III obtained as a by-product in the catalytic hydrogenation of IV.

Decomposition of II by Ferrous Ion.—A solution of 16.4 g. of II in 30 ml. of water was treated dropwise with 28 g. of ferrous sulfate heptahydrate dissolved in 85 ml. of water while keeping the temperature in the 20–25° range. Decomposition of peroxides appeared to be complete when approximately half of the ferrous sulfate solution had been added as evidenced by lack of temperature effect during the last half of the addition. A clear oily layer had separated. When addition of ferrous ion was complete (45 min.), 100 ml. of ether was added. The aqueous phase was extracted twice with 50-ml. portions of ether. The ether layers were combined, washed, dried with calcium sulfate, and the solvent was removed leaving 7.5 g. of clear oil. Gas chromatography showed the mixture to be composed of about 7% unidentified volatile products, 50% methyl 4-formoxybutyrate (III), about 3% aldehyde VI (both identified by their g.l.c. retention times and infrared spectra) and about 40% of a higher ester component which was subsequently identified as 1,6-hexanediol diformate (VIII). Over-all yields based on crude II were 25 and 34% for esters III and VIII, respectively.

A second ferrous ion-induced decomposition of II in which 16.4 g. of the hydroperoxide was added slowly to a 1 *M* sulfuric acid solution of ferrous sulfate (28 g. heptahydrate in about 80 ml. of water) at 0–5° gave essentially the same results as in the first experiment. Gas chromatography of the crude esters (6.4 g.) showed 44% III and about 48% VIII present as the major components giving over-all yields of 19 and 35% respectively, from hydroperoxide II.

The identity of VIII was conclusively established by distillation of 13 g. of the combined crude esters giving 4.3 g. of crude VIII, b.p. 78–83° (0.5 mm.). Redistillation gave 1.0 g., b.p. 68–70° (0.28 mm.), n^{25}_{D} 1.4289. Pure VIII prepared by esterification of 1,6-hexandiol with formic acid gave b.p. 68–69° (0.28 mm.), n^{25}_{D} 1.4289 and was identical in all respects with ester VIII prepared by the ferrous in decomposition of II.

Thermal Decomposition of 4-Hydroperoxy-4-methoxybutyl Formate (II) in Toluene.—A solution of 66 g. (0.4 mole) of II in 250 ml. of toluene was heated under gentle reflux using a water separator in the return line. Provision was made for collecting any gaseous products (b.p. below −75°). Reflux was continued for 13 hr. until a negative potassium iodide test indicated destruction of peroxides. During this interval approximately 2.1 l. of gas (corrected for water vapor and reduced to standard conditions) was obtained. A rough analysis of the gas mixture by infrared and mass spectroscopy indicated that it was approximately 42% hydrogen while carbon dioxide (10%), carbon monoxide (5%), air, and relatively minor amounts of methane and ethane made up the remaining components. Based on moles of II being decomposed the yield of hydrogen appeared to be slightly less than 10%.

After destruction of peroxide, toluene and volatile products were collected by distillation at atmospheric pressure (cut 1). A straw-colored liquid amounting to 35 g. remained. This was subjected to vacuum distillation giving 25 g., b.p. 65–95° (12 mm.) (cut 2). From the dark oily high boiling material remaining an additional 4 g. of oil, b.p. 100–185° (1.8 mm.), was collected (cut 3). Each of these fractions was examined by gas chromatography, and with the exception of cut 3, all products present in > 1% concentration were identified. These results are summarized in Table I. The dark residue remaining was discarded.

Intramolecular Reactions of Some Cyclic β-Diketones[1]

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The reaction of 2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinic acid with acetic anhydride resulted in an unusual decarboxylation and rearrangement reaction. This paper describes this reaction and discusses certain other reactions of β-diketones.

Although acetic anhydride frequently has been employed to convert carboxylic acids into their corresponding anhydrides, it has been observed that the reaction at times can take an entirely different course. For example, when phenylacetic acid was heated with acetic anhydride and sodium acetate, a good yield of phenylacetone was obtained.[3] In the synthesis of strychnine,[4] one of the key steps was the conversion of a carboxylic acid into a methyl ketone by means of acetic anhydride and sodium acetate. We have now observed this unusual decarboxylation and certain other reactions on a β-diketo acid, 2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinic acid (I).

When I was allowed to react with acetic anhydride, a neutral compound was obtained, which has lost the elements of carbon dioxide and water and has been substituted by an acetyl group. On the basis of its elemental analysis, ultraviolet and infrared spectra, this compound could have either structure IIa or IIb. A conclusion as to which of these represents the actual structure has been drawn from studies of model compounds VII and VIII, whose structures are similar to that of IIb. The model compound VII was prepared by the action of acetic anhydride on 2-(2-carboxyethyl)-5,5-dimethylcyclohexane-1,3-dione; this model (VII) exhibited strong infrared absorption at 1795 cm.$^{-1}$ and 1660 cm.$^{-1}$. The product obtained from the reaction of I with acetic anhydride exhibited infrared absorption at 1805 cm.$^{-1}$ and 1645 cm.$^{-1}$. However, one would expect three peaks in the infrared spectrum of IIb, but only two peaks

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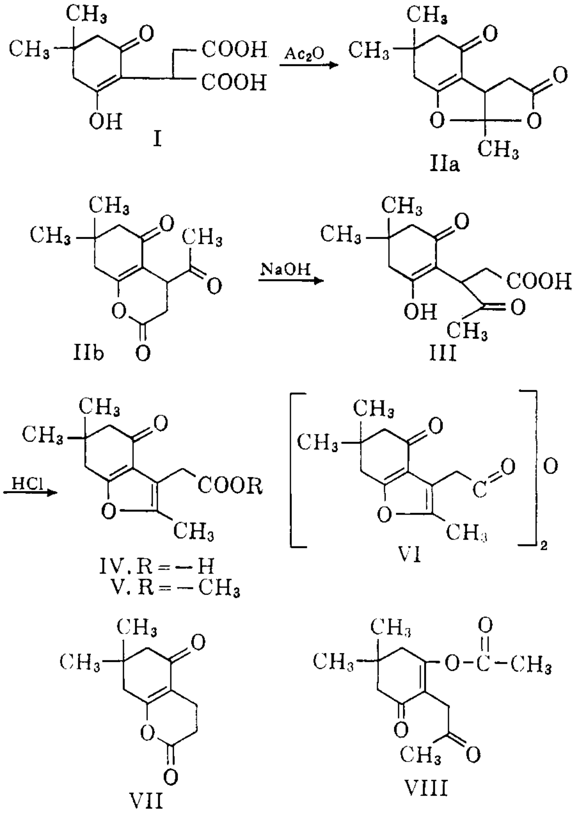
(2) Undergraduate research participant. The research described in this paper was used in partial fulfillment of the requirements for the Bachelor of Science degree.

(3) O. Yu. Magidson and G. A. Garkusha, *J. Gen. Chem. USSR*, **11**, 339 (1941).

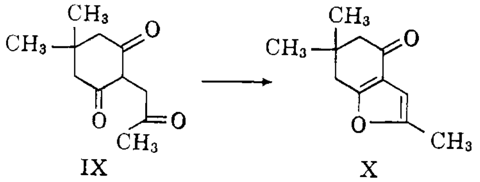
(4) R. B. Woodward, M. P. Cava, W. D. Ollis, H. U. Daeniker, and K. Schenker, *J. Am. Chem. Soc.*, **76**, 474 (1954).

for IIa. Furthermore, an examination of the infrared spectrum of a second model compound, 3-acetoxy-2-(2-oxopropyl)-5,5-dimethylcyclo-2-hexenone (VIII), revealed that it had three bands in the carbonyl region with absorption at 1775 cm.$^{-1}$, 1730 cm.$^{-1}$, and 1675 cm.$^{-1}$. On the basis of the infrared spectrum of VIII, we would not expect the third carbonyl band of IIb to be masked. On these grounds, we believe that the most probable structure for the compound obtained in the reaction of I with acetic anhydride is IIa.



When IIa was saponified, an acid (III) was obtained which exhibited the characteristic ultraviolet spectrum of a β-diketone. Treatment of III with acetic anhydride regenerated the neutral compound IIa. However, when III was allowed to react with dilute hydrochloric acid, an anhydro acid was obtained which no longer exhibited the characteristic ultraviolet absorption of a β-diketone. This material exhibited infrared absorption at 1740 cm.$^{-1}$, 1705 cm.$^{-1}$, 1675 cm.$^{-1}$, 1650 cm.$^{-1}$ (shoulder), and 1600 cm.$^{-1}$, ultraviolet absorption at 276 mμ[5] and was tentatively assigned structure IV.

In order to determine if structures similar to III would easily cyclize to a furan, a study was carried out on model compounds. Thus, 2-(2-oxopropyl)-5,5-dimethylcyclohexane-1,3-dione (IX) was prepared by the condensation of 5,5-dimethylcyclohexane-1,3-dione with chloroacetone. When IX was allowed to react with dilute hydrochloric acid, the corresponding furan (X) was obtained in good yield. The identity of X was established by its infrared, ultraviolet, and n.m.r. spectra.[6] The n.m.r. spectrum of X exhibited resonances at 6.22 p.p.m. (β-hydrogen of furan), 2.68 and 2.41 p.p.m. (methylene hydrogen), 2.34 p.p.m. (methyl), and 1.13 p.p.m. (*gem*-dimethyl). Integration of the n.m.r. signals from X revealed that the protons were in a ratio of 1 (6.22 p.p.m.): 2 (2.68 p.p.m.): 2 (2.41 p.p.m.): 3 (2.34 p.p.m.): 6 (1.13 p.p.m.) which is consistent with structure X.



An examination of the n.m.r. spectrum of IV revealed signals from the carboxylic hydroxyl proton at 10.58 p.p.m. and the methylene group adjacent to the carboxyl group at 3.58 p.p.m. The remainder of the spectrum was essentially identical with that of X with the exception that the signal from the β-hydrogen of furan was absent, a result which would be predicted on the basis of structure IV. Integration of the signals gave results which were consistent with structure IV.

One final point which requires comment concerning structure IV is the assignment of its infrared spectrum. The band at 1600 cm.$^{-1}$ and the shoulder at 1650 cm.$^{-1}$ are characteristic of a furan, the peak at 1675 cm.$^{-1}$ is characteristic of a ketone adjacent to an aromatic nucleus and the peaks occurring at 1705 cm.$^{-1}$ *and* 1740 cm.$^{-1}$ must be due to carboxyl absorption. The conclusion that both the 1740-cm.$^{-1}$ and the 1705-cm.$^{-1}$ peak must be assigned to the carboxyl group is based on three observations: (a) preparation of the methyl ester (V)[7] from IV caused the disappearance of both peaks and the formation of a new one at 1750 cm.$^{-1}$; (b) synthesis of the anhydride (VI) from IV caused the disappearance of both acid peaks with the formation of two new peaks, one at 1800 cm.$^{-1}$ and the other at 1760 cm.$^{-1}$; and (c) when the infrared spectrum of IV was determined using morpholine as a solvent, both the 1740-cm.$^{-1}$ and the 1705-cm.$^{-1}$ peaks were absent and two

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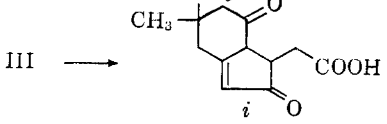
(5) Compound III could have formed the anhydro acid *i* by an acid-catalyzed aldol condensation, but both the infrared and ultraviolet data argue against this structure.

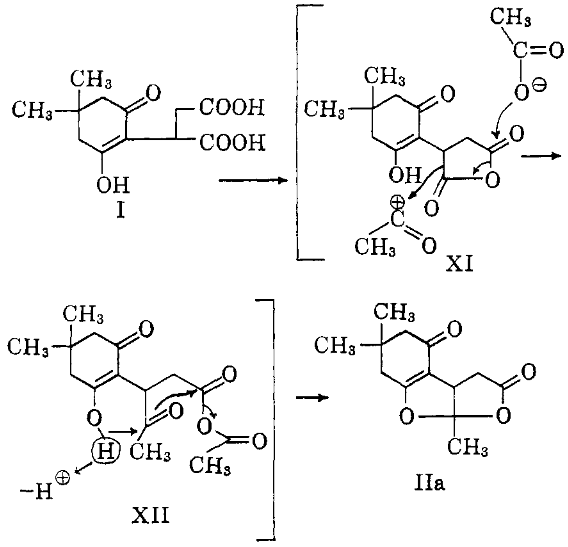


(6) The authors are indebted to Professor E. Wenkert who determined and interpreted the n.m.r. spectra reported in this paper. The shifts are reported as p.p.m. from tetramethylsilane.

(7) That no molecular rearrangement had occurred in the synthesis of V was shown by saponification of V to IV in good yield.

new peaks occurred at 1590 cm.$^{-1}$ and 1370 cm.$^{-1}$, a result which would be expected on the conversion of a carboxylic acid into the carboxylate anion[8] by morpholine. The origin of these two peaks from a carboxyl group is most probably due to absorption by both the monomer and the dimer but it may be also due to some new phenomenon.

The mechanism of the formation of IIa from I requires comment. One of several possible explanations requires that I is first converted into the anhydride XI, attack on XI by an $CH_3C{=}O^{\oplus}$ and $CH_3COO^{\ominus}$ would yield IIa *via* XII as shown below.



Experimental[9]

2-(4,4-Dimethyl-2,6-dioxocyclohexyl)succinic Acid (I).—A mixture of 65.4 g. (1.17 moles) of potassium hydroxide, 52.5 g. (0.375 mole) of 5,5-dimethylcyclohexane-1,3-dione, and 45.0 g. (0.387 mole) of maleic acid in 450 ml. of water was heated under reflux for 7 hr. and was allowed to stand overnight at room temperature. Acidification of the cold reaction mixture resulted in the formation of a precipitate which was collected by filtration and washed with 150 ml. of acetone; yield, 40.0 g. (41.6%), m.p. 215° in agreement with the literature.[10] $\bar{\nu}$ in cm.$^{-1}$ (KBr) 2800–2100 (acidic hydrogen), 1710 (C=O), 1645 and 1560 (enolic β-diketone).

Anal.[11] Calcd. for $C_{12}H_{16}O_6$: C, 56.24; H, 6.29. Found: C, 56.16; H, 6.59.

Action of Acetic Anhydride on 2-(4,4-Dimethyl-2,6-dioxocyclohexyl)succinic Acid.—A mixture of 601 mg. (2.34 mmoles) of 2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinic acid (I) and 3 ml. of acetic anhydride was heated under reflux for 1 hr. The reaction solution was concentrated *in vacuo* to 1 ml., cooled in an ice bath, and the crystals were collected by filtration; yield, 462 mg. (82.7%), m.p. 160°. One recrystallization from chloroform gave the analytical sample (IIa); yield, 371 mg. (67.2%), m.p. 164–166°; $\bar{\nu}$ in cm.$^{-1}$ (KBr) 1805 (enol lactone), 1645 (α,β-unsaturated ketone); $\lambda_{max}^{CHCl_3}$ ($\epsilon \times 10^{-3}$) 257 (12.9).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.82. Found: C, 66.04; H, 6.49.

3-(4,4-Dimethyl-2,6-dioxocyclohexyl)levulinic Acid (III).—A mixture of 2.14 g. (0.907 mmole) of IIa and 40 ml. of 7.5% sodium hydroxide solution was stirred at room temperature for 3 hr. During the first hour of reaction, solution gradually occurred. The chilled reaction mixture was acidified with hydrochloric acid, concentrated *in vacuo* until crystallization began, and the white solid was collected by filtration (III); yield, 1.79 g. (77.7%), m.p. 175–176°. For analysis, a small sample was recrystallized from water, m.p. 176–178°. $\bar{\nu}$ in cm.$^{-1}$ (KBr) 2650–2100 (acidic hydrogen), 1730 (C=O), 1695 (C=O), 1635 and 1565 (enolic β-diketone); λ_{max}^{EtOH} ($\epsilon \times 10^{-3}$) 264 (14.2); λ_{max}^{NaOH} ($\epsilon \times 10^{-3}$) 289 (18.7).

Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.00; H, 7.13. Found: C, 61.3; H, 7.09.

2,6,6-Trimethyl-3-carboxymethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (IV).—A solution of 262 mg. (1.03 mmoles) of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (III) in 3 ml. of 10% hydrochloric acid was heated under reflux for 35 min. during which time an oil gradually separated. The cooled reaction mixture was extracted with chloroform (3 × 5 ml.); the combined chloroform extracts were dried with anhydrous magnesium sulfate, filtered, and the volatile materials were removed *in vacuo*. The residual oil gradually crystallized; yield, 242 mg. (99.3%), m.p. 120–122°. Recrystallization from a mixture of benzene and hexane gave the analytical sample (IV); yield, 220 mg. (90.2%), m.p. 125–127°; $\bar{\nu}$ in cm.$^{-1}$ (KBr) 2700–2100 (acidic hydrogen) 1740 (C=O), 1705 (C=O), 1675 (C=O), 1650 shoulder and 1600 (furan); λ_{max}^{EtOH} ($\epsilon \times 10^{-3}$) 276 (3.69).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.82. Found: C, 65.78; H, 6.92.

2,6,6-Trimethyl-3-methoxycarbonylmethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (V).—A solution of 5.00 g. (21.2 mmoles) of 2,6,6-trimethyl-3-carboxymethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (IV) in 55 ml. of 1,2-dichloroethane containing 2.05 g. (64.0 mmoles) of methanol and 100 λ of ethanesulfonic acid was heated under reflux overnight. The cooled reaction mixture was concentrated *in vacuo* to half volume, 50 ml. of ether was added, and the mixture was extracted with 5% sodium bicarbonate solution (3 × 50 ml.). The organic phase was dried with anhydrous magnesium sulfate, filtered, concentrated *in vacuo* and gave 5.07 g. (95.8%) of crude product. Two distillations gave 3.09 g. (58.4%) of the analytical sample (V), b.p. 98–99°/0.08 mm.; $\bar{\nu}$ in cm.$^{-1}$ (film) 1750 (C=O), 1680 (C=O), 1645 and 1590 (furan); λ_{max}^{EtOH} ($\epsilon \times 10^{-3}$) 275 (3.81).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.82; H, 7.27.

The Anhydride of 2,6,6-Trimethyl-3-carboxymethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (VI).—A mixture of 700 mg. (2.96 mmoles) of 2,6,6-trimethyl-3-carboxymethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (IV) in 11 ml. of acetic anhydride was heated under reflux for 1 hr., evaporated *in vacuo* to dryness, and gave 620 mg. (96.1%) of a yellow solid, m.p. 118°. Several recrystallizations of the crude product from a mixture of benzene and hexane gave the pure product (VI), m.p. 126°; $\bar{\nu}$ in cm.$^{-1}$ (KBr): 1800 and 1765 (C=O, anhydride), 1670 (C=O), 1645 (shoulder) and 1595 (furan); λ_{max}^{EtOH} ($\epsilon \times 10^{-3}$) 272 (8.35).

Anal. Calcd. for $C_{26}H_{30}O_7$: C, 68.70; H, 6.65. Found: C, 68.43; H, 6.32.

The Enol Lactone of 2-(2-Carboxyethyl)-5,5-dimethylcyclohexane-1,3-dione (VIII).—A mixture of 5.00 g. (23.6 mmoles) of 2-carboxyethyl-5,5-dimethylcyclohexane-1,3-dione[10] (VII) in 30 ml. of acetic anhydride was heated under reflux for 1 hr. and then the volatile materials were removed *in vacuo*. Fractional distillation of the residue through a Vigreux column gave the analytical material (VIII), b.p. 82°/0.04 mm. The pure product solidified and was re-

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[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1956, p. 142.

[9] The ultraviolet spectra were determined on a Perkin–Elmer Model 4000A spectrophotometer, and the infrared spectra were determined on a Perkin–Elmer Model 137 spectrophotometer. The melting points were determined on a Kofler Heizbank and are corrected.

[10] I. N. Nazarov and S. I. Zavyalov, *J. Gen. Chem. USSR*, **25**, 508 (1955).

[11] The analyses reported in this paper were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

crystallized from *n*-hexane to a constant melting point of 58°; $\bar{\nu}$ in cm.$^{-1}$ (film) 1795 (C=O) and 1660 (C=O); λ_{max}^{EtOH} ($\epsilon \times 10^{-4}$) 255 (1.11).

Anal. Calcd. for $C_{11}H_{14}O_3 \cdot 1/4H_2O$: C, 66.48; H, 7.35. Found: C, 66.65; H, 7.15.

2-(2-Oxopropyl)-5,5-dimethylcyclohexane-1,3-dione (IX).—A mixture of 11.3 g. (0.210 mole) of sodium methoxide, 30 g. (0.214 mole) of 5,5-dimethylcyclohexane-1,3-dione, and 20.3 g. (17.5 ml., 0.221 mole) of chloroacetone in 145 ml. of ethanol was heated under reflux for 15 min. and then cooled. The sodium chloride which formed was removed by filtration, and the filtrate was concentrated *in vacuo*. The residual sirup was dissolved in a mixture of chloroform (50 ml.) and 10% sodium hydroxide (50 ml.). The aqueous phase was separated and reextracted with chloroform (50 ml.). The aqueous phase was cooled in an ice bath, made acidic with concentrated hydrochloric acid, and extracted with chloroform (3 × 50 ml.). The combined organic extracts were dried with anhydrous magnesium sulfate, filtered, and the filtrate was evaporated *in vacuo* to dryness. Recrystallization of the crude product from a mixture of chloroform and hexane gave 17.3 g. of the desired product (IX), m.p. 134–136°. Concentration of the mother liquor gave an additional 12.7 g. of IX, m.p. 132–133°. The total yield was 30.0 g. (71.5%). Recrystallization from a mixture of chloroform and hexane gave the analytical sample, m.p. 134–136°; $\bar{\nu}$ in cm.$^{-1}$ (KBr) 1725 (C=O), 1650 and 1570 (enolic β-diketone); λ_{max}^{EtOH} ($\epsilon \times 10^{-4}$) 262 (1.44); λ_{max}^{NaOH} ($\epsilon \times 10^{-4}$) 289 (2.46).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.33; H, 8.22. Found: C, 67.47; H, 8.22.

2,6,6-Trimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (X).—2-(2-Oxopropyl)-5,5-dimethylcyclohexane-1,3-dione (2.00 g., 10.2 mmoles) was added to a mixture of 22 ml. of water and 3.5 ml. of concentrated hydrochloric acid, and the mixture was heated under reflux for 75 min. The cooled reaction mixture was extracted with chloroform (2 × 20 ml.); the combined chloroform extracts were dried with anhydrous magnesium sulfate, filtered, and the filtrate was evaporated *in vacuo* to dryness; yield, 1.73 g. (95.1%), m.p. 72°. Sublimation from an oil bath at 60°/0.2 mm. gave the analytical material, m.p. 72°; $\bar{\nu}$ in cm.$^{-1}$ (KBr) 1690 (C=O), 1585 (furan); $\lambda_{max}^{CHCl_3}$ ($\epsilon \times 10^{-3}$) 271 (5.17).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.07; H, 7.91. Found: C, 73.92; H, 7.94.

3-Acetoxy-2-(2-oxopropyl)-5,5-dimethylcyclo-2-hexenone (VIII).—A mixture of 5.00 g. (25.5 mmoles) of 2-(2-oxopropyl)-5,5-dimethylcyclohexane-1,3-dione and 36.0 ml. of acetic anhydride was heated under reflux for 10 min., and the reaction mixture was concentrated *in vacuo*. Distillation of the residual oil gave 4.35 g. (71.6%) of pure product, b.p. 89°/0.03 mm.; $\bar{\nu}$ in cm.$^{-1}$ (film) 1775 (C=O, enol ester), 1720 (C=O), 1675 (α,β-unsaturated ketone); λ_{max}^{EtOH} in mμ ($\epsilon \times 10^{-3}$) 239 (8.80).

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.50; H, 7.61. Found: C, 65.56; H, 8.05.

Acknowledgment.—The authors are indebted to Professors B. R. Baker and E. Wenkert for their stimulating discussions and helpful criticism.

Synthesis of Amino Sugars by Reduction of Hydrazine Derivatives. 5-Amino-3,6-anhydro-5-deoxy-L-idose Derivatives[1-3]

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A comparison was made of the relative efficiencies of the nucleophilic reagents hydrazine and azide ion, for displacement of secondary *p*-tolylsulfonyloxy groups in certain sugar rings, as a preparative route to amino sugars. Both reagents appeared equally effective in displacing the 5-substituent of 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (I, Ia) to give derivatives with the L-idose configuration. In another derivative (V, VII), where approach of the attacking group was more sterically hindered, hydrazine was the more effective reagent.

The displacement of sulfonate esters of secondary hydroxyl groups in sugar rings, under conditions where neighboring group participation cannot assist the reaction, requires use of powerful nucleophilic reagents under forcing conditions, and proceeds with Walden inversion. The displacement of "isolated" secondary *p*-tolylsulfonyloxy groups by hydrazine is a typical reaction of this type, and has been useful as a synthetic route to new and rare amino sugars,[3,4] since the hydrazino derivatives are readily reduced to amino derivatives. Under suitable conditions the hydrazinolysis reaction gives hydrazino derivatives in high yield, but side reactions leading to unsaturated derivatives[5] may occur and the possibility exists that polysubstituted hydrazines might form. An alternative synthetic route, displacement of an isolated secondary *p*-tolylsulfonyloxy group by azide ion, a powerful nucleophile, would be expected to give an azido derivative with inversion, and formation of polysubstituted derivatives would be excluded. Azido groups are readily reduced to amino groups. Displacement of a *primary* *p*-tolylsulfonyloxy group by azide ion occurs readily[6] and is the procedure of choice for synthesis of ω-aminodeoxy sugars, such as 6-amino-6-deoxy-D-glucose[7] since the disubstituted derivatives formed as side products[8] in syntheses by the hydrazine method, cannot form.

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[1] Supported by Grant No. CY-3232 (C4) from the Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health, Bethesda 14, Md. (R. F. Project 759D).

[2] Reported in part in *Abstr. Papers Am. Chem. Soc.*, **141**, 7D (1962).

[3] Previous publication on this subject: D. Horton, M. L. Wolfrom, and A. Thompson, *J. Org. Chem.*, **26**, 5069 (1961).

[4] M. L. Wolfrom, F. Shafizadeh, and R. K. Armstrong, *J. Am. Chem. Soc.*, **80**, 4885 (1958); M. L. Wolfrom, F. Shafizadeh, R. K. Armstrong, and T. M. Shen Han, *ibid.*, **81**, 3716 (1959); R. Kuhn and G. Baschang, *Ann.*, **628**, 193 (1959); W. Roth and W. Pigman, *J. Org. Chem.*, **26**, 2455 (1961).

[5] K. Freudenberg and F. Brauns, *Ber.*, **55**, 3233 (1922).