followed by a rate-determining bimolecular reaction of the diazonium ion so produced with water, or with anions such as nitrate or chloride, to give glycolic ester or one of its derivatives. In nonpolar solvents, such as benzene, reaction with carboxylic acids again involves a preliminary reversible proton transfer, followed by reaction of the diazonium ion with a second mole of acid.[12] Roberts[13] has recently reported that the reaction of diphenyldiazomethane with acids in alcohol shows a general acid catalysis and has suggested for this reaction a mechanism involving the initial production of a diazonium ion which, after loss of nitrogen to give the benzhydryl carbonium ion, is ultimately converted to benzhydryl ethyl ether.

In view of these findings it is not unreasonable to suppose that the initial stage of the reactions studied here consists in a reversible proton transfer between diazoketone and solvent

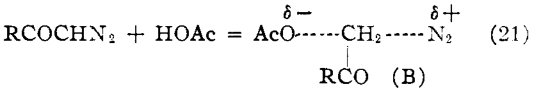
$$RCOCHN_2 + HOAc = \underset{(A)}{RCOCH_2N_2^{\oplus}} + OAc^{\ominus} \quad (19)$$

Several possibilities might be contemplated for the subsequent fate of the diazonium ion (A). Thus, it might undergo (a) bimolecular reaction with the solvent, (b) loss of nitrogen followed by reaction with the solvent of the carbonium ion so produced or (c) bimolecular reaction with the acetate ion

$$RCOCH_2N_2^{\oplus} + OAc^{\ominus} \longrightarrow RCOCH_2OAc + N_2 \quad (20)$$

We are inclined toward the third possibility for two reasons. First, the addition of a relatively large amount of sodium acetate has only a slight effect (Table V[1]) on the rate of decomposition of *p*-nitro-α-diazoacetophenone in acetic acid at 60°. The mechanisms involving (a) and (b) above, however, would lead to the prediction that added acetate ions, by repressing reaction (19), should markedly decrease the rate of decomposition. Second, the rate of decomposition of the diazoketone is markedly enhanced by the addition of chloride ions, and in this case the kinetics are demonstrably bimolecular, which is in harmony with the possibility (c) where chloride has replaced acetate.

According to this interpretation the over-all process of activation to which the thermodynamic quantities of Table VI refer, becomes



$$RCOCHN_2 + HOAc = \underset{\substack{| \\ RCO\ (B)}}{\overset{\delta-}{AcO}}\text{-----}CH_2\text{-----}\overset{\delta+}{N_2} \quad (21)$$

where B is the transition-state of the reaction (20). The relatively high negative values of the entropies of activation may well be associated with the fixation (freezing) in the process of solvent molecules on this polar transition-state.[16]

The plot of Fig. 6,[1] then, represents a linear free energy relationship between process (21) and the ionization of *p*-substituted benzoic acids. The negative values of the slopes (ρ) may be interpreted as indicating that the primary effect of the substituents is on the ability of the diazoketone to accept a proton in reaction (19).

Acknowledgments.—The authors wish to express their thanks to the Rutgers University Research Council for a grant-in-aid for the academic year 1949–1950 which materially expedited the completion of this research, and also to Dr. Edward L. Simons of this Laboratory for his assistance in the development of the graphical method for analyzing kinetic data presented in this paper.

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(16) The entropy of freezing one mole of acetic acid is −9.5 e.u.

NEW BRUNSWICK, NEW JERSEY
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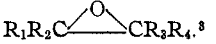
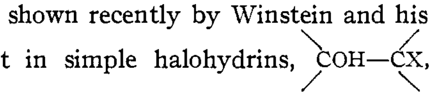
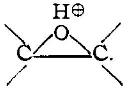
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Studies on the Pinacol Rearrangement. I. The Composition of Products Obtained in Some Reactions of 1,1,2-Triphenyl-2-bromoethanol

BY JOHN F. LANE AND DAVID R. WALTERS[1]

1,1,2-Triphenyl-2-bromoethanol (I), a new compound, has been synthesized, and the products formed when it is acted upon by various basic and electrophilic reagents, as well as aqueous dioxane, have been determined quantitatively. Bases produce pure triphenylethylene oxide (II) while silver and mercuric ion lead to the exclusive formation of phenyl benzhydryl ketone (III). Solvolysis in aqueous dioxane produces a mixture of ketone (III) and triphenylethylene glycol (IV) in which the former predominates. Structures for the transition states which lead to the formation of oxide, ketone and glycol are discussed.

That halohydrins, $R_1R_2COH{-}CXR_3R_4$, easily undergo the pinacol rearrangement to give ketones ($R_1COCR_2R_3R_4$) is well known.[2] Such transformations have been especially extensively studied by Tiffeneau and his students, who have shown that agents for rearrangement include silver and mercuric oxides and dry potassium hydroxide, the latter usually giving appreciable (often predominant) amounts of epoxides .[3]

It has been shown recently by Winstein and his students[4] that in simple halohydrins, , the hydroxyl group on C_β contributes a substantial driving force (L_0 = 1.34 kcal.) toward facilitating release of the halogen at C_α through formation of intermediates . Moreover, if the hydroxyl is converted by the action of a base to an alkoxide ion, an even larger driving force results (L_0 = 6 kcal.).

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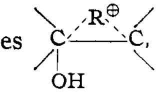
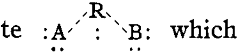
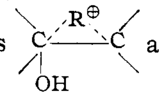
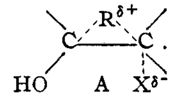
(1) du Pont Fellow in Chemistry, Rutgers University, 1946–1948.

(2) *Cf.* J. W. Baker, "Tautomerism," Routledge, London, 1934, p. 295 *et seq.*

(3) For typical examples see M. Tiffeneau, *et al.*, *Bull. soc. chim.*, **29**, 782 (1921); **33**, 725 (1923); **37**, 430, 1410 (1925); *Compt. rend.*, **134**, 1505 (1902); **145**, 811 (1907).

(4) *Cf.* S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948) and earlier papers.

When, in addition, such a system contains β-alkyl or aryl substituents capable of electron release, these may be expected to compete with the β-hydroxyl (less possibly with $\beta C-O^-$) through the formation of intermediates  which can, on loss of a proton and redistribution of the valence electrons of R, yield a carbonyl compound $-\overset{\overset{\displaystyle O}{\|}}{C}-CR$. Such intermediates are special examples of the generalized cyclic intermediate  which was proposed by Lane and Wallis[5] in discussing the stereochemistry of molecular rearrangements. The pair of electrons originally binding R to A is presumed to have entered into interaction with B in such a way that the R–A and R–B bonds acquire partial single bond character.[6] Lane and Wallis originally pictured this structure as arising *via* the "open sextet" structure $:\ddot{\underset{\cdot\cdot}{A}}:\ddot{\underset{\cdot\cdot}{B}}$ of Whitmore.[7] The existence of this "open" stage in the pinacol rearrangement is rendered doubtful, however, by evidence that C_α, when optically active, ordinarily does not racemize, but suffers inversion of configuration.[8] Accordingly, in the subsequent discussion the intermediates  are presumed to arise directly from the pinacolic systems *via* transition states of this type



The results of Tiffeneau and others of the French School provide abundant qualitative evidence that in halohydrins the participation, with attendant rearrangement, of C_β–R relative to C_β–OH is greatest when the capacity of R for electron release is high (*e.g.*, R = p-CH_3O–C_6H_4) and in general, less effective with alkyl than with aryl groups.[9] This is understandable on the above formulation, since in structures such as **A**, electron accession from R may be expected to increase the strength of the partial bonds $R\cdots C_\beta$, $R\cdots C_\alpha$, and migrating aryl groups can, through resonance, more easily absorb the positive charge.

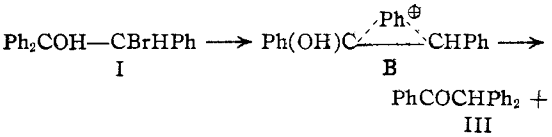
The data now available in the literature, however, do not suffice to provide a quantitative picture of the relative tendencies of C_β–OH, C_β–R, and C_β–O^- to participate in the release of anions from C_α. Tiffeneau's product compositions are only approximate and often are obtained by fractional distillation under atmospheric pressure, which is known in many instances to cause pinacolic rearrangement of epoxides.[10] In order to provide the quantitative data necessary for a general clarification, this Laboratory has undertaken a series of investigations on reactions of systems of the type $(R_2)_2COH$–$CHXR_1$. The first of these, concerning the products obtained from 1,1,2-triphenyl-2-bromoethanol (I, $R_1 = R_2 = C_6H_5$) under a variety of conditions is reported here.

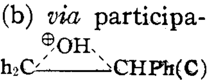
The bromohydrin (I) was prepared from 1,1,2-triphenylethanol by the action of N-bromosuccinimide. It was found to react instantaneously and quantitatively with hydroxyl ion in aqueous dioxane to give triphenylethylene oxide (II). The same product resulted quantitatively, though more slowly, from the action of acetate ion in aqueous dioxane and also from the action of dry potassium hydroxide on an ethereal solution of I.

The action of electrophilic reagents, such as silver nitrate and mercuric nitrate, in aqueous dioxane led, on the other hand, to the quantitative production of phenylbenzhydryl ketone (III). This ketone was also produced quantitatively from I: (a) in pure dioxane by the action of mercuric bromide and pyridine, (b) in ethereal solution by the action of moist silver oxide, and (c) in benzene solution by the action of anhydrous alumina (acid-washed to pH 3) dried at 185°.

Simple hydrolysis of I in 70% (aqueous) dioxane gave mixtures of the ketone (III) and triphenylethylene glycol (IV) in which the former predominated. Thus, the product composition was: at 40°, III, 86.3%, IV, 13.7%; at 50°, III, 84.5 ± 0.8%, IV, 15.5 ± 0.8%; at 70°, III, 80.8 ± 0.2%, IV, 19.2 ± 0.2%. In a solution 0.288 M in sodium perchlorate, however, the product composition at 40° was: III, 79.8 ± 2.0%, IV, 20.2 ± 2.0%. The epoxide was found to be rapidly converted to IV under mildly acidic conditions of the hydrolysis ($[H^+] \sim 0.02N$). Thus, estimation of the composition of products necessitated only a quantitative separation of IV from III. This, as described in detail in the experimental part, was readily achieved by chromatography over alumina.

While rearrangement is most probably to be explained in terms of the process



more than one possibility exists for the mechanism of the glycol formation: (a) *via* the intermediate **B**, *e.g.*, **B** + $H_2O \rightarrow$ IV + $H^\oplus$; (b) *via* participation of C_β–OH, *e.g.*, I $\xrightarrow{-Br^\ominus}$  $\xrightarrow{H_2O}$ IV + $H^\oplus$; (c) by direct interaction of I with water, *e.g.*, I + $H_2O \rightarrow$ IV + $\overset{\oplus}{H}\overset{\ominus}{Br}$. The ketone (III) is a product of great thermodynamic stability. Indeed, it is produced quantitatively from II, IV, and the isomeric triphenylacetaldehyde[11] by the action of moderately concentrated sulfuric acid. Since it may be produced from **B** by a very rapid

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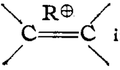
[5] J. F. Lane and E. S. Wallis, THIS JOURNAL, **63**, 1674 (1941).

[6] The significance of structures of this type  in enhancing their stability has more recently been pointed out by Pitzer, "The Protonated Double Bond," Gordon Research Conference Lecture, July 7, 1948.

[7] F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).

[8] H. I. Bernstein and F. C. Whitmore, *ibid.*, **61**, 1324 (1939).

[9] *Cf.* C. K. Ingold, *Ann. Repts. Chem. Soc. (London)*, **25**, 124 (1928).

[10] M. Tiffeneau and J. Levy, *Bull. soc. chim.*, **49**, 1161 (1931).

[11] A. Gardeur, *Chem. Zentr.*, **69**, II, 660 (1897).

process, namely, proton transfer to the solvent, we are inclined to the view that it is the sole product arising from this intermediate; hence to regard possibility (a) above as unlikely. Evidence bearing on the relative merits of (b) and (c) as correct explanations will be given in Part II of this series.

It is of interest that apparently there exists no ready path for the conversion of intermediate **C** to III, since the action of dilute acid on the epoxide (II) leads to the quantitative production of the glycol (IV). From the preparative standpoint this indicates that replacement of halogen by hydroxyl in a halohydrin is most safely achieved by converting it first through the action of a relatively strong base to the epoxide, followed by very mild acid hydrolysis of the latter to the glycol. Whether this principle is applicable to halohydrins of different structure from the one studied here is under investigation.

Experimental

Preparation of 1,1,2-Triphenyl-2-bromoethanol (I).—A mixture of 35 g. (0.128 mole) of 1,1,2-triphenylethanol, prepared in 95% yield by the method of Hell and Wiegandt,[12] 0.5 g. of benzoyl peroxide, 34.4 g. (0.192 mole) of N-bromosuccinimide and 200 ml. of anhydrous carbon tetrachloride was slowly refluxed on a water-bath until a copious amount of succinimide floated on the surface of the reaction mixture and N-bromosuccinimide was no longer consumed by additional refluxing. By removing the solvent from the filtered mother liquor there was obtained 37.3 g. of the bromohydrin. After two recrystallizations from ligroin it melted[13] at 124–126°; yield 32.5 g. (72%).

Anal. Calcd. for $C_{20}H_{17}OBr$: Br, 22.62. Found: Br, (Volhard), 22.45.

Preparation of Triphenylethylene Oxide (II).—This substance was prepared by the action of perbenzoic acid upon triphenylethylene.[14] The latter compound, m.p. 72°, was produced in 86% yield by refluxing 1,1,2-triphenylethanol with a twelve-fold excess of glacial acetic acid for one hour.

The olefin, 13 g., was added directly to 50 ml. of a 0.001 *M* solution of perbenzoic acid[15] at 0°, and the mixture was placed in the refrigerator overnight. The solution was then washed with 50-ml. quantities of 0.1 *N* sodium hydroxide and 0.1 *N* sodium bicarbonate and 100 ml. of water. After evaporation of the chloroform under reduced pressure, the residue was recrystallized twice from methanol; yield 9.3 g. (66%), m.p. 75–77°.[16]

Preparation of Triphenylethylene Glycol (IV).—This compound, m.p. 165–167°, was prepared in 78% yield by the method of Acree.[17]

Preparation of Phenyl Benzhydryl Ketone (III).—This ketone was prepared by the pinacol rearrangement of IV in the presence of 20% sulfuric acid.[18] A 78% yield was obtained after recrystallization from alcohol. The product melted at 137–139°.[19]

The substance absorbed light strongly in the near ultraviolet (320 mμ; $\epsilon_{max.}$ 0.632, in alcohol). At 340 mμ the absorption by II (ϵ 0.003) and IV (ϵ 0.0023) was negligible with respect to that of III (ϵ 0.534). The amounts of III in samples suspected of contamination by II and IV could therefore be determined by measurement of this property. That the absorption of III in dioxane conforms satisfactorily to Beer's law was evidenced by the following data (340 mμ).

III (g./liter)	*D*	
0.424	0.233	0.549
0.600	.338	.563
0.704	.392	.557
1.124	.613	.545
1.380	.770	.558
1.412	.813	.577
1.500	.820	.547

Action of Sodium Acetate.—A 50-ml. volumetric flask containing 423.6 mg. (1.2 mmoles) of the bromohydrin (I), 1.958 g. (14.4 mmoles) of sodium acetate trihydrate and 45 ml. of 70% (aqueous) dioxane[20] was placed in the thermostat at 50°. After ten minutes sufficient solvent was added to make the volume of solution exactly 50 ml. At the end of 48 hours the flask was removed from the bath and the solvent was partially removed under reduced pressure; the remainder was extracted twice with 25-ml. portions of chloroform. Evaporation of the combined extracts yielded 533 mg. (98%) of II as a viscous oil which crystallized when rubbed with petroleum ether; m.p. 74–75.5°.

Action of Sodium Hydroxide.—A mixture of 423.6 mg. (1.2 mmoles) of I, 2.75 ml. of 0.4393 *N* sodium hydroxide, 12.25 ml. of water and 35 ml. of dioxane was allowed to remain in the thermostat at 50° for 1.5 hours. After cooling to room temperature, one 10-ml. aliquot sample was diluted to 25 ml. with ethanol. A spectrophotometric analysis of the resulting solution, ϵ 0.005, failed to indicate the presence of any ketone III. Another 10-ml. portion of the original solution was extracted twice with 15-ml. portions of chloroform. The combined chloroform layers, after evaporation under vacuum, yielded 53.8 mg. (99%) of a viscous oil which crystallized upon standing overnight. The substance, melting at 75–76°, was triphenylethylene oxide.

A repetition of the above experiment substantiated these results.

Action of Dry Potassium Hydroxide.—The bromohydrin (1.00 g.) was dissolved in 10 ml. of anhydrous ether at room temperature. To this solution was then added 257 mg. of freshly pulverized potassium hydroxide. The mixture boiled vigorously for several seconds, and potassium bromide precipitated out immediately. After standing for two days at room temperature, the solution was filtered and the mother liquor was evaporated to dryness. The residue of triphenylethylene oxide weighed 763 mg. (99%); m.p. 75–77°.

Action of Silver Nitrate.—To the solvent composed of 10 ml. of 0.25 *N* silver nitrate and 40 ml. of dioxane was added 706 mg. (2 mmoles) of the bromohydrin (I). After standing for two hours to ensure complete precipitation of the silver bromide, the mixture was filtered and a portion of it analyzed spectrophotometrically. A specific extinction coefficient (ϵ) of 0.546, was determined, corresponding to 102.0% ketone.

In three additional experiments I (423.6 mg., 1.2 mmoles) was dissolved in a mixture of 15 ml. of 0.09841 *N* silver nitrate and 35 ml. of dioxane at 50°; the solution remained at this temperature for 12 hours. A 5-ml. aliquot sample was then diluted to a volume of 50 ml. with ethanol, and the resulting solution was subjected to a spectrophotometric analysis. From the specific extinction coefficients obtained for each of the three experiments (ϵ 0.0538, 0.0545 and 0.543) the percentages of III were calculated to be 100.6, 101.9 and 101.3, respectively.

Action of Silver Hydroxide.—Freshly precipitated silver hydroxide (500 mg.) was added to 10 ml. of an ethereal solution containing 100 mg. of I. Silver bromide precipitated very slowly, and the reaction mixture was shaken intermittently for three hours with negligible effect. After standing overnight, however, the silver hydroxide was covered with a layer of the silver halide; the mixture was stirred several times daily in order to present a fresh surface of silver hydroxide to the ethereal solution of the bromohydrin. At the end of five days no additional precipitation of silver bromide was observed so the solution was filtered and the mother liquor was evaporated to dryness. There remained 74 mg. of material, m.p. 133–136°, which was shown by spectrophotometric analysis (ϵ 0.516) to be 97% ketone (III).

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(12) C. Hell and F. Wiegandt, *Ber.*, **37**, 1429 (1904).

(13) This and subsequently reported melting points were determined on the Kofler micro hot-stage.

(14) A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

(15) "Organic Syntheses," Coll. Vol. I, edited by H. Gilman and A. Blatt, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

(16) R. Lagrave, *Ann. chim.*, [9] **8**, 363 (1927), reports m.p. 77°.

(17) S. Acree, *Ber.*, **37**, 2762 (1904).

(18) A. Orekhoff and M. Tiffeneau, *Compt. rend.*, **171**, 473 (1920).

(19) A. Biltz, *ibid.*, **26**, 1957 (1893), reports m.p. 136°.

(20) The dioxane was purified by the method of E. Eigenberger, *J. prakt. Chem.*, [2] **130**, 75 (1931), and distilled from sodium before use.

Action of Silver Ion and Hydrogen Ion on II in Aqueous Dioxane.—It was possible that in the preceding experiments, and also in the solvolyses to be described below, some ketone (III) could arise by the action of either hydrogen ion or silver ion on the oxide (II) or the glycol (IV), which are conceivable primary decomposition products of I. To check this possibility, samples of II were dissolved in 70% dioxane containing silver ion, hydrogen ion, or both. After a suitable reaction period the product was isolated by precipitation with water and extraction with ether. The specific conditions of these experiments and the results obtained are reported in Table I.

TABLE I

ACTION OF SILVER ION AND HYDROGEN ION ON II IN 70% (AQUEOUS) DIOXANE AT 25°

Reaction time, hr.	Volume, ml.	Reactants, mmole II	Ag$^+$	H$^+$	Products Identity	mmole	M.p. °C.
24	25	0.600	0.600	0.600	IV	0.594	164–166
24	50	1.20		1.20	IV	1.23	161–163
24	50	1.20	1.20		II	1.21	71–74

Action of Mercuric Nitrate.—To 100 ml. of 60% (aqueous) dioxane was added 847 mg. (2.4 mmoles) of I. After standing at room temperature for three days during which time mercuric bromide precipitated out slowly, the solution was neutralized with 201.6 mg. (2.4 mmoles) of sodium bicarbonate. The solvent was then partially removed under vacuum and the remaining solution was extracted with ether. Upon evaporation of the ethereal extract there was obtained 646 mg. (99%) of III; m.p. 137–139°.

A similar experiment at 25° involving 2.00 g. (5.66 mmoles) of I and 919 mg. (2.83 mmoles) of mercuric nitrate dissolved in 50 ml. of 70% (aqueous) dioxane yielded 1.523 g. (99%), m.p. 137–139°, of III.

Action of Mercuric Bromide and Pyridine.—In a 100-ml. volumetric flask were placed 212 mg. (0.6 mmole) of I, 216 mg. (0.6 mmoles) of mercuric bromide, 142 mg. (1.8 mmole) of pyridine; the reaction mixture was made to exact volume with pure dioxane. After standing for 12 days at room temperature, the solvent was partially removed and the remainder was extracted with chloroform. Evaporation of the chloroform extracts yielded 161 mg. (99%) of III; m.p. 137.5–139°.

Action of Alumina.—The alumina employed in this experiment was activated by acid-washing to a *p*H of 3 and igniting at 185°. The bromohydrin (I) (480 mg.) was dissolved in a mixture of 10 ml. of benzene and 25 ml. of ligroin. The solution was allowed to run slowly (1 ml. per minute) through a 9-cm. column containing 13.5 g. of the alumina. The mother liquor was recycled through the column four times and then allowed to remain over the column for 18 hours. Elution of all the material from the alumina was accomplished by 175 ml. of a solution containing 40% benzene in ligroin. The yield of ketone, m.p. 136–138°, was 367 mg. (99%).

Action of Aqueous Dioxane on II.—Under the conditions of this solvolysis II was shown to be converted quantitatively to IV; 653 mg. of II was dissolved in 100 ml. of 70% (aqueous) dioxane, containing 2.4 mmoles of hydrochloric acid, and heated for 30 hours at 50.5°; the residue from a 20-ml. aliquot sample, isolated by extraction with chloroform, weighed 137 mg. (theoretical weight based on glycol, 139 mg.) and melted at 165–167°. Thus, any oxide produced by solvolysis was finally present in the reaction product as IV, and the composition of products was determinable by chromatography.

Chromatographic Analysis of Mixtures of III and IV.—This method was developed for use in the experiment described below. The sample (300–400 mg.) was taken up in a mixture of 20 ml. of ligroin and 10 ml. of benzene, and the solution was allowed to pass through a 9-cm. (13.5 g.) column of alumina (80–200 mesh, acid-washed at *p*H 3 and previously ignited at 165°). The column was then diluted with a mixture of 30% benzene in petroleum ether (b.p. 35–70°) until evaporation of a 20-ml. sample of eluent failed to yield any residue. This ordinarily required about 125 ml. of solvent. Next, the column was eluted with 50 ml. of 50% benzene in ether. Evaporation of the first eluent to constant weight gave the amount of ketone present. Evaporation of the second gave the amount of glycol. Results of typical experiments on known mixtures are given in Table II.

TABLE II

CHROMATOGRAPHIC ANALYSIS OF KNOWN MIXTURES OF THE KETONE III AND GLYCOL IV

	Known				Determined			
	III		IV		III		IV	
Expt.	mg.	%	mg.	%	mg.	%[a]	mg.	%[a]
1	260	81.2	60	18.8	257.7	81.6	58.2	81.4
2	300	88.2	40	11.8	301.0	88.7	38.5	11.3
3	320	88.9	40	11.1	321.0	89.3	38.5	10.7
4	310	86.1	50	13.9	308.5	86.3	49.0	13.7

[a] Based on total weight of material obtained from chromatographic analysis.

Action of Aqueous Dioxane on I.—In these experiments solutions containing approximately one mmole of I dissolved in 50 ml. of aqueous dioxane were allowed to stand at the desired temperature until reaction was complete (four days at 70°, 12 days at 50°). Before final isolation of the product completeness of reaction was checked by removing an aliquot portion of solution and delivering it into an excess of dilute nitric acid, extracting the organic material with chloroform and determining the bromide ion in the aqueous solution by the Volhard method. Approximately one-half the solvent was removed from the reaction mixtures under reduced pressure, and the remaining solution was extracted twice with chloroform. The chloroform solution of the product was evaporated under vacuum and the residue weighed. It was then analyzed by the method (b) above. Results of several experiments under different conditions are given in Table III.

TABLE III

ACTION OF 70% (AQUEOUS) DIOXANE UPON THE BROMOHYDRIN I

Expt.	Temp. (°C.)	Wt. of residue (mg.)	III mg.	III %[a]	IV mg.	IV %[a]
1	50	340.8	274.3	85.3	47.2	14.7
2	50	342.0	272.3	83.2	54.8	16.8
3	50	349.0	271.1	84.9	48.3	15.1
4	70	341.0	256.5	81.2	59.5	18.8
5	70	341.0	257.4	79.8	65.3	20.2
6	70	341.0	261.1	81.4	59.5	18.6
7[b]	40	307.9	231.2	76.8	69.8	23.2
8[b]	40	311.5	228.8	80.7	54.7	19.3
9[b]	40	320.4	242.9	81.8	54.3	18.2

[a] Based on total weight of material obtained from chromatographic analysis. [b] Ionic strength adjusted to 0.288 by addition of sodium perchlorate.

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