

To obtain the chloromercuri compound, 2 g. of 2-acetoxymercuri-4-chloro-6-*n*-butylresorcinol was suspended in 10 cc. of water and 1 cc. of alcohol. The mixture was treated with 0.5 cc. of concd. hydrochloric acid and stirred for thirty minutes. A substance was produced which when crystallized from warm dilute alcohol gave 0.8 g. of a white solid melting at 144–145°. Mixed with the original acetoxymercuri compound it melted at 113–118°.

*Anal.* Calcd. for  $C_{10}H_{12}O_2Cl_2Hg$ : Hg, 46.05. Found: Hg, 46.68.

The same compound was obtained in 16% yield by pouring a solution of the acetoxy compound in hot 95% alcohol into a saturated sodium chloride solution.

An acetic acid or alcoholic solution of the chloromercuri compound did not give a precipitate of mercuric sulfide when treated with hydrogen sulfide. An alcoholic solution after standing for four months still gave no precipitate. A slight cloudiness was evident when the hydrogen sulfide was passed into a 0.01 *N* sodium hydroxide solution of the compound while a pyridine solution gave a heavy precipitate.

**Mercuration of 4-Chloro-6-*n*-butylresorcinol.**—Mercuration of 4-chloro-6-*n*-butylresorcinol carried out as with the *n*-butyl derivative and also according to the method of Sandin<sup>10</sup> gave a compound which was of the anhydro type. It melted at 227–230° when recrystallized from a mixture of acetic acid and alcohol. It was insoluble in alcohol alone.

*Anal.* Calcd. for  $C_{10}H_8O_3ClHg$ : Hg, 48.57. Found: Hg, 47.87.

Warming the above anhydro compound with dilute hydrochloric acid or pouring its solution in glacial acetic acid into a saturated sodium chloride solution gave a small amount of 2-chloromercuri-4-chloro-6-*n*-butylresorcinol, which when recrystallized from alcohol melted at 218–220°.

*Anal.* Calcd. for  $C_{10}H_{10}O_3Cl_2Hg$ : Hg, 44.62. Found: Hg, 44.3.

**Mercuration of *n*-Butylresorcinol.**—Mercuration in glacial acetic acid solution<sup>11</sup> gave 4-acetoxymercuri-6-*n*-butylresorcinol, m. p. 164–165°.

*Anal.* Calcd. for  $C_{12}H_{16}O_4Hg_2$ : Hg, 47.22. Found: Hg, 46.9.

By treatment with dilute hydrochloric acid the chloromercuri compound resulted. This melted at 105–107°. Only a trace of material was obtained.

Mercuration of *n*-butylresorcinol with an excess of mercuric acetate in alcohol gave a bright yellow compound melting above 230°.

*Anal.* Calcd. for  $C_{12}H_{14}O_4Hg$ : Hg, 64.38. Found: Hg, 63.6.

The analysis indicates this to be the anhydromercuri-acetoxymercuri compound.

**Mercury Analyses.**—The mercury analyses were effected by decomposing the compounds with hydrochloric acid and precipitating the mercury as the sulfide.<sup>20</sup>

### Summary

1. Previous evidence for the structure of 4-chlororesorcinol has been questioned and another proof of its structure given.
2. A number of halogen and mercury derivatives of 4-*n*-butylresorcinol has been prepared.
3. The bactericidal properties of these compounds have been investigated.

(20) Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, 1921, p. 382.

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RECEIVED JULY 27, 1934

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## The Acetoacetic Ester Condensation. IX. The Condensation of Ethyl $\alpha$ -Carbethoxy- $\beta$ -phenyl- $\gamma$ -isobutyrylbutyrate<sup>1</sup>

BY RICHARD F. B. COX AND S. M. McELVAIN

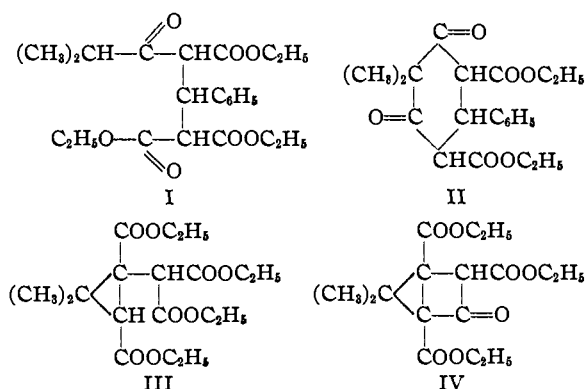
In a recent paper<sup>2</sup> it was suggested that the condensation of ethyl  $\alpha$ -isobutyryl- $\alpha'$ -carbethoxy- $\beta$ -phenylglutarate (I) to the cyclohexanedione (II) together with the reported condensation of 1,1-dimethyl-2,3-dicarbethoxy-3-diethylmalonate-cyclopropane (III) to the cyclobutane derivative<sup>3</sup> (IV) led to the conclusion that an acetoacetic ester condensation would take place between a carbethoxy group and a carbon carrying a single hydrogen atom only when the condensing carbethoxy group is a part of a mono-

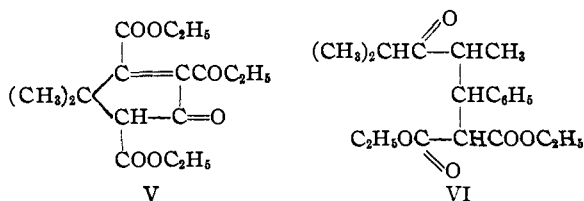
(1) This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

(2) Cox, Kroeker and McElvain, *THIS JOURNAL*, **56**, 1173 (1934).

(3) Perkin and Thorpe, *J. Chem. Soc.*, **79**, 736 (1901); *cf.* also ngold and Thorpe, *ibid.*, **115**, 330 (1919).

substituted malonic ester structure. However, the mechanism for the condensation which was





proposed as the result of this conclusion is not beyond criticism, in view of the doubt as to the structure of IV raised by Toivonen,<sup>4</sup> who claims that V rather than IV is produced by the action of sodium ethoxide on III. If Toivonen's contention be correct, then the only known condensation which involves a carbon carrying a single hydrogen atom is that of I to II and this one may be connected, as Dieckmann and Kron<sup>5</sup> have intimated, with the high enolic acidity of I which contains a  $\beta$ -keto ester as well as a mono-substituted malonic ester structure.

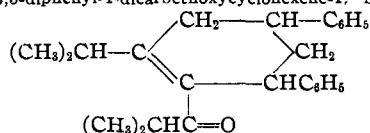
In order to determine whether or not the malonic ester structure alone was responsible for the internal condensation of I it seemed necessary to study the action of sodium ethoxide on such a compound as VI which does not contain the  $\beta$ -keto ester structure in question. Compound VI seemed most desirable for such a study because each of the carbon atoms that might enter into an acetoacetic ester condensation carries only one hydrogen atom. Unfortunately, the only apparently feasible method of preparation of VI, the addition of malonic ester to benzal ethyl isopropyl ketone, had to be given up because of the extremely low yields (12%) encountered in the preparation of the latter compound. Consequently, ethyl  $\alpha$ -carbethoxy- $\beta$ -phenyl- $\gamma$ -isobutyrylbutyrate (IX), which was readily prepared from malonic ester (VII) and benzalmethyl isopropyl ketone (VIII), was used instead of VI. Although this ester (IX) contains a methylene group adjacent to the carbonyl group it seemed unlikely that this group would function in an intramolecular condensation to produce a cyclobutane derivative.

Numerous products were obtained from the reaction of the ester IX with sodium ethoxide.<sup>6</sup>

(4) Toivonen, *Chem. Zentr.*, I 1356 (1923).

(5) Dieckmann and Kron, *Ber.*, 41, 1260 (1908).

(6) Dieckmann [*ibid.*, 41, 1276 (1908)] attempted the preparation of X from the reaction of VII and VIII with sodium ethoxide. He made no attempt to isolate the intermediate product (IX). He reported that the main product of the reaction was 1-isopropyl-2-isobutyryl-3,5-diphenyl-4-dicarbethoxycyclohexene-1. m. p. 190°:



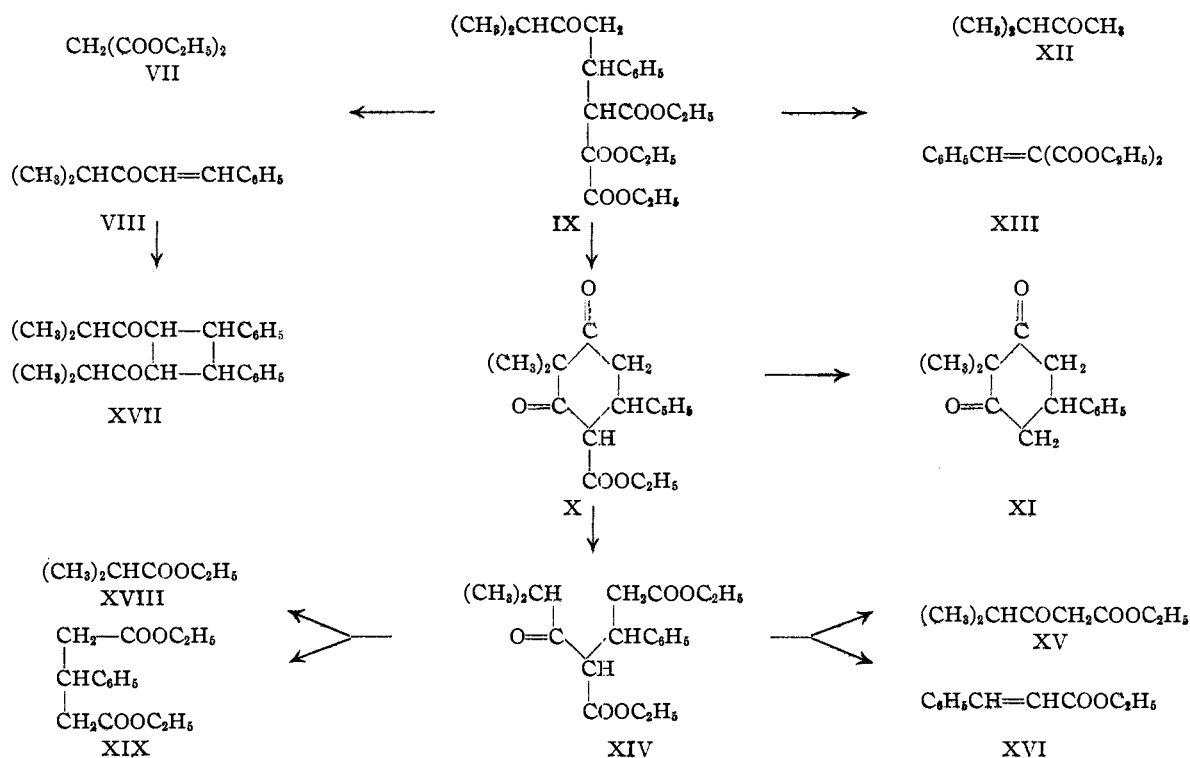
While the reaction was in progress about 1.5 moles of alcohol per mole of sodium ethoxide distilled out of the reaction mixture. A trace of ethyl isobutyrate was found in this alcohol. When the reaction mixture was worked up and fractionally distilled, the following products were identified in the various fractions: ethyl isobutyrylacetate (XV), malonic ester (VII), ethyl cinnamate (XVI), 2,2-dimethyl-5-phenylcyclohexanedione-1,3 (XI), two isomeric compounds which have been designated tentatively as diphenyldiisobutyrylcyclobutanes (XVII), benzal-malonic ester (XIII), methyl isopropyl ketone (XII) and ethyl isobutyrate (XVIII).

The formation of these various reaction products may be explained in the following manner. The ester IX, in the presence of sodium ethoxide, undergoes two distinct Michael retrogressions, one to give the materials VII and VIII from which IX was prepared and another to give methyl isopropyl ketone<sup>7</sup> (XII) and benzal-malonic ester (XIII). At the same time IX undergoes an internal acetoacetic ester condensation to produce the expected 2,2-dimethyl-4-carbethoxy-5-phenylcyclohexanedione-1,3 (X). This latter compound suffers alcoholysis to produce (a) 2,2-dimethyl-5-phenylcyclohexanedione-1,3 (XI) and (b) an intermediate open chain compound XIV which was found in the form of its retrogression products, ethyl isobutyrylacetate (XV) and ethyl cinnamate (XVI). A small amount of alcoholysis of XIV accounts for the small quantity of ethyl isobutyrate XVIII isolated. The other product of this alcoholysis (XIX) was not isolated. The dimerization of benzalmethyl isopropyl ketone (VIII) produces the diphenyldiisobutyrylcyclobutanes XVII which were isolated. These transformations may be illustrated as shown.

Although the carbethoxycyclohexanedione (X) was not obtained in pure form from the reaction mixture, the cyclic diketone (XI) derived from it was isolated. The fraction boiling within the range expected for X gave a strong coloration with ferric chloride but only XI could be caused to crystallize from it. When this fraction, after the removal of XI, was decarboxylated by heat—

None of this compound was found in the present investigation. The only evidence which Dieckmann found for the formation of X was a color test which one of the distillation fractions gave with ferric chloride.

(7) Connor, *THIS JOURNAL*, 55, 4599 (1933), has reported that simple ketones readily undergo the Michael condensation with unsaturated esters.



ing with benzoic acid, an additional quantity of the cyclic diketone (XI) was obtained. These results leave no doubt that the ester (IX) undergoes an internal acetoacetic ester condensation and accordingly give further support to the recently proposed<sup>2</sup> mechanism of the condensation.

The structures of the two cyclobutane derivatives (XVII) that were isolated from the reaction were not determined definitely. The boiling point of the fraction from which they were obtained together with the analyses of the recrystallized material indicate that they are dimers of benzalmethyl isopropyl ketone. One isomer melted at  $180^\circ$  and the other at  $155^\circ$ . When the lower melting isomer was heated with acetic anhydride at  $140^\circ$ , it was converted mainly into the higher melting isomer and partially into a third isomer which melted at  $182^\circ$ . An attempt was made to produce these compounds directly from benzalmethyl isopropyl ketone and sodium ethoxide, but only an uncrystallizable glassy solid was obtained. This material, however, boiled within the expected range and gave carbon and hydrogen analyses corresponding to a dimer of benzalmethyl isopropyl ketone.

### Experimental

**Materials Used.** Methyl isopropyl ketone was prepared according to the method described in "Organic

Syntheses."<sup>8</sup> Ethyl isopropyl ketone was obtained from the reaction of isobutyryl chloride and diethyl zinc.<sup>9</sup> Benzalmethyl isopropyl ketone was prepared in 57% yields by the method of Rupe and Hirschmann.<sup>10</sup> The product used boiled at  $140$ – $141^\circ$  (10 mm.). By the same procedure only a 12% yield of benzalethyl isopropyl ketone could be obtained from ethyl isopropyl ketone. This product boils at  $140$ – $141^\circ$  (12 mm.),  $n_D^{25}$  1.5530;  $d_4^{25}$  0.9824. *Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}$ : C, 82.98; H, 8.51. Found: C, 82.62; H, 8.55.

**Ethyl  $\alpha$ -Carbethoxy- $\beta$ -phenyl- $\gamma$ -isobutyrylbutyrate (IX).**—To 25 cc. of absolute alcohol in a 1-liter flask, fitted with a reflux condenser, a dropping funnel and a mechanical stirrer, was added 0.7 g. (0.03 atom) of sodium. When the sodium had dissolved, 54 g. (0.34 mole) of malonic ester in 100 cc. of dry ether was added. Then to this mixture 58 g. (0.34 mole) of benzalmethyl isopropyl ketone was added slowly with stirring. During this addition sufficient heat was generated to cause the ether to reflux. After all of the material had been added, refluxing was continued for two hours. The ether solution was then cooled, acidified with 10 cc. of a 10% hydrochloric acid solution and, after washing with sodium bicarbonate solution and with water, it was dried and distilled. The yield of IX was 88 g. (79% of theoretical). It boiled at  $192$ – $194^\circ$  (7 mm.) and solidified on cooling. After recrystallization from 70% alcohol it melted at  $42^\circ$ . *Anal.* Calcd. for  $\text{C}_{19}\text{H}_{26}\text{O}_5$ : C, 68.36; H, 7.78. Found: C, 68.54; H, 7.91.

**Reaction of IX with Sodium Ethoxide.**—To 13.16 g. (0.2 mole) of sodium ethoxide contained in a 200-cc. flask

(8) "Organic Syntheses," 1933, Vol. XIII, p. 68.

(9) Blaise and Herman, *Ann. chim. phys.*, [8] 17, 371 (1909).

(10) Rupe and Hirschmann, *Helv. Chim. Acta*, 14, 699 (1931).

fitted with a condenser for distillation and a stirrer to operate under diminished pressure was added 66.8 g. (0.2 mole) of the ester (IX). The reaction was carried out under diminished pressure as previously described.<sup>2</sup> After four hours of reaction at 125–130°, 14.3 g. (0.31 mole) of alcohol had distilled out of the reaction mixture. The alcohol from four such runs after refluxing with alkali and subsequent acidification gave an acid which was shown by DuClaux values to be isobutyric acid.

The mixture remaining in the reaction flask was poured out while still warm. After cooling it was powdered, dissolved in 300 cc. of ether, and treated with 100 cc. of ice water containing 15 cc. of acetic acid. The ether layer was separated, dried, and the ether removed by distillation from a water-bath. On cooling the residue crystals separated. After filtration and recrystallization from 95% alcohol these crystals melted at 180° (see fraction g, below).

The reaction mixture remaining after the removal of these crystals was fractionally distilled. The following fractions were collected and characterized: (a) 80–90° (745 mm.), 1.0 g. This fraction was methyl isopropyl ketone (XII); semicarbazone, m. p. 113–114°.

(b) 89–92° (16 mm.), 7.1 g. This fraction was shown by refractive index and carbon dioxide analyses<sup>11</sup> to contain 35% of ethyl isobutyrylacetate (XV) and 65% malonic ester (VII). The former was further characterized as the semicarbazone, m. p. 247–248°, and the latter by saponification to malonic acid, m. p. 133°.

(c) 145–160° (14 mm.), 3 g. This fraction was mainly ethyl cinnamate (XVI). It formed a dibromide, m. p. 74°, when treated with bromine in carbon tetrachloride and yielded cinnamic acid, m. p. 133°, upon saponification.

(d) 160–165° (14 mm.), 1 g. This fraction was benzal malonic ester (XIII). Mild hydrolysis yielded the half-ester, m. p. 85°. Further hydrolysis yielded cinnamic acid.

(e) 180–187° (14 mm.), 6 g. This fraction was probably a mixture of X, XI and other materials. It gave a strong coloration with ferric chloride. On standing in an ice box 0.7 g. of 2,2-dimethyl-5-phenylcyclohexanedione-1,3 (XI) crystallized out. After recrystallization from alcohol it melted at 86° and gave no coloration with ferric chloride; saponification equivalent 224 (calcd. 216); molecular weight (camphor) 202. XI has been prepared by Dieckmann and Kron<sup>6</sup> by the hydrolysis of 2,2-dimethyl-4,6-dicarbethoxy-5-phenylcyclohexanedione-1,3 (II) with 80% acetic acid. In this Laboratory it has been prepared by heating II with benzoic acid. A 1-g. sample of fraction (e) from which the crystals of XI were removed was heated with 1 g. of benzoic acid for two hours at 150°. After cooling it was washed until neutral with sodium bicarbonate solution and extracted with ether. The ether was evaporated and the residue allowed to crystallize; 0.05 g. of XI was isolated. By a similar procedure 0.2 g. of XI was obtained from 1 g. of II. Saponification of fraction (e) yielded only  $\beta$ -phenyl- $\gamma$ -isobutyrylbutyric acid, m. p. 106–107°.

(f) 190–192° (14 mm.), 1 g. This fraction yielded on recrystallization 0.8 g. of XI.

(g) 200–210° (14 mm.), 3 g. After several days of

standing a substance melting at 180° crystallized out of this fraction. It proved to be identical with the material isolated from the reaction mixture before distillation. The combined yield of this material amounted to 3.5 g. This compound gave no coloration with ferric chloride and was not saponified by 10% sodium hydroxide. Analyses indicate that it is a diphenyldiisobutyrylcyclobutane (XVII). *Anal.* Calcd. for C<sub>24</sub>H<sub>28</sub>O<sub>2</sub>: C, 82.70; H, 8.11. Found: C, 82.27; H, 8.11. In some of the experiments instead of the 180° melting material, a small quantity of a substance melting at 155° was obtained from fraction (g). Analyses indicated that this material is isomeric with the compound melting at 180°. *Anal.* Found: C, 82.54; H, 8.10.

(h) 210–300° (14 mm.), 27 g. This fraction was a very viscous liquid which could not be crystallized. Part of it could be saponified to give a non-crystallizable acid, which was not further characterized. The non-saponifiable material appeared to be the dimerization product of benzal-methyl isopropyl ketone.

(i) Residue, 10 g. No attempt was made to characterize this tar-like material.

**Interconversion of the Diphenyldiisobutyrylcyclobutanes (XVII).**—When 2 g. of the higher melting (180°) isomer (XVII) was heated for fifteen hours at 140° with 25 g. of acetic anhydride and the reaction mixture, after cooling, poured into 25 cc. of cold water, 1.8 g. of unchanged material was recovered. No other substance could be isolated. However, when 2 g. of the material melting at 155° was treated in a similar manner, 1.3 g. of the compound melting at 180° was obtained together with 0.3 g. of a substance that crystallized from alcohol in short needles and melted at 182°. A mixture of this latter substance and the 180° melting material melted about 19° lower than either of the components of the mixture. Analyses of the 182° melting material indicated that it was another isomer of XVII. *Anal.* Found: C, 82.34; H, 8.19.

**Reaction of Benzal-methyl Isopropyl Ketone (VIII) with Sodium Ethoxide.**—Eighty-seven grams (0.5 mole) of the ketone (VIII) was added to 12 g. (0.17 mole) of sodium ethoxide. A vigorous reaction ensued and the mixture became quite viscous. After heating for thirty minutes at 125° the mixture was cooled and washed with dilute hydrochloric acid. Upon distillation, after a small amount of benzal-methyl isopropyl ketone distilled over, the main reaction product was collected at 250–260° (14 mm.). This distillate set to an amorphous, glassy mass which could not be induced to crystallize. This amorphous material gave practically the same analyses (C, 82.90; H, 8.19) as were obtained for the three isomeric diphenyldiisobutyrylcyclobutanes described above.

### Summary

A study of the reaction occurring between sodium ethoxide and ethyl  $\alpha$ -carbethoxy- $\beta$ -phenyl- $\gamma$ -isobutyrylbutyrate has been made. Among the products of this reaction, 2,2-dimethyl-5-phenylcyclohexanedione-1,3 has been found. The isolation of this compound further substantiates the mechanism recently suggested for the acetoacetic ester condensation.

(11) Krocker and McElvain, *THIS JOURNAL*, **56**, 1173 (1934).

Among the other products obtained from this reaction are three isomeric compounds which appear to be diphenyldiisobutyrylcyclobutanes. MADISON, WISCONSIN RECEIVED JULY 27, 1934

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

### Three Crystalline Hexaacetates of *d*- $\alpha$ -Mannoheptose<sup>1</sup>

BY EDNA MONTGOMERY AND C. S. HUDSON

Hudson and Monroe<sup>2</sup> have described two hexaacetates of *d*- $\alpha$ -mannoheptose, of specific rotations  $[\alpha]_D^{20} +24$  and  $-31^\circ$  in chloroform, respectively. In a re-investigation of this subject we find that the dextrorotatory acetate, which was produced by acetylating the sugar with acetic anhydride and sodium acetate, was evidently not obtained pure in the earlier work because the pure substance is now found to have the rotation  $+34^\circ$ . This acetate is of the beta series because we have now transformed it in a mixture of acetic acid and acetic anhydride containing sulfuric acid as a catalyst, to a new crystalline hexaacetate of the sugar, of specific rotation  $+120.8^\circ$ , the alpha form. The difference between the molecular rotations of this  $\alpha, \beta$  pair is 40,000, in fair agreement with the values for many such pairs in the case of other sugars, for example, the  $\alpha$ - and  $\beta$ -glucose pentaacetates, which show a difference of 38,000. The levorotatory acetate, the rotation of which we now find to be  $-34^\circ$ , is not formed by rearrangement of the beta acetate, as reported by Hudson and Monroe; it accompanies the beta form as a product of the acetylation of the sugar with acetic anhydride and sodium acetate. We have now determined that it is of the open chain aldehyde type, since it is produced from *d*- $\alpha$ -mannoheptose ethyl mercaptal pentaacetate by the action of mercuric chloride in the presence of cadmium carbonate (Wolfrom's method<sup>3</sup>). This appears to be the first instance of the production of an aldehyde acetate from an aldose by direct acetylation of the sugar. The aldehyde acetate does not appear to be affected by the sulfuric acid transforming solution, as its rotation therein remains constant and it is recoverable therefrom. We now regard sulfuric acid as a preferable catalyst to zinc chloride in the transformation of alpha and beta acetates; there is less decomposition, the

reaction proceeds at room temperature, and the products are more readily isolated.

#### Experimental

**Preparation of  $\beta$ -*d*-[ $\alpha$ -Mannoheptose] Hexaacetate.**—Pure mannoheptose (40 g.) was acetylated with sodium acetate and acetic anhydride in the customary way, care being taken to keep the temperature of the solution below  $90^\circ$  so that a colorless sirup was obtained, which crystallized from aqueous alcoholic solution in 58% yield, of  $[\alpha]_D^{20} +26.4^\circ$  in chloroform. It was recrystallized four times from 10 parts of 50% ethyl alcohol. The product (25 g.), dried to constant weight at  $70^\circ$  and 5 mm., melted sharply at  $107^\circ$  and had an  $[\alpha]_D^{20}$  value of  $+34.1^\circ$  ( $c = 1.30$ , U. S. P. chloroform), and these properties remained unchanged after further recrystallizations.

*Anal.* Acetyl: 0.3169 g. used 41.14 cc. of 0.1 *N* NaOH. Calcd. for six acetyl groups, 41.17 cc. Calcd. for  $C_{19}H_{26}O_{13}$ : C, 49.33; H, 5.67. Found: C, 49.33; H, 5.67.

**Transformation of  $\beta$ -*d*-[ $\alpha$ -Mannoheptose] Hexaacetate to its Alpha Isomer.**—The pure beta hexaacetate (5 g.) was dissolved in the isomerizing reagent described below, making a 30-cc. solution. The change in  $[\alpha]_D^{20}$  value of the solution, complete in twenty-four hours at  $20^\circ$ , was from  $+33.9$  to  $+111^\circ$ . The transformed acetate was isolated and purified by the usual procedure, the dry sirup obtained crystallizing from ether (10 cc.) containing a few drops of petroleum ether in radiating clusters of long prisms (3.8 g.), which were recrystallized twice from the same solvent (3.2 g.), m. p.  $75-76^\circ$ ,  $[\alpha]_D^{20} +120.8^\circ$  ( $c = 1.30$ , U. S. P. chloroform). Further recrystallizations did not change its properties.

*Anal.* Acetyl: 0.4041 g. used 52.55 cc. of 0.1 *N* NaOH. Theoretical for six acetyl groups, 52.50 cc. Calcd. for  $C_{19}H_{26}O_{13}$ : C, 49.33; H, 5.67. Found: C, 49.39; H, 5.65.

**Isomerizing Reagent.**—A solution of sulfuric acid in acetic anhydride and acetic acid (2 to 1) was made by dropping 4.56 cc. of concentrated sulfuric acid (95%) into a mixture of 137.1 cc. of acetic anhydride (95%) and 58.5 cc. of acetic acid (99.5%) cooled to  $-17^\circ$ , slowly enough to avoid coloring.

**Aldehyde-*d*- $\alpha$ -Mannoheptose Hexaacetate by Acetylation of the Sugar.**—The crude acetate (10 g.) was crystallized from the concentrate of the combined alcoholic mother liquors obtained by recrystallizing the crude  $\beta$ -*d*-[ $\alpha$ -mannoheptose] hexaacetate (51 g.). The aldehyde acetate was extracted several times with warm ether and the insoluble portion was recrystallized twice from hot acetone (50 cc.). The tabular crystals (4.5 g.) melted at

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Hudson and Monroe, *THIS JOURNAL*, **46**, 978 (1924).

(3) Wolfrom, *ibid.*, **51**, 2188 (1929).