Reaction of the Ozonide with Potassium Hydroxide.—One gram (0.0035 mole) of the ozonide was refluxed for two hours in 50 cc. of 10% alcoholic potassium hydroxide. The mixture was poured into water, acidified with hydrochloric acid, and extracted with ether. The ether layer was extracted with sodium hydroxide solution and this was then acidified with hydrochloric acid. "Darco" was added and the water was heated and filtered. Benzoic acid crystallized from the filtrate, yielding 0.40 g., m. p. 121–122°.

Reaction of the Ozonide with Hydroxylamine.—One gram (0.0035 mole) of the ozonide was refluxed for two hours with 1 g. (0.014 mole) of hydroxylamine hydrochloride, 10 cc. of pyridine and 10 cc. of absolute ethanol. The solvents were removed by evaporation under an air jet and the residual crystals were triturated with water. The product (XI) was recrystallized from ethanol, forming 0.36 g. (58%) of fine white needles, m. p. 117–119°.

Anal. Calcd. for $C_{10}H_9N_2O$: N, 8.00. Found: N, 7.82.

Reaction of the Ozonide with Phenylhydrazine.—One gram (0.0035 mole) of the ozonide was heated at 235–240° for two hours with 4 cc. (0.041 mole) of phenylhydrazine. The reaction mixture was poured into dilute acetic acid and the resulting oil was separated and twice crystallized from ethanol. The yield of product, m. p. 110–112°, was 0.03 g. (2.5%).

Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.80; H, 5.60; N, 11.20. Found: C, 76.86; H, 5.74; N, 11.36.

***o*-Propionylbenzoic Acid (X).**—The method was that of Gottlieb,[8] in which 66 g. (0.625 mole) of freshly fused sodium propionate, 130 g. (1.0 mole) of propionic anhydride and 100 g. (0.675 mole) of phthalic anhydride were refluxed at 170° for two and one-half hours. The product, ethylidene phthalide, was obtained as an oil (97 g.). Of this 46 g. (0.29 mole) was refluxed with 10% aqueous sodium hydroxide. The yield of *o*-propionylbenzoic acid was 23.4 g. (44%), m. p. 96–97°.

4-Ethyl-1-keto-2,3,1-benzoxazine (XI).[6]—The method of Daube[7] was used, starting with 3 g. (0.017 mole) of *o*-propionylbenzoic acid, 3 g. (0.043 mole) of hydroxylamine hydrochloride and 10 cc. of 10% potassium hydroxide solution. The yield of product, m. p. 115–117°, was 1.9 g. (64%).

The melting point was not lowered when this compound was mixed with the reaction product of the ozonide with hydroxylamine.

1-Ethyl-3-phenylphthalazone (XII).[8]—One gram (0.0056 mole) of *o*-propionylbenzoic acid was refluxed with 4 cc. (4.4 g.; 0.041 mole) of phenylhydrazine at 235–240° for two hours. The reaction mixture was poured into dilute acetic acid, whereupon crystals formed. These were recrystallized from ethanol, forming 0.35 g. (40%) of long white needles, m. p. 111–112°.

The same product was formed when *o*-propionylbenzoic acid was treated with phenylhydrazine according to the directions of Shriner and Fuson[12] for preparing phenylhydrazones.

The melting point was not lowered when this compound was mixed with the reaction product of the ozonide with phenylhydrazine.

Summary

1. Seven new 2,3-disubstituted indones are described.

2. The dehydration products after the addition of the Grignard reagents of primary and secondary alkyl halides to 2-substituted indanediones have been shown to be indones rather than alkylidene indanones.

(12) Shriner and Fuson, "The Systematic Identification of Organic Compounds;" John Wiley and Sons, Inc., New York, N. Y., second edition, 1940, p. 64.

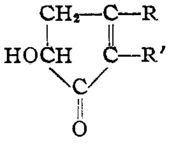
URBANA, ILLINOIS RECEIVED JULY 9, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation of Cyclopentenones from Lactones[1]

BY ROBERT L. FRANK, PETER G. ARVAN, JOHN W. RICHTER AND CLINTON R. VANNEMAN

A method for preparing substituted cyclopentenones has been reported by Plattner and St. Pfau[2] which consists in the removal of the elements of water from γ,δ-unsaturated acids or the corresponding lactones. This reaction has also been reported in the patent literature[3] and has been studied recently by Bryusova and Osipova.[4] It was thought that if the yields for this transformation on a laboratory scale could be improved, it might afford a means of preparing hydroxycyclopentenones similar to pyrethrolone (I, R = CH_3; R′ = C_5H_7), the alcohol portion of the pyrethrins, by the sequence of reactions shown on the following page.



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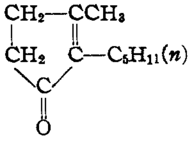

II

Such compounds could be used in studies relating chemical structure to pyrethrin-like insecticidal activity.

In order to investigate the reaction, γ-methyl-γ-decanolactone (III) was prepared in 28–31% yields by the addition of n-hexylmagnesium chloride or bromide to ethyl levulinate. The lactone was formed directly in this reaction due to the splitting out of ethoxymagnesium halide from the Grignard complex.[5] An attempt to prepare the lactone by the use of n-hexylzinc chloride was unsuccessful.

The use of phosphorus pentoxide as the dehydrating agent caused the transformation of γ-methyl-γ-decanolactone (III) to dihydrojasmone

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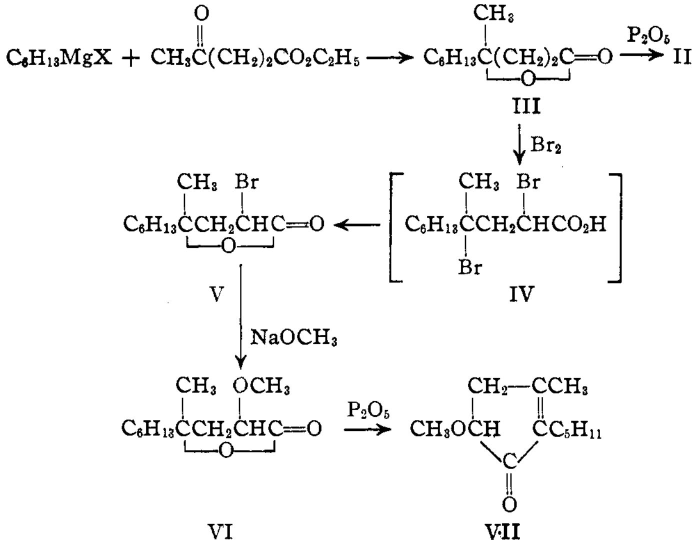
(1) Presented before the Organic Division at the Pittsburgh meeting of the American Chemical Society, September 6–10, 1943.

(2) Plattner and St. Pfau, *Helv. Chim. Acta*, **20**, 1474 (1937).

(3) Maschmeijer, French Patent 765,515 (June 12, 1934); I. G. Farbenindustrie, A.-G., French Patent 785,540 (Dec. 8, 1935); English Patent 453,518 (Aug. 10, 1936); Givaudan and Co., German Patent 639,455 (May 12, 1936).

(4) Bryusova and Osipova, *Sintezy Dushistykh Veshchestv. Sbornik Statei*, 295 (1939); *C. A.*, **36**, 3789 (1942).

(5) Grignard, *Compt. rend.*, **135**, 627 (1902).



(II)[6] to take place smoothly in yields of 50%. The product was identified by boiling point, density, refractive index, formation of its semicarbazone and its ultraviolet absorption spectrum. The spectrum, measured in 95% ethanol at a concentration of 2.5 × 10^{-5} moles per liter, showed a maximum at 235 mμ (log ϵ = 4.33) (Gillam and West[7] reported 237 mμ). While Plattner and St. Pfau mentioned the formation of dihydrojasmone (II) from γ-methyldecylenic acid, they did not give details of the transformation.

In order to apply this reaction to the preparation of the methoxycyclopentenone (VII) it was first necessary to prepare α-methoxy-γ-methyl-γ-decanolactone (VI). This was successfully accomplished by bromination of γ-methyl-γ-decanolactone (III) and subsequent treatment of the bromolactone (V) with sodium methoxide.

When the bromination product of γ-methyl-γ-decanolactone (III) was distilled, copious amounts of hydrogen bromide were evolved, with much foaming, even if the reaction mixture was first washed with sodium bicarbonate solution. It seems likely that this was due to the formation of α,γ-dibromo-γ-methylcapric acid (IV), which was then dehydrobrominated and cyclized to the desired product (V) during the distillation. This type of reaction is known to occur when γ-valerolactone is treated with hydrogen bromide.[8] The bromolactone (V), once obtained, showed no tendency to undergo dehydrobromination in subsequent distillations.

The reaction of the methoxylactone (VI) with phosphorus pentoxide did not yield the desired methoxycyclopentenone (VII).

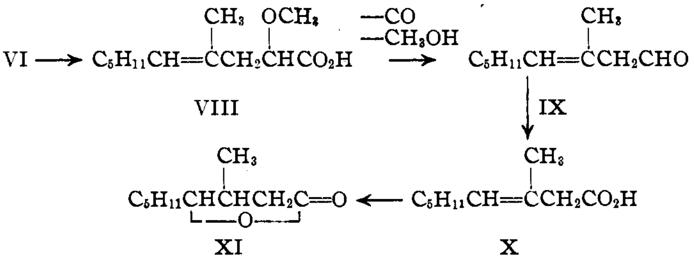
Twenty-three grams (0.112 mole) of the methoxylactone (VI) was poured onto 28.4 g. (0.20 mole) of phosphorus pentoxide in a 250-cc. Claisen flask connected to a receiver cooled by dry-ice. Heat was at once evolved and the contents turned black. The product was then distilled under reduced pressure, yielding 10.2 g. of a dark viscous liquid. This final product from three runs, totaling 19.0 g., was combined and redistilled in a 50-inch Podbielniak column.[9] Eleven fractions were collected varying in weight from 0.8 g. to 2.1 g.

Fraction 2, b. p. 74–82° (3–5 mm.), analyzing C, 87.72; H, 10.51; n^{20}_D 1.5190, was evidently an impure hydrocarbon and was found to decolorize both bromine and potassium permanganate.

Fraction 8, b. p. 112–115° (3–5 mm.), which showed the lowest refractive index of all the products, namely, n^{20}_D 1.4720, gave saponification equivalents 178 and 180 (seven hours of refluxing with 0.68 *N* sodium hydroxide was necessary).

Anal.[10] Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 71.04, 71.05; H, 11.18, 10.02.

It is suggested that Fraction 8 may be β-methyl-γ-pelargonolactone (XI), which could conceivably result from the following transformations (oxidation of the aldehyde (IX) could have taken place during the distillation).



The loss of two carbon atoms to form a lactone in this reaction is evidence that the bromine atom and methoxyl group in the bromolactone (V) and the methoxylactone (VI), respectively, are indeed in the expected *alpha* position.

Experimental Preparations

Ethyl Levulinate.—Five hundred eighty-one grams (5.0 moles) of levulinic acid, 583 cc. (460.7 g., 10.0 moles) of 95% ethanol, 500 cc. of benzene and 5 cc. of concentrated sulfuric acid were refluxed for fifteen hours in a 3-liter, round-bottomed flask equipped with a continuous water extractor and a reflux condenser. The reaction mixture was then fractionally distilled to yield 583 g. (81%) of product, b. p. 93–94° (18 mm.); n^{20}_D 1.4212.

γ-Methyl-γ-decanolactone (III).—A solution of *n*-hexylmagnesium chloride was prepared in the usual manner from 48.6 g. (2.0 moles) of magnesium turnings, 278 cc. (241.2 g.; 2.0 moles) of *n*-hexyl chloride (Sharples) and 500 cc. of anhydrous ether. It was then transferred to a 1-liter dropping funnel and added dropwise to a solution of 288.0 g. (2.0 moles) of ethyl levulinate in 700 cc. of anhydrous benzene and 200 cc. of anhydrous ether contained in a 3-liter, three-necked, round-bottomed flask fitted with the aforementioned dropping funnel, a stirrer and a reflux

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(6) Treff and Werner, *Ber.*, **66**, 1521 (1933).

(7) Gillam and West, *J. Chem. Soc.*, 671 (1942).

(8) Emmert, *Ber.*, **40**, 912 (1907); Fittig and Fränkel, *Ann.*, **255**, 31 (1889).

(9) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 177 (1931).

(10) The microanalyses reported in this paper were carried out by Miss Theta Spoor, Miss Margaret McCarthy and Miss Dorothy Schneider.

condenser. During the addition of the Grignard reagent a voluminous white precipitate formed in the yellow solution. Stirring and reflux were continued overnight, after which the mixture was cooled in an ice-bath and iced dilute sulfuric acid was added. The ether-benzene layer was then washed with water, dried over anhydrous calcium sulfate ("Drierite") and fractionally distilled in a carborundum-packed column. The first fraction after removal of the solvent consisted of 25.1 g. of ethyl levulinate, b. p. 63–70° (5 mm.); $n^{20}\mathrm{D}$ 1.4234. The desired product boiled at 120–125° (4–5 mm.) and the yield was 103.2 g. (28%, based on *n*-hexylchloride), $n^{20}\mathrm{D}$ 1.4487; d^{20}_{4} 0.950; [M]D calcd.,[11] 52.5; found, 52.0. It had a peach-like odor.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.59; H, 11.27.

A quantity of residue somewhat greater than the amount of product was left after the fractional distillation.

When *n*-hexyl bromide was used in the same molar amounts instead of the chloride and the reaction was carried out as described above, repeated runs gave yields of 113 g. (31%) of γ-methyl-γ-decanolactone.

Dihydrojasmone (II).—Into a glass-jointed, round-bottomed flask containing 28 g. (0.20 mole) of phosphorus pentoxide was poured 50 g. (0.27 mole) of γ-methyl-γ-decanolactone (III). The contents heated at once and turned black. The flask was quickly attached to a modified Widmer column and evacuated, whereupon 21.0 g. (50%) of product distilled in high purity, b. p. 91° (2 mm.); $n^{20}\mathrm{D}$ 1.4785; d^{20}_{20} 0.920.

The semicarbazone, prepared according to the directions of Shriner and Fuson,[12] melted at 173–174° (Staudinger and Ruzicka[13] reported 175–176°).

α-Bromo-γ-methyl-γ-decanolactone (V).—To 60 g. (0.33 mole) of the lactone (III) and 75 cc. of dry carbon tetrachloride in a 500-cc., three-necked, round-bottomed flask equipped with a mechanical stirrer, a 125-cc. dropping funnel and a reflux condenser to which was attached a gas trap was added 55 g. (0.34 mole) of bromine, dried with concentrated sulfuric acid. The mixture was stirred for five hours at room temperature after which it was heated at 70–75° for two hours. A mercury-vapor lamp was placed so that the maximum amount of light fell on the reaction vessel (ordinary white light gave much lower yields). The flask was cooled to room temperature and the contents washed successively with dilute aqueous sodium bisulfite, 5% aqueous sodium bicarbonate and water. It was then dried with anhydrous calcium sulfate ("Drierite"). At this point the solutions from two such runs were combined. The greater portion of the carbon tetrachloride was then distilled on a steam-bath and the residue heated at 150° under reduced pressure, using a water pump, until the pressure fell to 20 mm. The residue was then fractionally distilled in a carborundum-packed column and yielded 26.0 g. of starting material boiling at 128–134° (4–5 mm.), 27.0 g. of a mixture of starting material and product boiling at 134° (4–5 mm.)–160° (7 mm.) and 36.0 g. (27%, taking into account the recovered starting material) of nearly pure α-bromo-γ-methyl-γ-decanolactone, b. p. 160–165° (7 mm.). Redistillation gave a product with the following constants: b. p. 121–122° (1 mm.), 135–136° (3 mm.), 151–154° (5 mm.); $n^{20}\mathrm{D}$ 1.4890; d^{20}_{4} 1.243; [M]D calcd.,[11] 60.4; found, 60.9.

Anal. Calcd. for $C_{11}H_{19}O_2Br$: C, 50.20; H, 7.28; Br, 30.37. Found: C, 50.98; H, 7.12; Br, 30.11.

Judging from the analysis, the product still contained a trace of γ-methyl-γ-decanolactone, which was extremely difficult to remove completely.

α-Methoxy-γ-methyl-γ-decanolactone (VI).—To a solution of 9.2 g. (0.40 mole) of sodium in 250 cc. of absolute methanol was added 104 g. (0.396 mole) of α-bromo-γ-methyl-γ-decanolactone (V). The solution was allowed to stand at room temperature for ten hours, after which the precipitated sodium bromide was removed by filtration and the excess methanol by distillation *in vacuo*. The residue was poured into 1 liter of water and this was then extracted with two 500-cc. portions of ether. The ether extract was dried over anhydrous calcium sulfate and fractionally distilled in a modified Widmer column to give 64 g. of material boiling at 105–115° (3 mm.). This was redistilled to give 55 g. (65%) of product, b. p. 107–108° (3 mm.); $n^{20}\mathrm{D}$ 1.4408; d^{20}_{20} 0.964; [M]D calcd.,[11] 58.6; found, 58.7; saponification equivalent, calcd., 214; found, 216.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.94; H, 10.01.

In some runs the yields were lower and small amounts of a higher-boiling isomer were obtained, b. p. 151–170° (3–4 mm.); $n^{20}\mathrm{D}$ 1.4710; D^{20}_{4} 1.020; [M]D calcd.,[11] 58.6; found, 58.8; saponification equivalent, calcd., 214; found, 203.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 66.93; H, 9.85.

Summary

A convenient synthesis of dihydrojasmone is reported.

α-Methoxy-γ-methyl-γ-decanolactone has been prepared and its reaction with phosphorus pentoxide is discussed.

Urbana, Illinois Received August 12, 1943

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[11] Swientoslawski, This Journal, **42**, 1945 (1920).

[12] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., second edition, 1940, p. 142.

[13] Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 245 (1924).