

The aqueous mother liquor from which the 1,4-anhydro-2,3:5,6-dimethylene-D-mannitol had been removed was concentrated *in vacuo* to a sirup and treated with 25 ml. of carbon tetrachloride. About 1 ml. of the solvent was boiled off to remove traces of water; on cooling, fine needles separated: 80 mg. (7.5%), m.p. 109–117°. After recrystallization from 0.4 ml. of absolute ethanol the product melted at 120–121° either alone or in admixture with 1,4-anhydro-2,3-methylene-D-mannitol as prepared above. A rotation of -51.3° was observed in water (c 0.98).

5,6-Diacetyl-1,4-anhydro-2,3-methylene-D-mannitol.—One-half gram of 1,4-anhydro-2,3-methylene-D-mannitol was acetylated with acetic anhydride in pyridine in the usual fashion to give 0.51 g. (69%) of product melting at 87–88°; recrystallization from 6 parts of absolute alcohol failed to change this melting point. In chloroform the ester rotated -43.1° (c 0.80).

Anal. Calcd. for $C_{11}H_{16}O_7$: C, 50.76; H, 6.20. Found: C, 50.76; H, 6.14.

2,4-Methylene-D-mannitol (XIII) from 1,6-Dibenzoyl-2,4-methylene-D-mannitol (XII).—Fifteen grams of 1,6-dibenzoyl-2,4-methylene-D-mannitol (m.p. 156–157°, $[\alpha]_D^{20} +23.4^\circ$ in chloroform), prepared in 20 to 29% yield from 1,6-dibenzoyl-D-mannitol using the procedure of Haworth and Wiggins,¹³ was suspended in a mixture of 50 ml. of chloroform and 150 ml. of absolute methanol. When 5 ml. of 1 *N* barium methylate was added solution was rapid; after two hours at room temperature the reaction mixture was passed through a column (3.2 \times 30 cm.) of Amberlite IR-120²⁵ and the neutral barium-free effluent concentrated *in vacuo* to a volume of ca. 25 ml. A faint turbidity and slight color were removed by filtration through decolorizing carbon and the solution, after treatment with two drops of pyridine, concentrated *in vacuo* at 45–50° (bath) to a sirup which crystallized spontaneously. From 19 ml. of warm absolute alcohol there was obtained 6.18 g. (88%) of needles melting at 108–109°. Successive recrystallization

(25) A product of the Resinols Products and Chemical Co., Washington Square, Philadelphia 5, Pa.

from absolute alcohol and from dioxane failed to change this value; the pure 2,4-methylene-D-mannitol showed a rotation of $+25.9^\circ$ in water (c 2.04).

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.29; H, 7.27. Found: C, 43.55; H, 7.27.

A sample (206.2 mg.) of the 2,4-methylene-D-mannitol, dissolved in a small amount of water, was treated with 5.0 ml. of ca. 0.5 *M* sodium metaperiodate and the resulting solution diluted with water to 25 ml. After 17 hours at room temperature analysis showed that 1.07 molar equivalents of oxidant had been consumed and that no acid had been formed.

1,3:2,5:4,6-Trimethylene-D-mannitol from 2,4-Methylene-D-mannitol (XIII).—A sample (212.7 mg.) of pure 2,4-methylene-D-mannitol was dissolved in a mixture of 0.45 ml. of 37% formalin and 0.45 ml. of concentrated hydrochloric acid and the solution kept at 50°. The formation of crystals was first observed after 105 minutes. After 5 days at 50° there was obtained 206.5 mg. (86%) of well-formed needles melting at 229–232°; mixed with authentic 1,3:2,5:4,6-trimethylene-D-mannitol they melted at 232–233°.

1,3,5,6-Tetrabenzoyl-2,4-methylene-D-mannitol.—One gram of 2,4-methylene-D-mannitol was benzoylated in the usual fashion with benzoyl chloride and pyridine. From ca. 50 ml. of absolute alcohol there was obtained 2.9 g. (42%) of product melting at 100–101°; after recrystallization from 17 parts of absolute alcohol the product melted at 101–103° and showed -83.8° in chloroform (c 2.15).

Anal. Calcd. for $C_{33}H_{30}O_{10}$: C, 68.84; H, 4.95. Found: C, 68.74; H, 5.03.

Acknowledgment.—The authors wish to thank Dr. C. S. Hudson for his interest in this research. For the analytical determinations we are indebted to Dr. William C. Alford, Mrs. Evelyn G. Peake, Miss Paula M. Parisius and Miss Mary Jean Stockton.

BETHESDA, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Friedel-Crafts Reaction with Disubstituted Ethylene Oxides. III. The Rearrangement of α,α -Dimethylbibenzyl

BY WILLARD T. SOMERVILLE¹ AND PAUL E. SPOERRI

RECEIVED NOVEMBER 27, 1950

d,l-2,3-Diphenylbutane was shown to be converted to the *meso* isomer in the presence of anhydrous aluminum chloride or concentrated sulfuric acid. Both neophyl chloride and benzylidimethylcarbinyl chloride yield a mixture of α,α -dimethyldibenzyl and *meso*-2,3-diphenylbutane when condensed with aluminum chloride and benzene. In order to obtain information concerning the mechanism of the rearrangement, α,α -dimethyldibenzyl has been treated with aluminum chloride using both chlorobenzene and toluene as solvents. The solvent has been shown to participate in the rearrangement indicating that the reaction was intermolecular and probably preceded by cleavage of the α,α -dimethyldibenzyl molecule. Mechanisms consistent with the experimental data are presented.

The rearrangement of α,α -dimethyldibenzyl in benzene solution to *meso*-2,3-diphenylbutane by aluminum chloride and the formation of this isomer from both isobutylene dibromide and benzylidimethylcarbinol in benzene in the Friedel-Crafts reaction has been reported² previously. The present work presents some additional cases of this rearrangement as well as the results of studies on the mechanism of these rearrangements.

The relationship between *d,l*- and *meso*-2,3-diphenylbutane was investigated. It was found

(1) Taken in part from a dissertation presented by Willard T. Somerville to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

(2) W. T. Somerville and P. E. Spoerri, *THIS JOURNAL*, **72**, 2185 (1950).

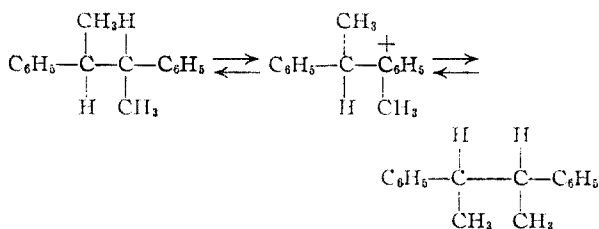
that the *d,l*-isomer is readily converted to the *meso* form when treated with aluminum chloride in benzene solution; the extent of conversion is dependent on the temperature and amount of aluminum chloride used. The results of these experiments are given in Table I.

TABLE I
ISOMERIZATION OF *d,l*-2,3-DIPHENYLBUTANE
(Time of reactions two hours.)

Expt. ^a	AlCl ₃ , moles	<i>t</i> , °C.	Yield of <i>meso</i> isomer, %
1	0.2	5–10	0
2	2.0	5–10	10.4
3	2.0	26–8	32

^a Using one mole of the *d,l*-isomer and 20 moles of benzene.

This may explain the absence of the *d,l*-isomer in the products of the Friedel-Crafts reaction with 2,3-butylene oxide as noted in the first paper of this series.² The *d,l*-isomer was also isomerized to the *meso* form when treated with concentrated sulfuric acid at 25°. Under these conditions, considerable sulfonation also took place. The isomerization may proceed by way of an intermediate carbonium ion



The use of sulfuric acid for racemization of substances containing asymmetric carbon atoms through the intermediate formation of a carbonium ion is well known³ but no examples of the use of aluminum chloride for this purpose have been found in the literature.

In an attempt to prepare α,α -dimethyldibenzyl free from rearranged product, other Friedel-Crafts reactions were investigated. The condensation of benzylmethylcarbinyl chloride (I) with benzene and aluminum chloride was found to give a mixture of α,α -dimethyldibenzyl (II) and *meso*-2,3-diphenylbutane (III). The same products were formed when neophyl chloride (IV) was used in this reaction.

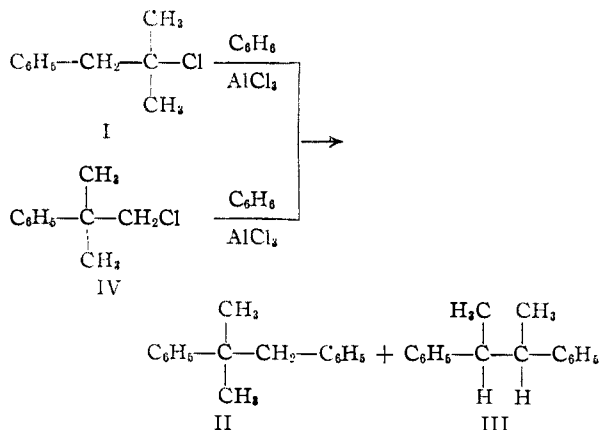
As in the case of *d,l*-2,3-diphenylbutane, the aluminum chloride rearrangement of α,α -dimethyldibenzyl proceeds to a greater extent in the presence of larger amounts of aluminum chloride and at higher temperatures.

To determine whether the rearrangement of α,α -dimethyldibenzyl occurred by an intramolecular shift of a methyl group and a hydride ion or by the cleavage of the molecule, followed by rearrangement and recombination, it was necessary to ascertain whether the solvent (benzene) participated in the reaction. The formation of the cleavage product, isobutylbenzene would indicate that the second course may be more likely. It was therefore essential to use a solvent which, if it entered into the reaction could be readily detected in the products. With a substituted benzene as solvent, rearrangement with solvent participation would be expected to give a product containing two different asymmetric carbon atoms and not a *meso* form.

In spite of its reduced activity, chlorobenzene was used as a reaction solvent for the rearrangement at 20–25°, since these conditions give a substantial amount of isomerized product in benzene solution and could be readily detected in the products. As the neophyl chloride-benzene Friedel-Crafts condensation also gave rearranged product, a neophyl chloride-chlorobenzene condensation was run simultaneously.

The reaction product from the rearrangement of

α,α -dimethyldibenzyl in chlorobenzene was a very complex mixture. The only product that could be isolated was *meso*-2,3-diphenylbutane equivalent to 0.4%. The neophyl chloride-chlorobenzene reaction gave as the principal product a colorless liquid containing chlorine having a density greater than water and a strong blue fluorescence. This was probably a mixture of 1-*p*-chlorophenyl-2-methyl-2-phenylpropane and 2-*p*-chlorophenyl-3-phenylbutane. It was not investigated further. In addition a very small amount of *meso*-2,3-diphenylbutane was also isolated. This was surprising in view of the complete absence of benzene in both reaction media.



The previously observed² rearrangement of α,α -dimethyldibenzyl in benzene solution was further studied. The extent of conversion to *meso*-2,3-diphenylbutane was found to be related to the temperature and amount of anhydrous aluminum chloride used in the reaction. The cleavage product of this reaction was identified as isobutylbenzene and not tertiary butylbenzene as previously reported² by a mixed melting point of the diacetyl-amino derivatives. The previously unknown diacetyl-amino derivative of isobutylbenzene was found to melt at 211–212° as compared with 210° for the diacetyl-amino derivative of *t*-butylbenzene.⁴ Bodroux⁵ has reported isobutylbenzene as a product of the reaction of isobutylene dibromide with benzene and aluminum chloride. Table II gives the results of the treatment of α,α -dimethyldibenzyl with aluminum chloride in benzene solution under various conditions.

TABLE II
REARRANGEMENT OF α,α -DIMETHYLDIBENZYL
Time of reaction five hours

Expt.	α,α -Dimethyl-dibenzyl, moles	AlCl ₃ , moles	Benzene, moles	<i>t</i> °	Yield of <i>meso</i> -2,3-diphenylbutane, %	Yield of isobutylbenzene, %
1	1	2	20	5–10	1.4	2.2
2	1.5	4.5	30	5–10	3.6	6.5
3	1	2	20	22–5	17	11.2

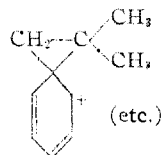
The rearrangement of α,α -dimethyldibenzyl was also conducted in toluene solution and again a neophyl chloride-toluene condensation was run as a control. In these reactions the following products were obtained:

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 178 ff., 315; R. L. Burwell, Jr., and G. S. Gordon, III, *This Journal*, **70**, 3128 (1948); G. S. Gordon, III, and R. L. Burwell, *ibid.*, **71**, 2355 (1949).

(4) V. N. Ipatieff and L. Schmerling, *ibid.*, **50**, 1056 (1937).
(5) F. Bodroux, *Compt. rend.*, **132**, 1333 (1901).

rearrangement of the α,α -dimethyldibenzyl in toluene solution.

The 1,2-shift of a phenyl group during the rearrangement of similar types of compounds has been previously observed. The pyrolysis of neophyl chloride has been shown by Whitmore to produce β,β -dimethylstyrene.¹⁰ Another case involves the rearrangement of a methyl analog of neophyl alcohol (2-methyl-2-phenyl-1-butanol) during treatment with thionyl chloride. The products obtained were 2-methyl-1-phenyl-1-butene, 2-chloro-2-methyl-1-phenylbutane as well as some of the corresponding alcohol.¹¹ A benzenium ion¹² such as



may be pictured as being an intermediate between carbonium ions VI and VII. The formation of II could occur by the action of benzene on this ion.

Experimental¹³

The anhydrous aluminum chloride used was the product of the Hooker Electrochemical Co. of Niagara Falls and contains a maximum of 0.05% iron. It was taken as needed from below the surface of a freshly opened 550 lb. drum.

***d,l*-2,3-Diphenylbutane.**—This compound was prepared by the coupling of α -chloroethylbenzene with magnesium in ether solution by a modification of the method of Lepin.¹⁴ The yield of *d,l*-isomer was 26.7%. It had the following physical constants: b.p. 110–111° (1.8 mm.); n_D^{20} 1.5557 and d_{4}^{20} 0.9766. The *meso* isomer was obtained in 28.2% yield; m.p. 125°.

Isomerization of *d,l*-2,3-Diphenylbutane. Isomerization with Sulfuric Acid.—One hundred grams of pure *d,l*-2,3-diphenylbutane was vigorously stirred with 100 ml. of concentrated sulfuric acid for 2.5 hours. The initial temperature was 25°; it rose to 37° within 10 minutes and then gradually subsided. The brownish-green reaction mixture was poured onto ice and water. The oily layer was carefully separated, washed free of acid with sodium carbonate solution and then dried with a small amount of anhydrous sodium sulfate. The yield of oil was 44 g. Upon refrigeration for several days, crystals were formed and removed. After recrystallization from alcohol 2.1 g. (2.1%) of pure *meso*-2,3-diphenylbutane melting at 125° was obtained.

Isomerization with Aluminum Chloride.—In the following experiments, the *d,l*-2,3-diphenylbutane was added all at once to a vigorously stirred suspension of the aluminum chloride in benzene. After stirring two hours at the desired temperature, the mixture was decomposed and worked up in the usual manner. The results are summarized in Table I.

Rearrangement of α,α -Dimethyldibenzyl in Benzene.—In the experiments, the α,α -dimethyldibenzyl was added all at once to a rapidly stirred suspension of aluminum chloride in benzene. After stirring for 5 hours at the proper temperature the reaction mixture was decomposed and worked up as above. The results are given in Table II.

Examination of the Butylbenzene Fraction.—Forty-eight grams of butylbenzene obtained from the rearrangement of α,α -dimethyldibenzyl was carefully fractionated. The major part of the distillate representing about 90% of the total had a b.p. of 172° at 757 mm. The boiling point of isobutylbenzene is 172.6°.¹⁵

(10) F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, Jr., *ibid.*, 65, 1469 (1943).

(11) E. S. Wallis and P. I. Bowman, *J. Org. Chem.*, 1, 383 (1936).

(12) D. J. Cram, *This Journal*, 71, 3863 (1949).

(13) The microanalyses were done by the Clark Microanalytical Laboratory, Urbana, Illinois.

(14) A. I. Lepin, *J. Russ. Phys. Chem. Soc.*, 44, 1190 (1912).

(15) Selected Values of Hydrocarbons, Bureau of Standards Circular C461 (1947).

The diacetylamino derivative was prepared from this material and a genuine sample. Both melted at 211–212°, and gave no depression when a mixed melting point was taken. The diacetylamino derivative of isobutylbenzene has not been previously reported.

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.74; H, 8.06; N, 11.29. Found: C, 67.24; H, 7.75; N, 11.32.

Condensation of Neophyl Chloride with Benzene.—Ten moles of neophyl chloride¹⁰ (1680 g.) dissolved in 3900 g. (50 moles) of benzene was gradually added over a period of 2.25 hours to a rapidly stirred mixture of 3900 g. (50 moles) of benzene and 133 g. (1 mole) of aluminum chloride at 10–12° in a 22-liter flask. The mixture became an orange brown in color, and 1.5 hours after the addition was complete, the evolution of hydrogen chloride ceased. The mixture was decomposed by pouring onto ice and water, washed free of acid and the excess benzene removed by distillation at 50 mm. pressure. The crude product had a very strong blue violet fluorescence. It was refluxed with 10% aqueous sodium hydroxide and finally vacuum distilled. The distillate boiling at 118–123° (3.5 mm.) contained crystals and amounted to 1403 g. The residue was 345 g. The crude α,α -dimethyldibenzyl was freed of crystalline material by repeated chilling to 0–5°. The yield of alcohol-washed crystals (*meso*-2,3-diphenylbutane) was 93 g. (4.4%).

The liquid portion was treated with an acetone solution of potassium permanganate to remove unsaturates and then carefully refractionated. The water white product (1014 g., 48.2%) boiled at 113–115° (1.8 mm.).

Condensation of Neophyl Chloride with Chlorobenzene.—One and one-half moles of neophyl chloride (252 g.) dissolved in 850 g. of chlorobenzene (7.5 moles) was added to a vigorously stirred suspension of 46.7 g. (0.35 mole) of aluminum chloride in 850 g. of chlorobenzene maintained at 10–12° over 1.25 hours. During the addition, the color of the reaction mixture changed from yellow to cherry red. It was then stirred for 3 hours at room temperature before decomposing and working up in the usual manner. Upon distillation, the fractions boiling at 125–139° (2 mm.) contained crystals. After chilling, filtering and recrystallization from alcohol, 0.8 g. of colorless crystals m.p. 125° was obtained. They were chlorine-free and did not depress the melting point of pure *meso*-2,3-diphenylbutane.

The main portion of the distillate was a colorless liquid giving a qualitative test for chlorine and having a strong blue fluorescence. It boiled at 145–65° (2.2 mm.), was heavier than water and amounted to 197 g. (53%). No further examination was made.

Rearrangement of α,α -Dimethyldibenzyl in Chlorobenzene.—Two hundred grams (0.95 mole) of α,α -dimethyldibenzyl dissolved in 500 g. (4.44 moles) of chlorobenzene was added all at once to an energetically stirred mixture of 1500 g. (13.32 moles) of chlorobenzene containing 26.6 g. (0.2 mole) of aluminum chloride at 10°. The mixture was stirred for 2.5 hours at this temperature during which the color changed from bright yellow to a dark red brown. The reaction mixture was decomposed by pouring onto ice and water and the solvent recovered at 50 mm. of pressure.

After a hot alkali treatment, the residual oil was vacuum distilled to yield: fraction 1, b.p. 117–130° (2 mm.), 38 g.; fraction 2, b.p. 130–153° (2 mm.), 26 g.; residue, 102 g. Fraction 1 on keeping in the refrigerator at 5° for 4–5 days slowly deposited crystals. These crystals were removed by filtration and recrystallized two times from alcohol. The yield of chlorine-free crystals amounted to 0.8 g. (0.4%). The melting point was 125° and was not depressed when mixed with an authentic specimen of *meso*-2,3-diphenylbutane.

Condensation of Neophyl Chloride with Toluene.—One and one-half moles (252 g.) of neophyl chloride dissolved in 920 g. (10 moles) of dry toluene was added to a vigorously stirred mixture of 1840 g. (20 moles) of toluene and 100 g. (0.75 mole) of aluminum chloride at 10–12°. After stirring for 4 hours at room temperature, the reaction mixture was decomposed and worked up as usual. Upon distillation at 2.0 mm. the following main fractions were obtained: fraction 1, b.p. 42°, 102 g.; fraction 2, b.p. 92–120°, 29 g.; fraction 3, b.p. 125–138°, 90 g.; residue, 48 g.

The first fraction was redistilled at atmospheric pressure. It was found to boil at 191–194° (757 mm.) with the major portion boiling at 193–194°. The yield of 85 g. is equivalent to 39% of *p*-isobutyltoluene having the following prop-

erties: d_{20}^{25} 0.8564; n_{20}^{25} 1.4885. *p*-Isobutyltoluene has been reported⁴ to have a boiling point of 191–192° (752 mm.); n_{20}^{25} 1.4888; d_{20}^{25} 0.8509. The semicarbazone of the acetyl derivative melts at 140–141° (141–142° reported).

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.34; H, 10.58.

Fraction 2, upon chilling, deposited crystals, which after recrystallization had a melting point of 125° (yield 0.8 g., 0.25%). The third fraction after refractionation boiled at 127–129° (1.8 mm.) and had an index of refraction n_{20}^{25} 1.5581; yield 71 g. (20.2%) of phenyltolylbutanes.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.30; H, 8.92.

Rearrangement of α, α -Dimethyldibenzyl in Toluene.—Two hundred grams (0.95 mole) of α, α -dimethyldibenzyl was added to 19 moles of toluene and 1.9 moles of aluminum chloride. After stirring for 5 hours at 25–30°, during which period the reaction mixture became brown, it was decomposed and worked up in the usual manner. Upon vacuum distillation, the following main fractions were obtained: fraction 1, b.p. 38–57° (1.8 mm.), 45 g.; fraction 2, b.p. 115–125° (1.8 mm.), 32 g.; fraction 3, b.p. 125–149° (1.8 mm.), 70 g.; residue, 30 g.

Fraction one upon redistillation at atmospheric pressure

boiled at 192–194° (757 mm.). The yield of 31 g. (22%) of *p*-isobutyltoluene had the following physical properties; d_{20}^{25} 0.8562; n_{20}^{25} 1.4880. The second fraction when chilled yielded 2.0 g. of crystals m.p. 125° (yield 1%). The third fraction was very carefully refractionated to yield 49 g. (22%) of phenyltolylbutanes boiling at 126–129° (1.8 mm.); n_{20}^{25} 1.5554.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.91; H, 9.19.

Friedel-Crafts Reaction on Benzylidimethylcarbinyl Chloride.—One hundred sixty-nine grams (1 mole) of benzylidimethylcarbinyl chloride was added to a vigorously stirred mixture of 266 g. (2 moles) of aluminum chloride in 1560 g. (20 moles) of benzene during a two-hour period keeping the reaction temperature at 5–10°. The mixture was stirred for one-half hour after the addition was completed and then poured on ice. After washing free of acid and recovering the excess solvent, the product was distilled. The portion of the distillate boiling at 112–115° (2.0 mm.) contained crystals. After processing in the usual manner, 15.8 g. (7.5%) of *meso*-2,3-diphenylbutane and 42.5 g. (20%) of α, α -dimethyldibenzyl were obtained.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

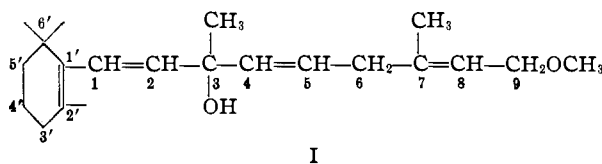
Synthesis of Polyenes. II. Allylic Rearrangements and Dehydrations in Substituted β -Ionols

BY WILLIAM OROSHNIK, GEORGE KARMAS AND ALEXANDER D. MEBANE

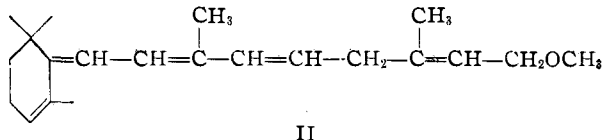
RECEIVED JANUARY 21, 1952

β -Ionols have been found, as a rule, to rearrange and dehydrate chiefly to *retro*ionylidene rather than β -ionylidene compounds. A notable exception was found in the case of the propargylic β -ionol, XIV. Possible mechanisms to explain these reactions, as well as the accompanying steric changes, are presented and discussed.

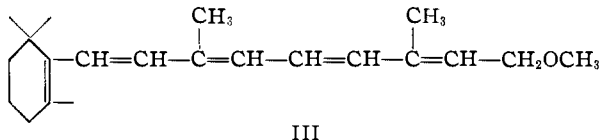
In Part I of this series¹ it was shown that the substituted β -ionol, 4,5-*cis*-I, undergoes a very facile allylic rearrangement and dehydration under the influence of acids, to give 4,5-*cis*- and 4,5-*trans*-II as well as a small quantity of vitamin A methyl ether, III.



I



II



III

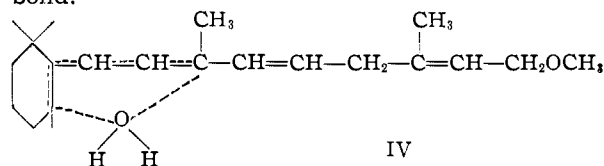
The rearrangement appears to follow the course established for simple divinylcarbinols, in which the hydroxyl group migrates toward the more alkylated double bond.² Braude and Jones,³ on the basis of

(1) W. Oroshnik, G. Karmas and A. D. Mebane, *THIS JOURNAL*, **74**, 295 (1952).

(2) I. M. Heilbron, E. R. H. Jones, J. T. McCombie and B. C. L. Weedon, *J. Chem. Soc.*, 85 (1945).

(3) E. A. Braude and E. R. H. Jones, *ibid.*, 128 (1946).

kinetic studies, have proposed a mechanism for this type of isomerization wherein an oxonium ion is formed in the initial stage and then isomerizes intramolecularly. In the case of I, which has a 4,5-*cis*-configuration, this mechanism would account only for the formation of 4,5-*cis*-II, since the transition state, IV, does not involve the 4,5-double bond.



IV

The simultaneous formation of the *trans*-isomer was previously thought to result from the stereoisomerizing effect of the dehydrating agent on the preformed *cis*-II.¹ However, it has now been found, by following the reaction spectrophotometrically, that the *cis-trans* ratio of the product is constant throughout the reaction, and is characteristic of the reaction medium. Thus, another mechanism involving the 4,5-double bond must be operating simultaneously. A reasonable explanation is afforded by assuming the formation of a carbonium ion which can be represented by resonance forms V and VI.⁴

(4) Because of the tendency toward conjugation, the contribution of

resonance forms of the type $-\text{CH}=\text{CH}-\overset{\text{CH}_3}{\underset{\oplus}{\text{C}}}-\text{CH}=\text{CH}-$ was considered as negligible.