

and dilute sulfuric acid (5%, 400 cc.) was refluxed for four and one-half hours. The cooled solution was neutralized with saturated barium hydroxide solution, centrifuged to remove barium sulfate, and concentrated under reduced pressure. The residue was dissolved in absolute ethanol, filtered and again concentrated. The product (28.0 g.) was fractionally distilled under reduced pressure and yielded 21.5 g. (67.4%) of product distilling at 207° (1.2 mm.) and possessing a n_D^{20} of 1.4885.^{1a}

Diglycerol from Isopropylidene- and Diisopropylidene-diglycerols.—Diisopropylidenediglycerol was hydrolyzed to diglycerol as previously described.^{1a} The monoisopropylidene derivative was hydrolyzed similarly to yield a theoretical quantity of the parent compound.

Summary

1. Diglycerol has been synthesized directly by the hydroxylation of allyl ether by the action

of permanganate and by the action of performic acid.

2. Diglycerol has also been synthesized by hydrolysis of the dichlorohydrin resulting from the addition of hypochlorous acid to allyl ether. The dichlorohydrin has likewise been converted to 2-epoxypropyl ether which has also been hydrolyzed to diglycerol.

3. Fractional distillation of diglycerol as diisopropylidenediglycerol has provided a simple means for isolating diglycerol from the reaction mixtures. Isopropylidenediglycerol forms as a by-product.

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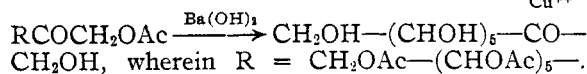
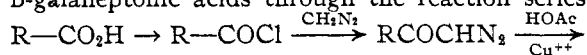
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

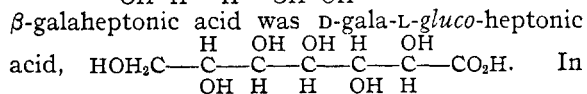
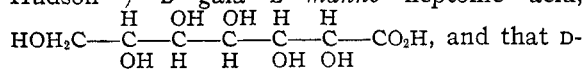
Two Ketoöctoses from the D-Galaheptonic Acids¹

BY M. L. WOLFROM AND PASCAL W. COOPER.

In continuation of our studies on the synthesis of higher ketoses, we report herein two new ketoöctoses prepared from the two isomeric D-galaheptonic acids through the reaction series



The more readily isolable form of D-galaheptonic acid, obtained through the cyanohydrin reaction on D-galactose, was described by Maquenne,² Kiliani³ and Fischer⁴ and was designated D- α -galaheptonic acid by the latter. The epimeric D- β -galaheptonic acid was first obtained by Fischer.⁴ Peirce⁵ proved that D- α -galaheptonic acid was configurationally (nomenclature of Hudson^{6,7}) D-gala-L-manno-heptonic acid,

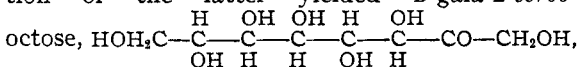


our work we followed the preparative directions of Hudson and co-workers^{8,9} for obtaining these two acids. Incidental to the isolation of D- α -galaheptonic acid as the amide, we describe the dihydrate of D-gala-L-manno-heptonamide.

D-Gala-L-manno-heptonic acid crystallizes in the unlactonized form and Robbins and Upson¹⁰ found it to be directly acetylatable to its crystalline hexaacetate. Treatment of the acetylated acid with phosphorus pentachloride yielded the crystalline hexaacetyl-D-gala-L-manno-heptonyl chloride which gave the crystalline acetylated diazomethyl ketone with diazomethane. The keto acetate resisted crystallization but was obtained in an analytically pure condition by chromatographic purification. Low temperature deacetylation with barium hydroxide yielded D-gala-L-tagato-octose, $HOH_2C-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CO-CH_2OH$.

This substance was unfortunately amorphous but was characterized further by a crystalline phenylosotriazole.

The crystalline epimeric hexaacetyl-D-gala-L-gluco-heptonic acid was obtained by the acetylation of the amorphous cadmium salt with acetic anhydride and hydrogen chloride according to the general procedure of Ladenburg, Tishler, Wellman and Babson.¹¹ It was further characterized as its methyl ester. The corresponding acetylated acid chloride failed to crystallize but the acetylated diazomethyl ketone and the keto acetate were obtained crystalline. Deacetylation of the latter yielded D-gala-L-sorbo-



again unfortunately not crystallized. It was characterized further by its known phenylosazone.

D-Gluco-L-tagato-octose has been described.¹² Its properties and those of two derivatives are

(10) G. B. Robbins and F. W. Upson, *ibid.*, **62**, 1074 (1940).

(11) K. Ladenburg, M. Tishler, J. W. Wellman and R. D. Babson, *ibid.*, **66**, 1217 (1944).

(12) M. L. Wolfrom and A. Thompson, *ibid.*, **63**, 1453 (1946).

(1) Paper No. 11 in the series entitled "The Action of Diazomethane upon Acyclic Sugar Derivatives"; previous communication, M. L. Wolfrom, J. M. Berkebile and A. Thompson, *THIS JOURNAL*, **71**, 2360 (1949).

(2) L. Maquenne, *Compt. rend.*, **106**, 286 (1888).

(3) H. Kiliani, *Ber.*, **21**, 915 (1888).

(4) E. Fischer, *Ann.*, **288**, 139 (1895).

(5) G. Peirce, *J. Biol. Chem.*, **22**, 327 (1915).

(6) C. S. Hudson, *THIS JOURNAL*, **60**, 1537 (1938).

(7) C. S. Hudson, *Advances in Carbohydrate Chem.*, **1**, 28 (1945).

(8) R. M. Mann, Alice T. Merrill and C. S. Hudson, *THIS JOURNAL*, **67**, 2100 (1935).

(9) R. M. Hann and C. S. Hudson, *ibid.*, **59**, 548 (1937).

TABLE I
COMPARATIVE PROPERTIES OF D-GLUCO-L-TAGATO-OCTOSE AND D-GALA-L-TAGATO-OCTOSE

Derivative	D-GlucO-L-tagato-octose ¹² M. p., °C.	$[\alpha]_D^{20}$ (c <5)	D-Gala-L-tagato-octose M. p., °C.	$[\alpha]_D^{20-25}$ (c <5)
Free sugar	Amorphous	+31° (H ₂ O)	Amorphous	-17° (H ₂ O)
Keto heptaacetate	77-79	+35 (CHCl ₃)	Amorphous	+31 (CHCl ₃)
Hexaacetyl diazomethyl ketone	Amorphous	+85 (CHCl ₃)	120-122	+22 (CHCl ₃)

shown in Table I in comparison with those of D-gala-L-tagato-octose. Although both of these keto octoses have the upper configuration of L-tagatose, the optical rotatory properties tabulated, save for those of the keto acetates, are very different. It is of interest that none of the three known keto octoses exhibit the Seliwanoff¹³ ketose test or are fermentable by yeast. Although it is a matter of keen disappointment to this Laboratory that none of these three keto octoses have as yet crystallized, they are nevertheless to be added to the list of six known aldo octoses⁷ to make a presently existent series of nine isomeric octoses.

Experimental

D-Gala-L-manno-heptonamide Dihydrate.—Crude D-gala-L-manno-heptonamide, prepared from D-galactose according to the procedure of Hann, Merrill and Hudson,⁸ was recrystallized from hot water and dried under reduced pressure at 56°; m. p. 102-105° (dec.), $[\alpha]_D^{24}$ +11° (c 1.84, water). For the anhydrous amide Hudson and Komatsu¹⁴ report the constants: m. p. 204-206°, $[\alpha]_D^{24}$ +14° (c 0.43, water).

Anal. Calcd. for C₇H₁₃O₇·2H₂O: C, 32.20; H, 7.32; N, 5.36; H₂O, 13.78. Found: C, 32.28; H, 7.06; N, 5.32; H₂O (loss in wt. at 110° under reduced pressure), 13.68.

Hexaacetyl-D-gala-L-manno-heptonyl Chloride Hexaacetate.—D-Gala-L-manno-heptonamide dihydrate was converted to D-gala-L-manno-heptonic acid according to the procedure of Hann, Merrill and Hudson⁸ and this was transformed into hexaacetyl-D-gala-L-manno-heptonic acid by low temperature acetylation with acetic anhydride and zinc chloride according to the directions of Robbins and Upson¹⁰; m. p. 176-177°, $[\alpha]_D^{29}$ +15° (c 3.94, chloroform). Hexaacetyl-D-gala-L-manno-heptonic acid (1.9 g.) suspended in 30 ml. of anhydrous ether, was treated with 1.8 g. of phosphorus pentachloride and the mixture was shaken mechanically at room temperature for several hours. Crystallization (1.8 g.) occurred when the resultant solution was maintained overnight at ice-box temperature. A further quantity (0.2 g.) was obtained from the mother liquor by concentration to one-half volume and cooling to 0°; total yield 1.8 g. (91%), m. p. 130-131°, $[\alpha]_D^{21}$ +26° (c 4.3, abs. chloroform). Several recrystallizations from anhydrous ether failed to alter these constants. The substance was soluble in acetone and chloroform, moderately so in ether, and was insoluble in water and petroleum ether.

Anal. Calcd. for C₇H₇O₇Cl(CH₃CO)₆: C, 45.93; H, 5.27; Cl, 7.13; sapon. value (8 equivs.), 16.11 ml. 0.1 N NaOH per 100 mg. Found: C, 45.93; H, 5.29; Cl, 7.06; sapon. value, 16.10 ml.

1-Diazo-1-desoxy-keto-D-gala-L-tagato-octose Hexaacetate.—A solution of D-gala-L-manno-heptonyl chloride hexaacetate (20.0 g.) in dry ether (200 ml.) was poured slowly with stirring into 275 ml. of anhydrous ether containing 4.5 g. of diazomethane. There was a slow evolution of nitrogen gas during the addition and subsequent precipitation of the product. The mixture was allowed to stand at 0° for four hours and was then permitted to warm

gradually to room temperature to effect a complete reaction. The crude material was isolated by distillation of the ether at atmospheric pressure; yield 14.0 g. (69.3%), m. p. 116-118°, $[\alpha]_D^{26}$ +19.5° (c 4.1, abs. chloroform).

The product (1 g.) was dissolved in 40 ml. of benzene and placed on a chromatographic column (270 mm. long × 44 mm. diam.¹⁵) containing 100 g. of Magnesol¹⁶-Celite¹⁶ (5:1 by wt.) and developed with 600 ml. of benzene-ethanol (100:1 by vol.). The main zone¹⁶ containing the diazomethyl ketone was near the middle of the column. After elution from the cut zone by 200 ml. of acetone, 0.5 g. of material was obtained on recrystallization from five parts of acetone by the addition of ten parts of petroleum ether; m. p. 120-122°, $[\alpha]_D^{21}$ +22° (c 4.5, chloroform), unchanged on further recrystallization effected in the same manner. This diazomethyl ketone formed slightly yellow crystals. It was soluble in acetone and chloroform, moderately so in warm ether and warm alcohol, and was insoluble in water and petroleum ether. It reduced warm Fehling solution.

Anal. Calcd. for C₂₀H₂₈O₁₃N₂: C, 47.81; H, 5.22; N, 5.57. Found: C, 47.86; H, 5.22; N, 5.82.

keto-D-Gala-L-tagato-octose Heptaacetate.—A solution of 1-diazo-1-desoxy-keto-D-gala-L-tagato-octose hexaacetate (4.6 g.) in 50 ml. of glacial acetic acid containing a trace of cupric acetate (0.015 g.) was heated to reflux. As soon as the violent reaction had subsided, the solution was evaporated under reduced pressure at 50° to about 10 ml. The solution was then diluted with 75 ml. of chloroform, washed three times with water, dried with anhydrous sodium sulfate and evaporated under reduced pressure to a sirup. Since Wolf from and Thompson¹² had shown that considerable deacetylation takes place in this general procedure, the sirup was completely acetylated by treatment with 50 ml. of acetic anhydride containing 0.5 g. of zinc chloride. After standing overnight at room temperature, the acetic anhydride was hydrolyzed with 200 g. of ice and water. The acetate was extracted with chloroform, the chloroform solution washed with water, dried and evaporated under reduced pressure to a sirup. The sirup failed to crystallize.

The sirup (1 g.) was dissolved in 40 ml. of benzene and placed on a chromatographic column (270 mm. long × 44 mm. diam.¹⁶) containing 100 g. of Magnesol¹⁶-Celite¹⁶ (5:1 by wt.) and developed with 600 ml. of benzene-ethanol (100:1 by vol.). The principal zone,¹⁶ near the top, after elution with 300 ml. of acetone, failed to crystallize. This procedure was repeated two more times, but still the material failed to crystallize. The pure material was obtained after dissolving in acetone (decolorizing charcoal) and drying the resulting sirup at 56° under reduced pressure and over phosphorus pentoxide; $[\alpha]_D^{25}$ +31° (c 3.9, abs. chloroform). It was readily soluble in acetone and chloroform, moderately so in alcohol and was insoluble in water and petroleum ether. It reduced warm Fehling solution and gave the Pacsu¹⁷ keto acetate test.

Anal. Calcd. for C₈H₈O₈(CH₃CO)₇: C, 49.43; H, 5.65; CH₃CO, 13.10 ml. 0.1 N NaOH per 100 mg. Found: C, 49.46; H, 5.44; CH₃CO, 13.20 ml.

D-Gala-L-tagato-octose.—The general procedure of Wolf from, Thompson and Evans¹⁸ was followed in preparing

(15) Adsorbent dimensions.

(16) W. H. McNeely, W. W. Binkley and M. L. Wolf from, *THIS JOURNAL*, **67**, 527 (1945).

(17) E. Pacsu and F. V. Rich, *ibid.*, **55**, 3018 (1933); F. B. Cramer and E. Pacsu, *ibid.*, **59**, 1467 (1937).

(18) M. L. Wolf from, A. Thompson and E. F. Evans, *ibid.*, **67**, 1793 (1945).

(13) T. Seliwanoff, *Ber.*, **20**, 181 (1887).

(14) C. S. Hudson and S. Komatsu, *THIS JOURNAL*, **41**, 1141 (1919).

this compound. To a solution, cooled to 0°, of 22 g. of barium hydroxide octahydrate in 220 ml. of water, was added 5 g. of amorphous *keto*-D-gala-L-tagato-octose heptaacetate. The mixture was maintained at 0° and shaken occasionally until the acetate had dissolved, which required about sixty minutes. The mixture was kept at 0° for two hours longer. The inorganic ions were then removed and the sirupy product was isolated as described in the previous publication¹⁸; yield 2.0 g., $[\alpha]^{21}_D -17^\circ$ (c 4.0, water, no mutarotation).

The amorphous product was very soluble in water and was insoluble in ethanol and acetone. It reduced hot Fehling solution. It exhibited a negative Seliwanoff ketose test. The new ketoöctose was not fermented by bakers' yeast. It possessed a sweet taste. The product has so far resisted crystallization.

Anal. Calcd. for $C_8H_{16}O_8$: C, 40.00; H, 6.72. Found: C, 40.07; H, 6.74; ash, absent.

D-Gala-L-tagato-octose Phenylsazone and Phenylsotriazole.—D-Gala-L-tagato-octose was converted to the phenylsazone; m. p. 225–229°, in fair agreement with the value 224° (cor.) cited by Fischer.⁴ Following the general procedure of Haskins, Hann and Hudson,¹⁹ this phenylsazone (1.8 g.) and 1.17 g. of cupric sulfate pentahydrate in 50 ml. of water was refluxed for two hours. The reaction mixture was filtered hot and on cooling the material crystallized. Pure material was obtained on two recrystallizations from water; 0.8 g., m. p. 200–202°, $[\alpha]^{25}_D +26^\circ$ (c 1.5, pyridine).

Anal. Calcd. for $C_{14}H_{19}O_8N_3$: C, 51.68; H, 5.88; N, 12.92. Found: C, 51.67; H, 5.66; N, 13.16.

Hexaacetyl-D-gala-L-gluco-heptonic Acid.—The filtrate from the D-gala-L-manno-heptonamide⁸ was employed for the preparation of D-gala-L-gluco-heptonic acid, isolated through its phenylhydrazide (m. p. 183–185°, $[\alpha]^{25}_D -8^\circ$ in water at c 3.86) according to the procedure of Hann and Hudson.⁹ The aqueous solution of the acid so prepared was treated under mechanical stirring with an excess of cadmium hydroxide at 50–60° for four hours and the mixture was then maintained overnight at room temperature. The filtered solution was concentrated to a volume of 200 ml. and the salt was precipitated by pouring the aqueous solution into 1000 ml. of methanol. The amorphous solid was dried to constant weight, under reduced pressure, over phosphorus pentoxide at room temperature.

Following the general acetylation procedure of Ladenburg and associates,¹¹ a suspension of 40 g. of cadmium D-gala-L-gluco-heptonate in 200 ml. of acetic anhydride was cooled to 10° and dry hydrogen chloride was passed through the suspension for three hours with stirring. The temperature of the reaction mixture was raised to 50° and so maintained for one hour. The mixture was concentrated under reduced pressure and the residue was slurried with 200 ml. of ice and water to dissolve the inorganic salts. The product was obtained by filtering and washing with cold water; yield 47.0 g. One recrystallization from acetone gave pure material; m. p. 210–212°, $[\alpha]^{25}_D +16.5^\circ$ (c 1.1, acetone). This substance was sparingly soluble in hot acetone, ether and chloroform. It was insufficiently soluble in chloroform for polarization purposes.

Anal. Calcd. for $C_7H_8O_8(CH_3CO)_6$: C, 47.70; H, 5.47; sapon. value (7 equivs.), 14.63 ml. 0.1 N NaOH per 100 mg. Found: C, 47.88; H, 5.49; sapon. value, 14.68 ml.

Methyl Hexaacetyl-D-gala-L-gluco-heptonate.—A suspension of 1 g. of hexaacetyl-D-gala-L-gluco-heptonic acid in 20 ml. of dry ether was added to 50 ml. of an ethereal solution of diazomethane (slightly in excess of 1 mole) and allowed to stand at room temperature for six hours. Crystals were obtained on filtration and solvent removal; yield 0.8 g. Two recrystallizations from acetone-petroleum ether gave pure material; m. p. 125–127°, $[\alpha]^{25}_D +20^\circ$ (c 4.47, chloroform).

(19) W. T. Haskins, R. M. Hann and C. S. Hudson, *THIS JOURNAL*, **67**, 939 (1945).

Anal. Calcd. for $C_{20}H_{28}O_{14}$: C, 48.77; H, 5.73. Found: C, 48.73; H, 5.84.

1-Diazo-1-desoxy-keto-D-gala-L-sorbo-octose Hexaacetate.—Hexaacetyl-D-gala-L-gluco-heptonic acid (10 g.) was suspended in 100 ml. of benzene containing 6 ml. of purified²⁰ thionyl chloride and 5 drops of pyridine and the mixture was refluxed for two hours, filtered hot and maintained at room temperature overnight. The crude acid chloride was isolated by solvent removal under reduced pressure at room temperature, the last traces of thionyl chloride being removed by co-distillation under reduced pressure at 35–40°, with absolute ether. No suitable method for purifying this substance was found and the crude, amorphous solid was used directly in the next step.

An amount of 9 g. of the above acid chloride was converted to the crude diazomethyl ketone and the crude product (8.2 g.) was purified chromatographically as described above for the synthesis of 1-diazo-1-desoxy-keto-D-gala-L-tagato-octose hexaacetate. The sectioned main zone, located near the bottom of the column, was eluted with acetone; yield 0.4 g. Pure material was obtained on further crystallization from acetone-petroleum ether; m. p. 133–135°, $[\alpha]^{25}_D -29.5^\circ$ (c 4.5, chloroform). This diazomethyl ketone formed yellow needles that were insoluble in ether and petroleum ether but were very soluble in acetone, chloroform and ethanol.

Anal. Calcd. for $C_{20}H_{26}O_{13}N_2$: C, 47.81; H, 5.22; N, 5.57. Found: C, 47.88; H, 5.21; N, 5.58.

keto-D-Gala-L-sorbo-octose Heptaacetate.—This substance was prepared from 1-diazo-1-desoxy-keto-D-gala-L-sorbo-octose hexaacetate (3.44 g.) as described above for the synthesis of *keto*-D-gala-L-tagato-octose heptaacetate and the further acetylated product was isolated in the same manner, the final product being crystalline; yield 3.29 g. Pure material was obtained on further crystallization from acetone-petroleum ether; m. p. 104–106°, $[\alpha]^{25}_D +11^\circ$ (c 5.5, chloroform). *keto*-D-Gala-L-sorbo-octose heptaacetate crystallized in beautiful, white, elongated needles. It was readily soluble in acetone and chloroform, moderately so in ethanol and ether, and was insoluble in petroleum ether and water. It reduced hot Fehling solution, gave the Pacsu¹⁷ keto acetate test, and exhibited an absorption band with a maximum at 2870 Å.; $\log \epsilon_{\max} = 1.67$ (c 0.0308 M in U. S. P. chloroform, 1-cm. cell, Beckman quartz spectrophotometer, model DU).

Anal. Calcd. for $C_{22}H_{30}O_{15}$: C, 49.45; H, 5.66. Found: C, 49.61; H, 5.50.

D-Gala-L-sorbo-octose and its Phenylsazone.—*keto*-D-Gala-L-sorbo-octose heptaacetate (2.5 g.) was deacetylated as described above for the synthesis of D-gala-L-tagato-octose and the product was isolated in the same manner; yield 0.8 g., $[\alpha]^{25}_D -45^\circ$ (c 5.0, water, no mutarotation).

The white, amorphous product was soluble in water, hot acetic acid and methanol but was insoluble in ethanol and acetone. It reduced hot Fehling solution and possessed a sweet taste. The new ketoöctose was not fermented by bakers' yeast. It exhibited a negative Seliwanoff test. The product has so far resisted crystallization.

Anal. Calcd. for $C_8H_{16}O_8$: C, 40.00; H, 6.72. Found: C, 40.07; H, 6.65; ash, absent.

The crystalline phenylsazone of this octose was prepared: m. p. 200–205° (dec., cor.), $[\alpha]^{25}_D -4.3^\circ$ (0.5 hr.) → -43° (4 days, c 2.3, pyridine), in agreement with the values cited by Hann, Merrill and Hudson.²²

Anal. Calcd. for $C_{20}H_{26}O_8N_4$: C, 57.40; H, 6.26; N, 13.39. Found: C, 57.45; H, 6.23; N, 13.48.

Acknowledgment.—We are pleased to acknowledge the counsel of Dr. A. Thompson of this Laboratory.

(20) D. L. Cottle, *ibid.*, **68**, 1380 (1946).

(21) $\epsilon_{\max} = E_{\max} \times \text{mol. wt.}/C \times D$; C = g./l., D = cell thickness in cm.

(22) R. M. Hann, Alice T. Merrill and C. S. Hudson, *ibid.*, **66**, 1912 (1944).

Summary

1. The two D-galaheptonic acids have been converted to amorphous ketoöctoses, designated D-gala-L-tagato-octose and D-gala-L-sorbo-octose. The former has been characterized by its crystalline phenylosazone and phenylosotriazole and the latter by its crystalline keto acetate and phenylosazone.

2. Crystalline 1-diazo-1-desoxy-keto-D-gala-L-

tagato-octose hexaacetate, 1-diazo-1-desoxy-keto-D-gala-L-sorbo-octose hexaacetate and the amorphous keto-D-gala-L-tagato-octose heptaacetate are described.

3. D-Gala-L-manno-heptonamide dihydrate, hexaacetyl-D-gala-L-manno-heptonyl chloride, hexaacetyl-D-gala-L-glucio-heptonic acid (and its methyl ester) are described in crystalline condition.

COLUMBUS, OHIO

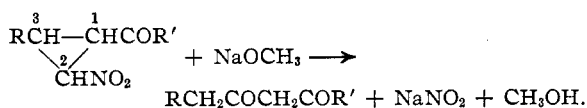
RECEIVED MARCH 18, 1949

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

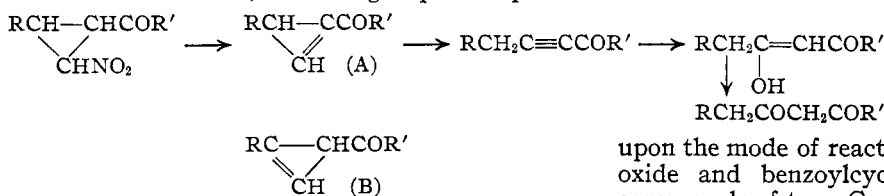
Cyclopropanes. I. The Reaction between Nitrocyclopropyl Ketones and Alkali

BY LEE IRVIN SMITH AND VAUGHN A. ENGELHARDT¹

Kohler and his students, in a long series of researches,² found that nitrocyclopropyl carbonyl compounds, having one hydrogen atom attached to the carbon atom holding the nitro group, reacted with alkaline reagents to produce ultimately 1,3-dicarbonyl compounds.



In the reaction, the ring was opened between carbon atoms 1 and 3, the nitro group was replaced

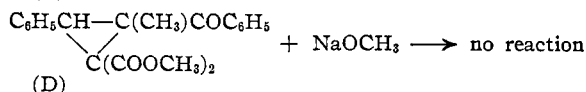
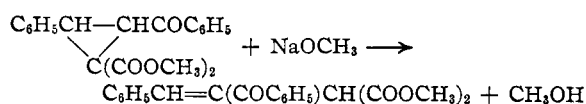


by the hydroxyl- or alkoxy- group, giving the enol form (or a derivative of it) of the diketone which was transformed into the diketone itself. A mechanism was proposed for this transformation,^{2d} and considerable evidence was accumulated to support it, although the presence of certain of the key intermediates was not established directly. The mechanism involved conversion of the nitrocyclopropyl ketone, by loss of the elements of nitrous acid, into a cyclopropene derivative and isomerization of the latter to an α,β -acetylenic ketone which, by addition of the elements of water, would lead to the enol of the 1,3-diketone.

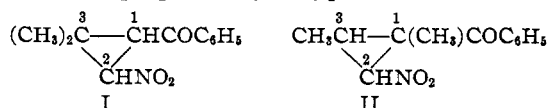
All of the nitrocyclopropyl ketones investigated by Kohler were so constituted that there was at

least one hydrogen atom attached to each of carbon atoms 1 and 3; hence, each of these, by loss of the elements of nitrous acid, could give rise to a cyclopropene of either type A, in which the double bond was conjugated with the carbonyl group, or type B, in which the double bond was not so conjugated.

One of the first problems to be solved, therefore, in a study of Kohler's mechanism is the question as to whether the double bond in the hypothetical cyclopropene must lie in the α,β - or β,γ -position to the carbonyl group; this paper is concerned with the results of an investigation designed to decide the point. In addition, it was hoped that the study might lead to results having a bearing upon the mode of reaction between sodium methoxide and benzoylcyclopropyl esters³ whereby compounds of type C react, but those of type D are unaffected.



Two nitrocyclopropyl ketones, I and II, were synthesized: I is so constituted that loss of the elements of nitrous acid could give a cyclopropene only of type A (α,β), whereas II could give a cyclopropene only of type B (β,γ).



When the 3,3-dimethyl-2-nitro-1-cyclopropyl phenyl ketone (I) was added to methanol containing four equivalents of sodium methoxide,

(3) Kohler and Conant, *THIS JOURNAL*, **39**, 1404, 1699 (1917).

(1) Abstracted from a thesis presented to the Graduate Faculty of the University of Minnesota by Vaughn A. Engelhardt, in partial fulfillment of the requirements for the Ph.D. degree, August, 1948. Presented at the 115th meeting of the American Chemical Society, San Francisco, California, March 27-April 1, 1949.

(2) (a) Kohler and Engelbrecht, *THIS JOURNAL*, **41**, 1379 (1919). (b) Kohler and Williams, *ibid.*, **41**, 1644 (1919). (c) Kohler and Rao, *ibid.*, **41**, 1697 (1919). (d) Kohler and Smith, *ibid.*, **44**, 624 (1922). (e) Kohler and Allen, *ibid.*, **50**, 884 (1928).