted with ether. The ether solution was washed with three small portions of sodium carbonate solution and saved. The combined sodium carbonate extracts were treated with Norite and neutralized with hydrochloric acid. The precipitated benzoylbenzoic acid was collected on a filter and recrystallized from aqueous alcohol, dried and assayed for radioactivity. All of these *p*-benzoylbenzoic acid fractions possessed sharp melting points of 196–197°, when observed on a Kofler hot-stage. The experiments are summarized in Table VI. The ether solution from above was concentrated to recover benzophenone. This was converted to its 2,4-dinitrophenylhydrazone. In many cases five crystallizations were not sufficient to raise the m.p. above 210°. For this reason assays for the benzophenone fractions could not always be obtained and thus are not included in all of the experiments of Tables II, III and VI.

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[22] J. F. Eastham, private communication.

[23] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509.

TABLE V

SUMMARY OF YIELD DETERMINATION EXPERIMENTS

Starting compound	Radioactivity, mc./mole	Wt., g.	Experimental conditions	Time, hr.	Aliquot used to determine yield of ketone		Weight of dead ketone added to aliquot		Radioactivity of diluted ketone	
					VII	VIII	VII	VIII	VII	VIII
Va, β-form	2.286 ± 0.008	3.1163	40 ml. of 96% H_2SO_4 at 0°	4	1/10	1/5	0.5411	1.2506	0.6950 ± 0.0051	0.1572 ± 0.0016
Va, β-form	2.243 ± .036	0.6085	20 ml. of 96% H_2SO_4 at 0°	3.5	1/4	3/4	.4841	0.9768	.4392 ± .0028	.1246 ± .0004
Vb, α-form	0.8630 ± .0006	0.6185	20 ml. of 96% H_2SO_4 at 0°	2	1/4	3/4	.5706	.9580	.1523 ± .0002	.0543 ± .0002
Va, β-form	2.270 ± .031	1.0398	10 ml. boiling formic acid	21	1/8	3/8	.6545	1.5906	.3223 ± .0023	.0631 ± .0006
Vb, α-form	0.8848 ± .0053	1.1075	40 ml. boiling formic acid	22	1/8	3/8	.5115	0.9587	.1616 ± .0001	.0400 ± .0003
VIa	3.812 ± .010	2.9987	50 ml. of 96% H_2SO_4 at 0°	1	1/5	1/5	1.2480	1.1280	1.046 ± .002	.301 ± .001
VIa	3.812 ± .010	1.1218	30 ml. boiling formic acid	2	1/4	1/4	1.4656	1.2012	0.7052 ± .0024	.3742 ± .0007
VIa	3.812 ± .010	0.8407	30 ml. boiling formic acid	2	1/4	3/4	1.7409	1.9556	.2859 ± .0001	.3092 ± .0013
IV	3.800 ± .013	1.0988	40 ml. of 96% H_2SO_4 at 0°	2	1/5	1/5	1.0311	1.0181	.5390 ± .0010	.1310 ± .0006
IV	3.800 ± .018	0.8767	20 ml. boiling formic acid	3	1/5	1/5	0.8246	0.8573	.5505 ± .0001	.1697 ± .0005
Va, β-form	2.031 ± .010	1.0742	150 ml. formic acid at 27.6°	24	1		1.1857		.6153 ± .0003	
Va, β-form	2.031 ± .010	0.8715	140 ml. formic acid at 27.6° for 24 hr. then boil 2 hr.		2/5	3/5	1.1256	1.0700	.4182 ± .0018	.1050 ± .0002
VIa	3.812 ± .010	1.0160	150 ml. formic acid at 27.6°	24	1		1.0177		0.1728 ± .0017	

TABLE VI

SUMMARY OF RADIOACTIVITY DISTRIBUTION DETERMINATIONS

Starting compound	Radioactivity of starting compound, mc./mole	Radioactivity at tertiary carbon position, mc./mole	Experimental conditions	Radioactivity of benzoylbenzoic acid fraction of products	Radioactivity of benzophenone fraction of products
IV	3.800 ± 0.013		96% H_2SO_4 at 0°	0.0392 ± 0.0001	
IV	3.800 ± .013		Boiling formic acid	.4377 ± .0001	
Va, β form	2.286 ± .008	0.001	96% H_2SO_4 at 0°	.0419 ± .0004	0.0336 ± 0.0001
Vb, α form	0.8848 ± .0053	.702 ± .0034	Boiling formic acid	.6710	.6744 ± .0042
Va, β form	2.270 ± .031	.001	Boiling formic acid	.0913	.0799
Vc, β form	1.209 ± .001	1.204 ± .001	96% H_2SO_4 at 0°	.6805 ± .0001	
Vc, β form	1.209 ± .001	1.204 ± .001	Boiling formic acid	0.925 ± .001	
VIa	3.812 ± .010	0.0121	96% H_2SO_4 at 0°	1.059 ± .004	
VIa	3.812 ± .010	.0121	Boiling formic acid	0.6637 ± .0014	
VIa	3.812 ± .010	.0121	Boiling formic acid	.626 ± .001	
VIa	3.812 ± .010	.0121	Boiling formic acid	.625 ± .001	
VIa	3.812 ± .010	.0121	Formic acid at 27.6° for 24 hr.	.158 ± .002[a]	

[a] The benzoylbenzoic acid was obtained by degradation of the *p*-tolyldesoxybenzoin from the isotope dilution experiment in the last line of Table V.

Calculations of the Contributions of Each Path of Charts I, II and III. A. Chart I. The Sulfuric Acid-catalyzed Reaction of Glycol V.—If c is the mole fraction of VII formed through path C (Chart I), then $(0.98 - c)$ is the mole fraction of VII formed through path D (since 2% of the reaction is assumed from line 3, Table II, to proceed through paths A and B). It then follows from Chart I that

$$c + (0.98 - c)0.5 = 0.563 \text{ (line 10, Table II)}$$

and $c = 0.146$, $(0.98 - c) = 0.834$. Since ketone VII, formed through paths A, C and D, represents 84.9% of the product and ketone VIII, formed through paths B and E, represents 15.1% of the product (see Table I, lines 3, 4 and 5) it readily follows that the mole fractions of reactant converted to the products through each path are: $m_a = 0.017$, $m_b = 0.003$, $m_c = 0.124$, $m_d = 0.708$, $m_e = 0.148$.

B. Chart II. The Formic Acid-catalyzed Reaction of Glycol V.—If c, d and f are the mole fractions, respectively, of ketone VII formed through paths C, D and F (Chart II), then

$$\begin{aligned} 0.765 &= c + 0.5d + 0.5f \text{ (line 11, Table II)} \\ d + f &= 1 - c \\ f &= (1 - c)0.115 \\ d &= (1 - c)0.885 \end{aligned}$$

and $c = 0.530$, $d = 0.416$ and $f = 0.054$, thus m_c, m_d, m_e and m_f, the contributions of paths C, D, E and F, are

$$\begin{aligned} m_c &= 0.530\ (0.88) = 0.466 \\ m_d &= 0.416\ (0.88) = 0.366 \\ m_e &= 0.120 \\ m_f &= 0.054\ (0.88) = 0.048 \end{aligned}$$

C. Chart III. The Formic Acid-catalyzed Reaction of Glycol VI.—If m_j, m_d and m_f are the mole fractions of the total reaction product proceeding to ketone VII through paths J, D and F, and m_k and m_e are the mole fractions of total reaction product proceeding to ketone VIII through paths K and E, then

$$\begin{aligned} m_j + m_d + m_f &= 0.714 \text{ (lines 9 and 10, Table I)} \\ m_k + m_e &= 0.286 \text{ (lines 9 and 10, Table I)} \\ \frac{m_j + m_f}{m_j + m_f + m_d} &= 0.165 \text{ (line 8, Table II)} \\ m_d + m_f &= m_d \left[\frac{0.414}{0.366}\right] \text{ (from Chart II, see Section B above)} \end{aligned}$$

and

$$\frac{m_d + m_f}{m_e} = 3.5 \text{ (line 2, Table I)}$$

from which: $m_j = 0.040$, $m_k = 0.093$, $m_d = 0.596$, $m_e = 0.193$, $m_f = 0.078$.

Analytical Determinations.—The carbon and hydrogen analyses were performed by the Huffman Microanalytical Laboratories, Wheatridge, Colorado. The carbon-14 assays were performed in the usual[1,9] manner.

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