

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, THE HEBREW UNIVERSITY]

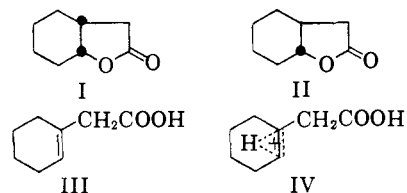
## The Iodolactonization of Cyclohexeneacetic Acids

BY J. KLEIN

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The stereochemistry of iodolactonization of cyclohexene-1- and -2-acetic acids has been established on the basis of the catalytic hydrogenolysis of the iodolactones and of elimination reactions with them. Several other reactions of the iodolactones are reported.

The lactone I of *cis*-2-hydroxycyclohexaneacetic acid, previously obtained indirectly<sup>1</sup> from the *trans*-lactone II, has been prepared in a one-step reaction from cyclohexene-1-acetonitrile *via* the unsaturated acid<sup>2</sup> III. The conditions of the reaction (presence of mineral acid) and the steric homogeneity of the product obtained point to a  $\pi$ -complex intermediate IV between a proton and the double bond of the unsaturated acid III. However, it now has been found that 50% sulfuric acid isomerizes II to I. This isomerization, observed previously in the case of similar lactones,<sup>3</sup> does not allow conclusions to be drawn on the stereochemistry of the acid-catalyzed lactonization. No equilibrium conditions were obtained during the acid treatment, since about 50% of the lactone was destroyed and it is probable that II, being more reactive,<sup>1</sup> is destroyed preferentially.

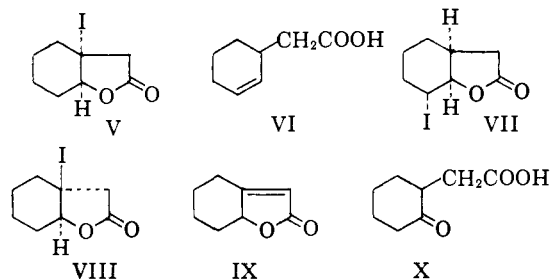


It seemed that the stereochemistry of lactone ring formation could be studied more easily in a related reaction, the iodolactonization. This reaction can be carried out under such conditions<sup>4</sup> that the iodolactone, which is obtained at room temperature in a neutral aqueous solution, precipitates immediately on its formation. Consequently, equilibration is avoided.

A  $\pi$ -complex between iodine and the double bond of the unsaturated acid was assumed previously to explain the formation of  $\beta$ -iodo- $\gamma$ -lactones from  $\beta,\gamma$ - and of  $\delta$ -iodo- $\gamma$ -lactones from  $\gamma,\delta$ -unsaturated acids.<sup>5</sup> The steric consequence of the occurrence of such an intermediate would be in the case of the iodolactonization of cyclohexene-1-acetic acid, the formation of the *cis*-lactone V. Catalytic hydrogenolysis of carbon-oxygen and carbon-halogen bonds has been shown<sup>6</sup> to proceed with retention of configuration. Similarly, hydrogenolysis of V in the presence of Raney nickel

afforded I under conditions in which II was recovered unchanged. Palladium-on-charcoal was ineffective as catalyst for this hydrogenolysis, while zinc and acetic acid reverted V to the acid III.

A proof for the formation of *cis*-lactones during iodolactonization was found in the production of I by hydrogenolysis of the  $\delta$ -iodo- $\gamma$ -lactone prepared from cyclohexene-3-acetic acid (VI). As this hydrogenolysis obviously can not affect the configuration of the asymmetric atoms of the lactone ring, the *cis*-lactone configuration is present in the iodolactone too. The configuration VII



is assigned to this iodolactone on the basis of a  $\pi$ -complex intermediate during its formation. The retention of configuration during catalytic hydrogenolysis is confirmed indirectly, if a similar mechanism is assumed for the iodolactonization of the two unsaturated acids III and VI. Should the hydrogenolysis proceed with *inversion* of configuration, then the iodolactone V would necessarily have the lactone ring linked *trans* to the cyclohexene ring. By analogy, the iodolactone VII also would have the lactone ring in the *trans* configuration and give after hydrogenolysis II, which is not the case.

The possibility was considered that V was not the primary product of the iodolactonization reaction, but formed by the isomerization of its unknown isomer VIII. However, a bimolecular displacement of iodine on the tertiary carbon atom of VIII by an iodine anion is probably very slow and the  $S_N1$  mechanism for this isomerization is excluded by our results on the exchange reaction between V and radioactive sodium iodide.<sup>7</sup> Similarly, path 1 for this isomerization (which possibility is emphasized by our observation that 56% of the iodine present initially in V appears in the form of molecular iodine after 27 days of "equilibrating" of V with a great excess of a concentrated ethanolic sodium iodide solution) can be ruled out on the strength of a stereochemical argument. If VIII is the primary product and V formed by equilibra-

(7) The rate of ionization of VIII is expected to be comparable to that of V. These results will be published separately.

(1) M. S. Newman and C. A. VanderWerf, *THIS JOURNAL*, **67**, 233 (1945).

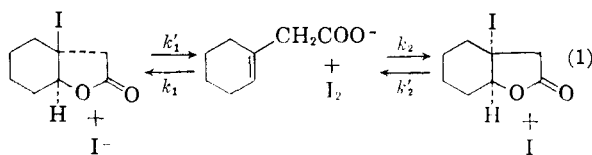
(2) J. Klein, *J. Org. Chem.*, **23**, 1209 (1958).

(3) D. H. R. Barton, *ibid.*, **15**, 467 (1950).

(4) J. Bougault, *Ann. chim.*, **14**, 145 (1908); *Compt. rend.*, **139**, 864 (1904).

(5) E. E. van Tamelen and M. Shamma, *THIS JOURNAL*, **76**, 2315 (1954).

(6) W. A. Bonner, J. A. Zderic and G. A. Casaletto, *ibid.*, **74**, 5086 (1952); J. H. Brewster, *ibid.*, **78**, 4061 (1956); J. Klein and G. Lewin, *ibid.*, **80**, 1707 (1958).



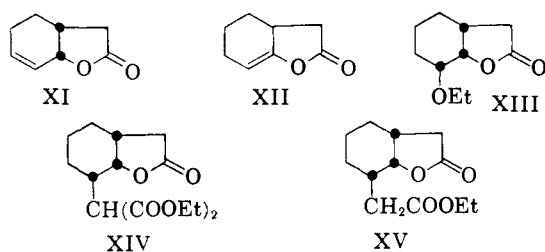
tion, then  $k_1 > k_2$  and  $k_2/k_2' > k_1/k_1'$ , which implies that  $k_1' \gg k_2'$ , and that the reaction of VIII with iodide ion (*cis* elimination) would be more rapid than the reaction of V with iodide ion (*trans* elimination), which is not probable.

It appears that the iodolactone V is not only the kinetically favored product, but also the more stable isomer, since hydrogenolysis of "equilibrated" solution of V and sodium iodide gave only I.

The stereospecificity of the iodolactonization and of the catalytic hydrogenolysis makes possible the assignment of configurations to lactones or  $\gamma$ -hydroxy acids, when the unsaturated acids are also available.

The iodolactone V yields with pyridine the unsaturated conjugated lactone IX, which is known<sup>1</sup> to give with sodium hydroxide solution the keto-acid X. This series of reactions represents a method to oxidize *selectively* a  $\gamma$ -position in a  $\beta,\gamma$ -unsaturated acid, when other oxidizable groups are also present in the molecule. We have tried to obtain X directly from the iodolactone V by the action of sodium hydroxide; the product was not obtained in pure form, but yielded easily the known semicarbazone of X. The lactone IX has been used recently as starting material for the total synthesis of vitamin D model compounds.<sup>8</sup> Our synthesis of IX is shorter and gives a higher over-all yield than the previous method.<sup>2</sup>

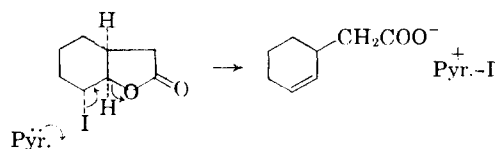
The iodolactone V is dehydrohalogenated even by potassium cyanide, but VII has to be boiled with pyridine in order to eliminate hydriodic acid, and then gives a mixture of an unsaturated lactone XI and of the acid VI. The constitution of XI was based on the carbonyl frequency at 1765  $\text{cm}^{-1}$ <sup>9</sup>; it confirms incidentally also the con-



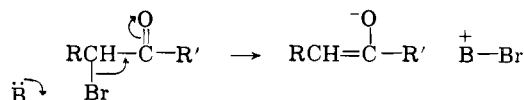
figuration assigned to VII. The formation of the acid VI in the treatment of VII by pyridine can be explained by the presence of an electron-accepting group on the neighboring carbon atom. Such a reaction would also be favored by the *trans* configuration of the iodine and oxygen substituents. Pyridine or possibly iodide anions, formed in the parallel dehydroiodination, drive this transformation, reverse to iodolactonization.

(8) I. I. Harrison and B. Lythgoe, *J. Chem. Soc.*, 843 (1958).

(9) An unsaturated lactone of constitution XII is expected to absorb at a higher frequency than V, *viz.*, at about 1800  $\text{cm}^{-1}$ ; *cf.* R. S. Rasmussen and R. R. Brattain, *THIS JOURNAL*, **71**, 1073 (1949).



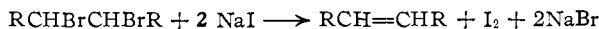
The displacement of halogen by hydrogen on heating an  $\alpha$ -bromoketone with pyridine can be compared with this reaction<sup>10</sup>



The iodolactone VII reacts slowly with diethyl sodiomalonate in anhydrous alcohol to give the ethoxylactone XIII and the malonate XIV; the latter undergoes decarboxylation on heating to give the lactone ester XV, in a manner observed in similar cases.<sup>11</sup> The fact that I absorbs strongly at 944 and 993  $\text{cm}^{-1}$  and II at 1033 and 1080  $\text{cm}^{-1}$  has been useful in their identification. Both lactones show a band at 882  $\text{cm}^{-1}$  which is stronger in the *trans* isomer. Similar bands have been found<sup>12</sup> recently in the santonin series and ascribed to specific vibrations in the molecule. The differences in absorption between I and II are particularly evident in chloroform solution, in which the bands of I at 944 and 993  $\text{cm}^{-1}$  are stronger than in the pure liquid, while all the bands of II are weaker or non-existent in this solution. The iodolactone V has bands at 940 and 993  $\text{cm}^{-1}$ , which can be considered as a proof of its *cis* configuration. The corresponding bands of the iodolactone VII are at 943 and 972  $\text{cm}^{-1}$ . Differ-

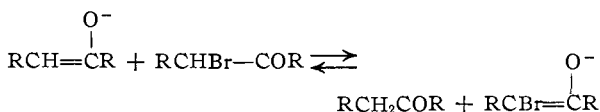
(10) E. Schwenk and B. Whitman, *ibid.*, **59**, 949 (1937); R. P. Jacobsen, *ibid.*, **62**, 1620 (1940); H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

One of the referees suggested that the reaction



is a better analogy for the formation of the unsaturated acid from VII, since the brominating agent could not exist in appreciable concentration in the presence of an enolate of a ketone. He suggested also that the formation of the debrominated ketone in the reaction with bases can be explained by oxidation-reduction equilibria (formation of dibromoketones, see F. Kröhnke, *Ber.*, **69**, 614, 921 (1936); **70**, 864 (1937)).

These arguments are strong indeed, especially in the case when the reaction is carried out in an aprotic solvent containing only a small amount of proton donors, where the ketonization will no doubt be much slower than the halogenation. We think, however, that the analogy of the debromination of ketones can be retained and the results of Kröhnke explained when it is realized that the debromination occurs when the enol is stabilized by conjugation and the halogenation slowed down by neighboring groups. The *trans*-bromination could be explained by the reaction



In our case, we have not found free iodine at the end of the reaction, and it probably reacted with the double bond of a part of the substance.

The possibility that pyridine itself could bring about the deiodination of VII is supported by the fact that (i) proceeds in some cases when sodium hydroxide is used instead of sodium iodide.

(11) H. Meerwein, *Ann.*, **398**, 242 (1913); W. S. Johnson, B. Banister, R. Pappo and J. E. Pike, *THIS JOURNAL*, **78**, 6354 (1956).

(12) T. Kanazawa, H. Kamio, M. Sumi and M. Nishikawa, *ibid.*, **80**, 3705 (1958).

ences in the carbonyl stretching frequencies of I and II also have been found recently.<sup>13</sup>

The procedures for the preparation of the starting materials have been improved during this work. The unsaturated acid III was prepared by the alkaline saponification of its ethyl ester. This ester was obtained by heating cyclohexene-1-acetonitrile with ethanol and concentrated hydrochloric acid. The lactone I was obtained by a modification of the previous procedure,<sup>2</sup> which consumes less solvent and reagent.

### Experimental

The infrared spectra were taken on films for liquids and in potassium bromide pellets for solids, unless stated otherwise.

**Ethyl Cyclohexene-1-acetate.**—A mixture of 120 g. of cyclohexene-1-acetonitrile,<sup>14</sup> 330 ml. of ethanol and 200 ml. of concentrated hydrochloric acid was refluxed for 8 hours, cooled and after addition of water extracted with benzene. The benzene layer was washed with 10% aqueous sodium carbonate and with water, and gave upon distillation 100 g. (60%) of ethyl cyclohexene-1-acetate boiling at 120° (40 mm.),<sup>16</sup>  $\nu_{\max}$  1735 cm.<sup>-1</sup> (ester carbonyl). The alkaline solution gave on acidification, extraction with benzene and distillation, 6 g. (4%) of the acid II, b.p. 153–155° (30 mm.).<sup>16</sup>

**Cyclohexene-1-acetic Acid (III).**—To a solution of 86 g. of ethyl cyclohexene-1-acetate in 250 ml. of ethanol a solution of 50 g. of sodium hydroxide in 150 ml. of water was added and the mixture refluxed for 4 hours. Water was added and the mixture extracted with benzene. The aqueous layer then was acidified and extracted with benzene. Distillation of the benzene layer yielded 45 g. (62%) of the acid II, b.p. 150–155° (25 mm.), m.p. 33–34°.<sup>16</sup>

**Cyclohexene-3-acetic acid (VI)** was prepared by the method of Eijkman<sup>17</sup> from 1,2-dibromocyclohexane and diethyl sodiomalonate.

The *trans*-lactone of 2-hydroxycyclohexaneacetic acid (II) was obtained by the procedure of Newman and Vander-Werf<sup>1</sup>; infrared spectrum: 795, 828, 850, 882, 1033, 1080, 1120, 1137, 1176, 1192, 1260, 1305, 1367, 1387, 1400, 1428, 1457, 1785, 2880, 2945 cm.<sup>-1</sup>.

The *cis*-lactone of 2-hydroxycyclohexaneacetic acid (I) was prepared as reported previously.<sup>2</sup> The obtained lactone is the pure *cis* isomer. The yield of 4% *trans*-lactone reported in one of the experiments<sup>2</sup> probably was due to a contamination. A modified procedure was also used: To a solution of 20 g. of cyclohexene-1-acetonitrile in 70 ml. of acetic acid, 40 ml. of concentrated hydrobromic acid and 20 ml. of 50% sulfuric acid were added and the mixture refluxed for 6 hours. Water then was added and the product extracted with benzene. The benzene solution was washed with 10% sodium carbonate solution and water, and gave on distillation 7.5 g. (32.5%) of I, b.p. 140–145° (20 mm.). The alkaline solution gave on acidification, extraction with benzene and distillation, 1 g. (4%) of the acid III, b.p. 150–155° (20 mm.); infrared spectrum of I: 800, 833, 852, 860, 882, 910, 944, 993, 1004, 1024, 1053, 1104, 1144, 1176, 1231, 1262, 1300, 1350, 1428, 1457, 1775, 2880, 2945 cm.<sup>-1</sup>.

**Isomerization of II under Acid Conditions.**—To a solution of 5 g. of II in 35 ml. of glacial acetic acid, 25 ml. of 50% aqueous sulfuric acid was added and the mixture refluxed for 4 hours. Water was added and the product extracted with benzene. The benzene solution was washed with 10% aqueous sodium carbonate solution and water, and gave upon distillation 2.8 g. (46%) of an oil boiling at 143° (30 mm.); according to its infrared spectrum it was identical with I.

**Iodolactone V.**—The iodolactone was prepared essentially by the procedure of Linstead<sup>18</sup> and van Tamelen<sup>6</sup>: At room temperature a solution of 10 g. of cyclohexene-1-

acetic acid and 19 g. of sodium bicarbonate in 300 ml. of water was added to a solution of 38 g. of iodine and 75 g. of potassium iodide in 600 ml. of water. The oily precipitate was extracted after 4 hours with ether, and the ether extract washed with sodium bisulfite solution until the coloration of iodine disappeared, and with saturated sodium bicarbonate solution. The dried ethereal solution was evaporated *in vacuo*; the oily residue gave, on trituration with petroleum ether, 8.2 g. (43%) of a white solid melting at 56°; infrared spectrum: 693, 706, 804, 855, 893, 940, 993, 1104, 1133, 1159, 1211, 1242, 1430, 1780, 2890, 2975 cm.<sup>-1</sup>.

When the reaction time was only 45 min., the yield was 38%. The iodolactone, dissolved in the petroleum ether filtrate, gave on treatment with pyridine 0.7 g. (7%) of the unsaturated lactone IX.

The iodolactone VII was prepared by the same procedure as V. After 4 hours, there was obtained a white product, m.p. 65°, in a yield of 88%; infrared spectrum: 688, 850, 861, 892, 943, 972, 1022, 1053, 1144, 1167, 1182, 1230, 1290, 1309, 1430, 1460, 1780, 2890, 2975 cm.<sup>-1</sup>.

**Reduction of V with Zinc and Hydrochloric Acid.**—To a solution of 5 g. of V in 50 ml. of acetic acid, 10 g. of zinc powder and, in portions, 5 ml. of concentrated hydrochloric acid were added within 3 hours. Benzene was added to the reaction mixture, and the solution filtered. The filtrate was washed twice with water and 10% aqueous sodium carbonate solution, acidified and extracted with benzene. Distillation gave 1.7 g. (65%) of the acid III, b.p. 150° (20 mm.), m.p. 32–33°.

**Hydrogenolysis of V.**—To a solution of 8 g. of V in 100 ml. of ethanol, 5 g. of sodium bicarbonate and about 10 g. of Raney nickel in 20 ml. of ethanol was added. The mixture was hydrogenated at room temperature and 3 atm. pressure for 20 hours, and the solution filtered and distilled; 3.1 g. (74%) of an oil, b.p. 145° (20 mm.), was thus obtained. The infrared spectrum showed it to be I. When a solution of 6 g. of V and 3 g. of sodium iodide in 100 ml. of ethanol was left for 2 days and then hydrogenolyzed as above, Compound I was obtained in 83% yield.

**Hydrogenolysis of VII** was carried out as for V. From 6 g. of VII there was obtained 2 g. (50%) of an oil, b.p. 145° (25 mm.); it was identified as I, as above.

**Attempted Isomerization of II.** (a) **By Zinc and Hydrochloric Acid.**—To a solution of the *trans*-lactone II in 30 ml. of glacial acetic acid, 5 g. of zinc powder and, in portions during 3 hours and with stirring, 2 ml. of concentrated hydrochloric acid was added. The mixture was stirred for 5 more hours, benzene added and the solution filtered. The filtrate was washed with water and 10% aqueous sodium carbonate solution, and distilled. Thus, 3.3 g. of an oil, b.p. 143–144° (25 mm.), was obtained, which was identified by its infrared spectrum as unchanged starting material.

(b) **By Sodium Bicarbonate and Iodide.**—A mixture of 4 g. of II, 3 g. of sodium bicarbonate, 0.5 ml. of concentrated hydriodic acid and 30 ml. of ethanol was stirred for 18 hours. Benzene and water were added and the layers separated, and the benzene solution was distilled; 2.8 g. of an oil, b.p. 145° (25 mm.), identified as unchanged II, as above, was obtained.

(c) **By Raney Nickel and Sodium Bicarbonate.**—A mixture of 5 g. of II, 3 g. of sodium bicarbonate, 3 g. of Raney nickel and 30 ml. of ethanol was stirred under hydrogen at 3 atm. pressure for 18 hours. The solution then was filtered and distilled to give 3 g. of unchanged II, b.p. 145° (25 mm.).

**Dehydrohalogenation of V.**—A solution of 5 g. of V in 10 ml. of pyridine was kept for 2 days at room temperature. Ethanol (30 ml.), zinc powder (5 g.) and (during one hour) 10 ml. of concd. hydrochloric acid were added with stirring and cooling. The solution was filtered after addition of benzene and the organic layer washed successively with 10% hydrochloric acid, 10% sodium carbonate solution and water. Distillation of the benzene layer gave 1.4 g. (54%) of IX, b.p. 152–153° (30 mm.), m.p. 28–30°;  $\lambda_{\max}^{\text{EtOH}}$  216 m $\mu$  ( $\epsilon$  15,000);  $\nu_{\max}^{\text{CHCl}_3}$  1750 (conjugated  $\gamma$ -lactone carbonyl), 1650 (conjugated C=C), 1450, 1340, 1300, 1176, 1124, 1090, 1070, 1040, 940, 915, 892, 856, 845 cm.<sup>-1</sup>.

**Reaction of V with Sodium Hydroxide.**—A solution of 8 g. of sodium hydroxide in 50 ml. of water was added to a solution of 7 g. of V in 10 ml. of ethanol and the mixture refluxed for 3 hours. The ethanol was distilled off and the solution acidified and extracted continuously with ether for 5 hours. The ether layer was extracted with saturated

(13) J. H. Brewster and C. H. Kucera, *THIS JOURNAL*, **77**, 4564 (1955).

(14) A. C. Cope, *et al.*, *Org. Syntheses*, **31**, 25 (1951).

(15) K. Auwers and Ph. Ellinger, *Ann.*, **387**, 227 (1912).

(16) O. Wallach, *ibid.*, **343**, 51 (1905).

(17) J. F. Eijkman, *Chem. Weekblad*, **6**, 699 (1909).

(18) R. P. Linstead and C. J. May, *J. Chem. Soc.*, 2565 (1927).

sodium bicarbonate solution, and the extract then acidified and extracted continuously with ether. Distillation of the ethereal solution gave 1.6 g. (39%) of an oil, b.p. 140–145° (1.5 mm.);  $\bar{\nu}_{\max}$  3500–2500 (carboxyl), 1710  $\text{cm}^{-1}$  (carbonyl).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_3$ : C, 61.5; H, 7.7. Found: C, 62.1; H, 8.0.

The oil was identified as X by its semicarbazone of m.p. 196°.<sup>1</sup>

**Dehydrohalogenation of VII.**—A solution of 6 g. of VII in 10 ml. of pyridine was refluxed for 10 hours. Benzene and, with cooling, hydrochloric acid were added and the benzene solution was washed with 10% hydrochloric acid and 10% sodium carbonate solution. Distillation of the benzene layer gave 1.1 g. (36%) of XI as an oil boiling at 109–112° (4 mm.);  $\bar{\nu}_{\max}$  1070 (vinyl hydrogen), 1765 ( $\gamma$ -lactone carbonyl), 1668 (C=C stretching), 1621, 1430, 1337, 1303, 1231, 1178, 1100, 1077, 1057, 1000, 970, 937, 905, 885  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_2$ : C, 69.6; H, 7.3. Found: C, 69.2; H, 7.6.

The alkaline solution was acidified and extracted with benzene. Distillation yielded 0.7 g. (22%) of an oil, b.p. 117–118° (5 mm.),  $\bar{\nu}_{\max}$  3500–2500 (carboxyl), 3040 (vinyl hydrogen), 1705  $\text{cm}^{-1}$  (C=O). Analysis and infrared spectrum showed that VI had formed.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_2$ : C, 68.6; H, 8.6. Found: C, 68.3; H, 8.2.

**Reaction of VII with Ethyl Sodiomalonnate.**—To a solution of 2.5 g. of sodium metal in 50 ml. of absolute ethanol, 8.5 g. of diethyl malonnate and then, dropwise during 7 hours at reflux, 13.3 g. of VII dissolved in 50 ml. of absolute ethanol was added. The heating was continued for 3 hours more, and the solution cooled, acidified, diluted with water and extracted with ether. The ethereal layer was distilled and gave 0.8 g. of an oil boiling at 110–115° (1.5 mm.), 2.5 g. of an oil XV, b.p. 150–160° (1 mm.), and 0.8 g. of an oil (XIV), b.p. 180–185° (1 mm.). The first fraction XIII showed the characteristic infrared peak at 1780  $\text{cm}^{-1}$  (carbonyl of a  $\gamma$ -lactone).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{16}\text{O}_3$ : C, 65.2; H, 8.7. Found: C, 65.1; H, 8.8.

The product XV absorbed at 1780 ( $\gamma$ -lactone) and 1730  $\text{cm}^{-1}$  (ester carbonyl).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{18}\text{O}_4$ : C, 63.7; H, 8.0. Found: C, 63.4; H, 8.3.

The oil XIV showed a peak of 1780 ( $\gamma$ -lactone) and 1730  $\text{cm}^{-1}$  (ester carbonyl).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{22}\text{O}_6$ : C, 60.4; H, 7.4. Found: C, 61.0; H, 7.7.

The product boils, on slow distillation, at 150–155° (0.8 mm.), to give a product identical with XV.

JERUSALEM, ISRAEL

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

## Molecular Rearrangements. XVI. The Pinacol Rearrangement of the Diphenyl-*m*-tolylethylene Glycols<sup>1</sup>

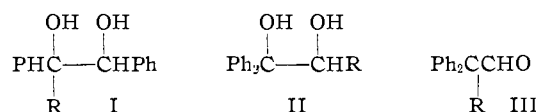
BY CLAIR J. COLLINS AND NEWELL S. BOWMAN<sup>2</sup>

RECEIVED JANUARY 16, 1959

The rearrangements of *threo*- and *erythro*-1,2-diphenyl-1-*m*-tolylethylene glycol (I) and 1,1-diphenyl-2-*m*-tolylethylene glycol (II) in concentrated sulfuric acid at 0° have been examined. The yields of the two ketones (IV and V) produced have been determined by the isotope dilution method, and the fates of various carbon-14 labels of I and II have been established. From the foregoing data the contributions of several paths to the rearrangements of I and II were calculated, and it is shown from these that the *m*-tolyl/phenyl migration ratio in the rearrangement of the conjugate acid of diiphenyl-*m*-tolylacetaldehyde is no less than 1. The present results support in every detail the mechanism previously<sup>8–12</sup> proposed for the rearrangements of triaryl glycols and triarylacetaldehydes.

### Introduction

From 1930 to 1933, McKenzie and his co-workers,<sup>3,5</sup> Roger and McKay<sup>4,7</sup> and Koelsch<sup>6</sup> reported the identities of the products formed during the acid-catalyzed rearrangements of the tolyl-substituted glycols I (R = *o*, *m* or *p*-tolyl). In five recent papers<sup>8–12</sup> we have studied the rearrangements of the diphenyl *o*-tolyl<sup>10</sup> and of the diphenyl *p*-tolyl<sup>9</sup> compounds I, II and III (R = *o*-tolyl and *p*-tolyl) plus the analogous phenyl di-*p*-tolyl system.<sup>11</sup> Thus: (1) the effect of acid



catalyst upon the rearrangements has been elucidated<sup>8,12</sup>; (2) the relationship between the pinacol and the aldehyde-ketone rearrangements has been demonstrated<sup>9</sup> and (3) the question of the apparent reversal of migratory abilities of the groups involved during the aldehyde-ketone rearrangement<sup>9–11</sup> has been answered.

Of the compounds (I) studied by the earlier investigators,<sup>3–7</sup> we had previously neglected the rearrangement of 1,2-diphenyl-1-*m*-tolylethylene glycol<sup>4,7</sup> (I, R = *m*-tolyl). We therefore undertook the study of the rearrangements, in cold, concentrated sulfuric acid, of *threo*- and *erythro*-1,2-diphenyl-1-*m*-tolylethylene glycol (I) and of 1,1-diphenyl-2-*m*-tolylethylene glycol (II), since it appeared from our prior work<sup>8–12</sup> that we should be able to make certain predictions concerning the expected yields of the two ketones IV and V. Roger and McKay,<sup>7</sup> for example, state that in concentrated sulfuric acid at –2°, the “ $\beta$ -form” (*erythro*) of 1,2-diphenyl-1-*m*-tolylethylene glycol

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

(2) Research Participant from the University of Tennessee, June–Sept., 1958.

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