

fractions indicated the presence of silicon-methyl and silicon-phenyl groups. The solvent was removed from the original mother liquor and the residue heated at 100° under a pressure of 0.5 mm. to give 1.5 g. (25.9%) of sublimate, identified as dodecamethylcyclohexasilane, m.p. 250–253° (m.m.p.). Attempts to obtain products from the sublimation residue were unsuccessful.

**2,2-Dimethyl-1,1,1,3,3,3-hexaphenyltrisilane. Preparation.**—To 2.6 g. (0.02 mole) of dichlorodimethylsilane, there was added 0.04 mole of triphenylsilyllithium in 50 ml. of tetrahydrofuran. The reaction mixture was hydrolyzed in dilute acid and filtered. The solids were washed with water, methanol, and ether, and dried to give 8.2 g. (71.4%) of product, m.p. 222–226°. Two recrystallizations from a mixture of benzene and cyclohexane gave 5.5 g. (47.7%) of pure 2,2-dimethyl-1,1,1,3,3,3-hexaphenyltrisilane, m.p. 223–227°.

*Anal.* Calcd. for  $C_{38}H_{36}Si_3$ : Si, 14.60. Found: Si, 14.48, 14.58.

**Reaction with Lithium.**—A few milliliters of tetrahydrofuran was added to a stirred mixture of 5.8 g. (0.01 mole) of the trisilane and 0.7 g. (0.1 g.-atom) of lithium. The reaction mixture became yellow after 5 min. A total of 25 ml. of tetrahydrofuran was added over a 30-min. period and the reaction mixture was stirred for an additional 3 hr. To the resulting dark green mixture, 3.4 g. (0.03 mole) of chlorotrimethylsilane was added rapidly. The colorless solution was decanted away from the lithium and hydrolyzed in dilute acid. Subsequent to the usual work-up, the solvents were removed and the residue crystallized from ethanol to give 4.3 g. (65.1%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106–108° (m.m.p.). The solvents were removed from the mother liquor and the residue heated to 100° (12 mm.) to yield 0.4 g. (66%) of impure dodecamethylcyclohexasilane, m.p. 200–230°. Recrystallization from acetone afforded 0.3 g. (50%) of pure product, m.p. 250–252° (m.m.p.).

**Cleavage of Dodecamethylcyclohexasilane with Lithium in Tetrahydrofuran.**—Triphenylsilyllithium was prepared by the reaction of 0.13 g. (0.00025 mole) of hexaphenyldisilane and 0.7 g. (0.1 g.-atom) of lithium in a small volume of tetrahydrofuran.

To this, 5.25 g. (0.015 mole) of dodecamethylcyclohexasilane was added in 25 ml. of tetrahydrofuran.<sup>12</sup> The resulting mixture was stirred at room temperature for 24 hr. Titration of the brown solution showed the silyllithium content to be 0.009 mole.<sup>6</sup> Chlorotriphenylsilane, 3.5 g. (0.012 mole), was added. The colorless solution was hydrolyzed and filtered to give 0.2 g. of hexaphenyldisilane, m.p. 360–365° (m.m.p.). The filtrate was worked up in the usual manner and the solvents were removed. Petroleum ether (b.p. 60–70°) was added to the residue and filtration afforded 1.6 g. (50%) of triphenylsilanol, m.p. 150–155° (m.m.p.). The solvent was removed from the filtrate and the residue crystallized from acetone to give 1.9 g. (36.4%) of recovered dodecamethylcyclohexasilane, m.p. 250–252° (m.m.p.). Attempts to isolate other pure products were unsuccessful.

**Reaction of Lithium with the Insoluble Dimethylsilylene Polymer.**—About 0.7 g. (0.1 g.-atom) of lithium, which had been used for the preparation of triphenylsilyllithium, and 5.8 g. of the insoluble dimethylsilylene polymer<sup>13</sup> were stirred for 52 hr. in 20 ml. of tetrahydrofuran. The dark brown reaction mixture was hydrolyzed in excess dilute acid and filtered to give 0.7 g. (12%) of recovered polymer. Subsequent to the usual work-up, the solvents were removed and the residue distilled under reduced pressure and afforded a large number of fractions boiling in the range 65° (0.4 mm.) to 100° (0.003 mm.). The total amount of distillable material was 4.5 g. (77.8%). All of these fractions showed strong absorption bands in their infrared spectra for silicon-hydrogen and silicon-methyl groups. One fraction, b.p. 100–105° (0.4 mm.), partially solidified. Recrystallization from acetone afforded 1.8 g. (32%) of dodecamethylcyclohexasilane, m.p. 250–252° (m.m.p.).

(12) An attempt to cleave dodecamethylcyclohexasilane with untreated lithium in tetrahydrofuran gave no indication of a reaction after 48 hr., and starting material was recovered in a 90% yield.

(13) Obtained from the uncatalyzed reaction of dichlorodimethylsilane with lithium in tetrahydrofuran.<sup>4</sup>

## Intramolecular Reactions of Some Cyclic $\beta$ -Diketones<sup>1</sup>

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The reaction of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (I) with bromine resulted in an unusual intramolecular reaction. The structure of this product and the reactions of some related model compounds are discussed.

The investigation of the reaction of bromine with ketones has resulted in an understanding of the mechanism of this reaction. It has been shown that the rate of reaction is dependent on the concentration of the ketone and catalyst (acid or base) but is independent of the concentration of the halogen. From this and other data, it is believed that the rate-determining step is the formation of the enol which is then rapidly attacked by halogen.<sup>3</sup> In connection with our structural studies on some cyclic  $\beta$ -diketones,<sup>4</sup> we became interested in the reaction of bromine with certain  $\beta$ -diketones, and this paper describes some novel reactions which we have observed with this system.

When 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (I) was allowed to react with an aqueous solution of bromine, a *neutral product* (II) was obtained which had undergone substitution of a bromine for a hydrogen atom. An examination of the infrared spectrum of the brominated product revealed hydroxyl absorption at 3620 and 3340  $\text{cm}^{-1}$  and carbonyl absorption at 1785 and 1725  $\text{cm}^{-1}$ . Furthermore an examination of the ultraviolet spectrum revealed that the  $\beta$ -diketone system was no longer capable of enolization since the characteristic absorption of an enolizable  $\beta$ -diketone was absent; in fact, the only absorption exhibited was at 298  $\text{m}\mu$  with an  $\epsilon$  of 90 which is characteristic of an isolated ketone.<sup>5</sup> In addition, the bromine must be located in this compound in a unique position since when it is allowed to react with sodium hydroxide, a 25% yield of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (I) is obtained. In order to obtain more

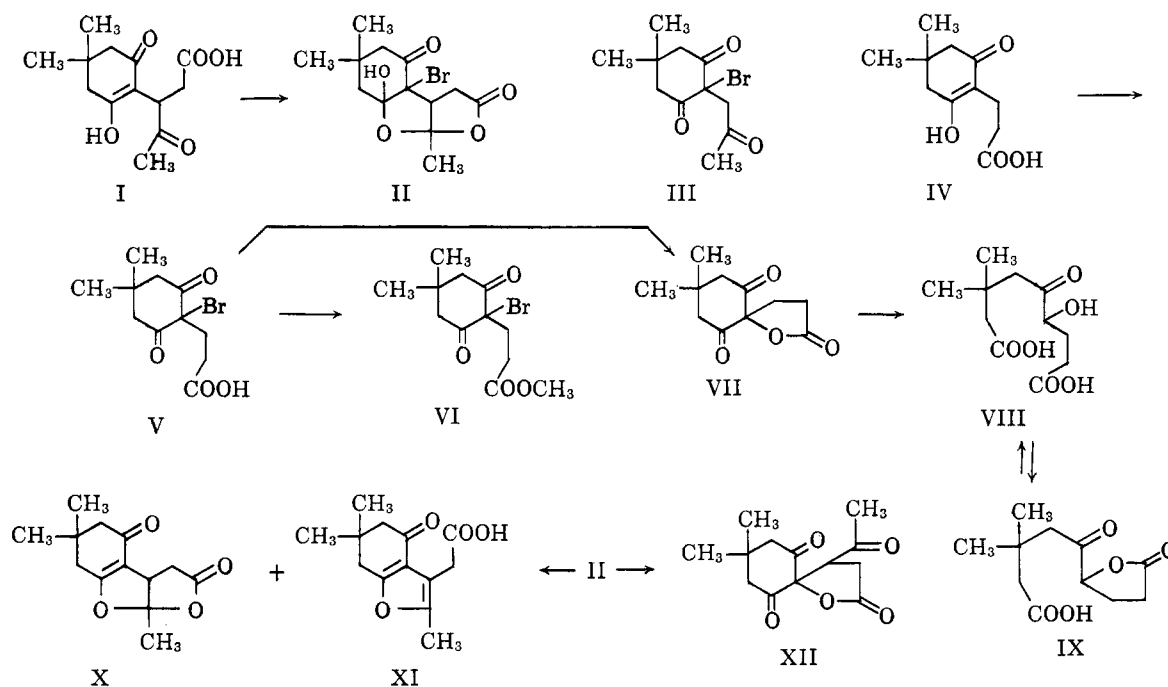
(1) This investigation was supported generously by research grant CY5527 from the National Cancer Institute, National Institutes of Health, Public Health Service.

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

(3) A number of reviews on this subject have been published; see, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 372.

(4) For the previous paper of this series, see H. J. Schaeffer and R. Vince, *J. Org. Chem.*, **27**, 4502 (1962).

(5) W. R. Brode, "Chemical Spectroscopy," 2nd Ed., John Wiley and Sons Inc., New York, N. Y., 1943, p. 221–226.



information about these reactions, a study of model systems which are related to I was undertaken.

In order to assess the effect of an exocyclic ketone on the bromination of cyclic  $\beta$ -diketone, the model compound, 2-(2-oxopropyl)-5,5-dimethylcyclohexane-1,3-dione, was treated with bromine; the resultant product (III) lost the typical ultraviolet absorption of an enolizable  $\beta$ -diketone.<sup>6</sup> Its infrared spectrum did not exhibit hydroxyl absorption but did exhibit typical carbonyl absorption at 1740 and 1715  $\text{cm}^{-1}$ . Thus, the exocyclic ketone did not alter the course of this reaction, as is evidenced by the isolation of the normal bromination product III.

The effect of a  $\beta$ -carboxyethyl chain on the bromination of a  $\beta$ -diketone was investigated by allowing 2-(2-carboxyethyl)-5,5-dimethylcyclohexane-1,3-dione (IV) to react with bromine. The product of this reaction was assigned structure V on the grounds that it lost the typical ultraviolet absorption of an enolizable  $\beta$ -diketone and that it exhibited typical infrared absorption due to acidic hydrogen (2650–2000  $\text{cm}^{-1}$ ), and C=O of a  $\beta$ -diketone and carboxylic acid at 1745 and 1710  $\text{cm}^{-1}$ , but it did not exhibit hydroxyl absorption that was found in II. Thus, a  $\beta$ -carboxyethyl does not affect the formation of the expected product on bromination of a  $\beta$ -diketone. Only in the case where as exocyclic ketone and a  $\beta$ -carboxyethyl group are present in a  $\beta$ -diketone, as in I, do we find participation by these groups in the bromination reaction.

Several interesting reactions were observed on V. For example, when V was recrystallized from absolute methanol, a neutral compound was obtained in a 72% yield which was shown to be the methyl ester (VI). The structure of VI was shown to be correct by an alternate synthesis; *i.e.*, when the methyl ester of IV was allowed to react with bromine, a good yield of VI was obtained. The formation of the methyl ester (VI) from the acid (V) merely by heating

of V in methanol most probably occurs by the elimination of a small amount of hydrogen bromide from V, which thereby catalyzes the esterification. If, however, V is heated in water, rather than methanol, a different neutral compound is obtained which has lost the elements of hydrogen bromide. This product exhibited infrared absorption at 1790, 1750, and 1715  $\text{cm}^{-1}$  and has been assigned structure VII.

Compound VII can also be obtained by allowing compound V to react with either sodium bicarbonate or magnesium hydroxide. If VII is allowed to react with excess sodium hydroxide at 0°, the  $\beta$ -diketone system is cleaved and the lactone is opened to generate the dicarboxylic acid VIII whose infrared spectrum exhibited the predicted peaks at 1730 (C=O, ketone) and 1700 (C=O, acid). Distillation or sublimation of VIII gave the corresponding lactone (IX). An attempt to prepare the diester of VIII gave the corresponding monoester of IX. As expected, IX was recovered unchanged upon treatment with sodium bicarbonate but regenerated VIII upon treatment with sodium hydroxide solution. Finally, it was found that when V was allowed to react with sodium hydroxide, a 30% yield of IV was obtained. The reversal of the bromination reaction by sodium hydroxide also occurs with II and III and can be explained by assuming the release of  $\text{Br}^+$  to the attacking base, followed by protonation of the corresponding enolate anion.<sup>7</sup>

As a consequence of our studies on model compounds, we felt that in the bromination of I, the bromine must have attacked carbon-2 as the initial reaction, followed by further intramolecular reaction to give the neutral product (II). In an attempt to determine the carbon skeleton of the brominated product, II was treated with zinc dust and acetic acid. The major product of the reaction was 2,6,6-trimethyl-3-carboxymethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (XI) which,

(6) The ultraviolet spectrum of a typical cyclic  $\beta$ -diketone, for example I or IV, exhibits absorption at 264  $\text{m}\mu$  when determined in ethanol and at 289  $\text{m}\mu$  when determined in 0.1 N sodium hydroxide. The molecular extinction coefficient for the maxima are of the order of  $10^3$  to  $10^4$ .

(7) The generation of  $\text{Br}^+$  or its equivalent from a bromo ketone by the attack of a nucleophile has ample precedence; see, for example, H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955). Other related reactions are the generation of  $\text{Br}^+$  when N-bromosuccinimide is allowed to react with sodium hydroxide.

as we have shown earlier,<sup>4</sup> is the product formed when I is treated with acid; however, a second product was isolated in low yield which was found to be X<sup>4</sup>. In order to remove the bromine atom from II under neutral conditions, II was allowed to react with hydrogen using a palladium-on-charcoal catalyst in the presence of magnesium oxide which caused the formation of X in good yields. Finally, treatment of II with a suspension of magnesium oxide in 95% ethanol resulted in the formation of XII, a compound whose infrared spectrum was similar to the infrared spectrum of VII. On these grounds, the assignment of structure II to the bromination product I is the most probably justified. The formation of XII from II establishes that the bromine atom is at carbon-2, and the formation of X from II establishes the gross carbon skeleton. That X is formed from II also establishes the location of the hydroxyl group in II since we visualize the reaction as proceeding in two steps: (a) hydrogenolysis of the bromine atom and (b) dehydration of the resulting  $\beta$ -hydroxy ketone to give X.

### Experimental<sup>8</sup>

**Bromination of 3-(4,4-Dimethyl-2,6-dioxocyclohexyl)levulinic Acid.**—To a solution of 513 mg. (2.01 mmoles) of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid<sup>4,9</sup> (I) in 50 ml. of water was slowly added a saturated solution of bromine in water until a yellow color persisted. The precipitate which formed was collected by filtration, washed with water, and dried *in vacuo* at room temperature; yield, 606 mg. (90.9%), m.p. 120° dec. Recrystallization from a mixture of benzene and hexane gave the analytical sample; yield, 404 mg. (60.7%), m.p. 117–118 dec.  $\bar{\nu}$  in cm.<sup>-1</sup> (chloroform): 3620 and 3340 (OH), 1785 and 1725 (C=O).

*Anal.*<sup>10</sup> Calcd. for C<sub>13</sub>H<sub>17</sub>O<sub>5</sub>Br: C, 46.88; H, 5.15; Br, 23.98. Found: C, 46.99; H, 5.22; Br, 24.11.

This compound is sensitive to heat since it decomposed on drying *in vacuo* at 65°. The melting point is a poor criterion for purity; we have found that the melting point of the analytical sample may vary from 115 to 124° dec. when determined in an oil bath and may be as high as 150° dec. when determined on the Kofler Heizbank.

**2-(2-Oxopropyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione (III).**—To a solution of 500 mg. (2.54 mmole) of 2-(2-oxopropyl)-5,5-dimethylcyclohexane-1,3-dione<sup>4</sup> in 25 ml. of water was added a solution of bromine water until a yellow color persisted, and the reaction mixture was chilled. The white precipitate which formed was collected by filtration and washed with water; yield, 667 mg. (96.8%), m.p. 112°. One recrystallization of the crude product from methanol gave the analytical material, m.p. 111°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 1740 and 1715 (C=O).

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub>Br: C, 48.02; H, 5.49; Br, 29.04. Found: C, 47.82; H, 5.52; Br, 29.33.

**2-(2-Carboxyethyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione (V).**—2-(2-Carboxyethyl)-5,5-dimethylcyclohexane-1,3-dione<sup>11</sup> (1.00 g., 4.72 mmoles) was dissolved in 25.0 ml. of water and 10.0 ml. of methanol with heating. After cooling to room temperature the clear solution was treated with bromine water until a slight yellow persisted. The reaction solution was chilled, and the white product which precipitated was collected by filtration and washed with water; yield, 1.06 g. (72%), m.p. 127°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 2650–2000 (acidic hydrogen), 1745 and 1710 (C=O);  $\lambda_{\text{max}}^{\text{EtOH}}$  300 ( $\epsilon$  214).

(8) The infrared spectra were determined on a Perkin-Elmer Model 137 spectrophotometer, and the ultraviolet were determined on a Perkin-Elmer Model 4000A spectrophotometer. Except where noted, the melting points were determined on a Kofler Heizbank and are corrected.

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

(10) The analyses reported in the paper were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(11) H. Stetter, H. Kessler, and H. Meisel, *Ber.*, **87**, 1617 (1954).

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>4</sub>Br: C, 45.39; H, 5.19; Br, 27.45. Found: C, 45.47; H, 5.06; Br, 27.52.

**Reaction of 2-(2-Carboxyethyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione with Methanol.**—A solution of 0.602 g. (2.07 mmoles) 2-(2-carboxyethyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione (V) in 25.0 ml. of methanol was refluxed for 1 hr., concentrated *in vacuo* to about 10 ml., and chilled. The white solid which precipitated was removed by filtration and washed with water; yield, 0.450 g. (72%), m.p. 70°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 1745 and 1710 (C=O);  $\lambda_{\text{max}}^{\text{EtOH}}$  262 ( $\epsilon$  442).

*Anal.* Calcd. for C<sub>12</sub>H<sub>17</sub>O<sub>4</sub>Br: C, 47.23; H, 5.61; Br, 26.18. Found: C, 47.50; H, 5.69; Br, 26.11.

**2-(2-Carbomethoxyethyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione (VI).**—2-(2-Carbomethoxyethyl)-5,5-dimethylcyclohexane-1,3-dione (100 mg., 0.442 mmole) was dissolved in 1 ml. of ethanol and 1 ml. of water at room temperature. Bromine water was added dropwise to the solution until a slight yellow color persisted. Addition of water (5 ml.) to the reaction mixture caused precipitation of a white solid which was collected by filtration; yield, 101 mg. (75%), m.p. 71°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 1745 and 1710 (C=O). The product obtained in this reaction was identical in all respects with the product obtained by esterification of V.

**The Lactone of 3-(4,4-Dimethyl-2,6-dioxo-1-hydroxycyclohexyl)propionic Acid (VII).**—(a) To 477 mg. (1.64 mmoles) of 2-(2-carboxyethyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione (V) was added 5 ml. of water and 0.1 ml. of methanol. The mixture was refluxed for 5 min. during which time solution did not occur, but the pH dropped to approximately 1. The reaction mixture was chilled, and the white solid was collected by filtration; yield, 260 mg. (75%), m.p. 210°. The crude product was sublimed from an oil bath at 120° (0.10 mm.) and gave 256 mg. of the analytical sample (VII), m.p. 210°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 1790 (C=O,  $\gamma$ -lactone), 1750, and 1710 (C=O).

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>: C, 62.84; H, 6.71. Found: C, 62.90; H, 6.68.

(b) To a solution of 200 mg. (0.686 mole) of 2-(2-carboxyethyl)-2-bromo-5,5-dimethylcyclohexane-1,3-dione (V) in 20 ml. of ether was added 20 ml. of 5% sodium bicarbonate solution. After the mixture was stirred for 10 min., a white solid formed at the interface of the ether and water. The mixture was chilled, and the solid (VII) was removed by filtration; yield, 103 mg. (71.5%), m.p. 211°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 1790, 1750, and 1710. This product was identical in all respects with the neutral compound obtained by refluxing V with water.

**3,3-Dimethyl-5-oxo-hydroxyazelaic Acid (VIII).**—A mixture of 1.62 g. (7.71 mmoles) of 3-(4,4-dimethyl-2,6-dioxo-1-hydroxycyclohexyl)propionic acid lactone (VII) and 16 ml. of 10% sodium hydroxide was stirred for 1 hr. in an ice bath. The cold reaction mixture was acidified with hydrochloric acid, and the white solid which precipitated was collected by filtration; yield, 1.29 g. (68.0%), m.p. 121°. Recrystallization from a mixture of *p*-dioxane and hexane gave the pure product, m.p. 122°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 3320 (OH), 1730 (C=O, ketone), 1700 (C=O, acid);  $\lambda_{\text{max}}^{\text{EtOH}}$  290  $\mu$  ( $\epsilon$  40.3).

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>6</sub>: C, 53.65; H, 7.35; neut. equiv., 123.0. Found: C, 53.35; H, 7.57; neut. equiv., 124.5, 124.3.

**The  $\gamma$ -Lactone of 3,3-Dimethyl-5-oxo-6-hydroxyazelaic Acid (IX).**—3,3-Dimethyl-5-oxo-6-hydroxyazelaic acid (VIII) (406 mg., 1.58 mmoles) was sublimed from an oil bath at 130° (0.1 mm.) and 270 mg. (71.6%) of a white solid was collected, m.p. 64–66°. Resublimation gave the pure product (IX), m.p. 64–66°.  $\bar{\nu}$  in cm.<sup>-1</sup> (potassium bromide): 2650–2100 (acidic hydrogen), 1780 (C=O,  $\gamma$ -lactone), 1730 (C=O, ketone), 1700 (C=O, acid).

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>5</sub>: C, 57.88; H, 7.06. Found: C, 57.71; H, 7.14.

**The Lactone of 8-Carbomethoxy-7,7-dimethyl-5-oxo-4-hydroxy-octanoic Acid.**—A mixture of 500 mg. (2.03 mmoles) of 3,3-dimethyl-5-oxo-6-hydroxyazelaic acid (VIII), 205 mg. (6.40 mmoles) of methanol, and 10  $\lambda$  l. of ethanesulfonic acid in 5.5 ml. 1,2-dichloroethane was refluxed for 18 hr. To the cold reaction mixture was added 20 ml. of water and 25 ml. of ether. The two phases were separated, and the aqueous portion was extracted with ether (2  $\times$  25 ml.). The combined ether extracts were washed with 5% sodium hydroxide solution. The organic phase was dried with anhydrous magnesium sulfate, filtered, concentrated *in vacuo* and gave 485 mg. (99%) of crude product. Distillation in a micro distillation apparatus (oil bath temperature,

110°, 0.07 mm.) gave 266 mg. of pure product.  $\bar{\nu}$  in  $\text{cm.}^{-1}$  (film): 1790 (lactone), 1740 ( $\text{C}=\text{O}$ , ester).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{O}_5$ : C, 59.47; H, 7.48. Found: C, 58.95; H, 7.40.

**Action of Zinc and Acetic Acid on the Bromination Product of 3-(4,4-Dimethyl-2,6-dioxocyclohexyl)levulinic Acid (II).**—A mixture of 276 mg. (0.830 mmole) of II and 425 mg. of zinc dust in 10 ml. of glacial acetic acid was stirred for 1.5 hr. at 80°. After filtration, 25 ml. of water was added to the filtrate, and the mixture was extracted with ether (3 × 25 ml.). The combined ether extracts were washed with water (3 × 25 ml.) and then extracted with 5% sodium bicarbonate solution (3 × 25 ml.). The ethereal layer, after drying with magnesium sulfate, was evaporated to dryness and gave 16 mg. (8.2%) of X, m.p. 167°.  $\bar{\nu}$  in  $\text{cm.}^{-1}$  (potassium bromide): 1805 (enol lactone), 1645 ( $\alpha,\beta$ -unsaturated ketone). This product was identical with X prepared by a different method.<sup>4</sup> The bicarbonate extracts were acidified with concentrated hydrochloric acid and extracted with ether (3 × 25 ml.). The combined ether extracts after the usual processing gave 101 mg. (52.0%) of 2,6,6-trimethyl-3-carboxymethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (XI) (m.p. 125°), which was identical with the product previously prepared by a different procedure.<sup>4</sup>

**Hydrogenolysis of the Bromination Product of 3-(4,4-Dimethyl-2,6-dioxocyclohexyl)levulinic Acid (II).**—A mixture of 666 mg.

(2.00 mmoles) of II, 100 mg. of magnesium oxide, and 150 mg. of 5% palladium-on-charcoal catalyst in 200 ml. of absolute ethanol was hydrogenated at an initial pressure of 60 p.s.i. until the theoretical amount of hydrogen had been absorbed. After filtration, the reaction mixture was concentrated *in vacuo* to 10 ml., and the white solid (X), which precipitated from solution, was collected by filtration; the yield of X was 321 mg. (68.2%), m.p. 167°.  $\bar{\nu}$  in  $\text{cm.}^{-1}$  (potassium bromide): 1805 (enol lactone), 1645 ( $\alpha,\beta$ -unsaturated ketone). This product was identical in all respects with compound X prepared by a different procedure.<sup>4</sup>

**The Lactone of 3-Acetyl-3-(4,4-dimethyl-2,6-dioxo-1-hydroxycyclohexyl)propionic Acid (XII).**—A solution of 333 mg. (1.00 mmole) the bromination product of 3-(4,4-dimethyl-2,6-dioxocyclohexyl)levulinic acid (II) and 50 mg. of magnesium oxide in 100 ml. in 95% ethanol was stirred for 2.5 hr. and allowed to stand overnight. The solution was filtered to remove excess magnesium oxide. The filtrate was concentrated to 50 ml. *in vacuo*, chilled, and the white solid product which precipitated was removed by filtration; yield, 167 mg. (66.2%), m.p. 212°. Sublimation from an oil bath at 130° (0.1 mm.) gave the analytical material, m.p. 210°.  $\bar{\nu}$  in  $\text{cm.}^{-1}$  (potassium bromide): 1790 (lactone), 1745 and 1720 ( $\text{C}=\text{O}$ ).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_5$ : C, 61.89; H, 6.39. Found: C, 62.05; H, 6.58.

### Furazan Oxides. III. An Unusual Type of Aromatic Substitution Reaction<sup>1,2</sup>

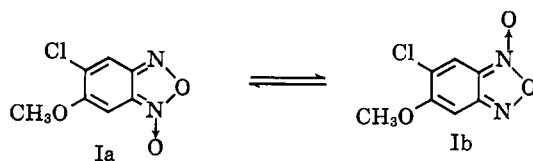
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Treatment of either 2,4- or 2,3-dinitroaniline in alkaline methanol solution at 50° with aqueous sodium hypochlorite gives rise to an unusual substitution reaction which proceeds by way of the corresponding nitrobenzofurazan oxide as an intermediate. The product in each case is a chloromethoxybenzofurazan oxide in which the nitro group in the nitrobenzofurazan oxide intermediate has been replaced by a chloro group and an adjacent ring hydrogen in this intermediate has been replaced by a methoxy group. An analogous reaction takes place with each of the two nitrobenzofurazans. The structures of the chloromethoxy products were proved by spectral and chemical means. A mechanism for this reaction is suggested.

In 1912 Green and Rowe reported<sup>4</sup> that 2,4-dinitroaniline underwent an unexpectedly complex reaction when it was treated in alkaline methanol solution at 50° with aqueous sodium hypochlorite. Such treatment constitutes a well known method for the preparation of benzofurazan oxides from *o*-nitroanilines; however, the product from 2,4-dinitroaniline was found not to be the corresponding nitrobenzofurazan oxide but rather a chloromethoxybenzofurazan oxide. The chloro and methoxy groups were formulated by Green and Rowe as having the positions relative to the heterocycle which are indicated in structure I,<sup>5</sup> although the structural evidence consisted only in satisfactory analyses for N, Cl, and  $\text{CH}_3\text{O}$  and also the observations



(1) Part II: F. B. Mallory and C. S. Wood, *J. Org. Chem.*, **27**, 4109 (1962).

(2) Presented before the Organic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(3) National Science Foundation Cooperative Graduate Fellow, 1960-1961.

(4) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2452 (1912).

(5) The furazan oxide structure for molecules in this family and the Ia  $\rightleftharpoons$  Ib type of equilibration by way of *o*-dinitrosobenzenes have been demonstrated by recent work. (See ref. 1 for pertinent references.)

that the compound underwent several reactions typical of furazan oxides.

The use of ethanol in place of methanol in hypochlorite oxidation of 2,4-dinitroaniline was found<sup>4</sup> to give a chloroethoxybenzofurazan oxide whose structure was formulated on similar grounds to be analogous to I.

There appears to be only one other mention in the literature of this unusual type of substitution reaction in which an aromatic nitro group and a ring hydrogen are replaced by chloro and alkoxy groups; in 1958 Dyall and Pausacker reported<sup>6</sup> that treatment of 2,3-dinitroaniline in alkaline ethanol with aqueous sodium hypochlorite gave a product which they formulated solely on the basis of analyses for C, H, and Cl as X-chloro-4-ethoxybenzofurazan oxide.

We have reinvestigated these reactions and have found that in each case the structure which previously was assigned<sup>4,6</sup> to the product is incorrect. Thus, we have established that the product from 2,4-dinitroaniline in methanol has structure II and the product from 2,3-dinitroaniline in methanol has structure III. It is suggested that in substituted benzofurazan oxides of this sort steric compression of the exocyclic oxygen and the adjacent substituent on the six-membered ring may destabilize significantly the configurations such as IIa and IIIa so that the equilibrium mixture would contain predominantly the configurations such as IIb and

(6) L. K. Dyall and K. H. Pausacker, *Australian J. Chem.*, **11**, 491 (1958).