Attempts to prepare the cyclic succinhydrazide by alternative methods; such as the reaction of diethyl succinate and hydrazine at high dilution, intramolecular cyclization of succindihydrazide in refluxing butyl cellosolve, and the reaction of hydrazine with *N*-benzylsuccinimide were unsuccessful.

EXPERIMENTAL[7]

1,2-Dibenzoylhexahydropyridazine. A solution of 1.8 g. (0.008 mole) of tetramethylene bromide in 30 ml. of absolute alcohol was added slowly with stirring to a refluxing solution of 2 g. (0.008 mole) of dibenzoylhydrazine[8] in 100 ml. of 60% ethanol. Sufficient concentrated sodium hydroxide was added throughout the reaction to maintain a *p*H of 8–9. After 8 hr. the alcohol was removed by distillation during which water was added to replace the alcohol. The aqueous solution was extracted several times with chlorofrom and the combined extracts dried over anhydrous sodium sulfate. After removal of the solvent by evaporation, the residue (0.5 g., 20%) consisted of white crystals melting at 124–127°. An analytical sample was prepared by recrystallization from a mixture of hexane and chloroform followed by 2 sublimations. The melting point of the hygroscopic crystals was raised to 130°.

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.46; H, 6.15; N, 9.51. Found: C, 73.06; H, 6.08; N, 8.99.

Only starting material was isolated from the reaction of 1,2-dibenzoylhydrazine and trimethylene bromide under similar conditions.

Hexahydropyridazine-3,6-dione. This compound was prepared by catalytic reduction of maleic hydrazide by a modification of the method of Feuer, Bachman, and White.[6] Practical grade maleic hydrazide was recrystallized from water, refluxed with 4% of its weight of Raney nickel in water, and recrystallized again from water. By use of this procedure the amount of platinum oxide catalyst necessary for the reduction of maleic hydrazide could be reduced to half that previously required, the reaction time shortened, and the reductions made consistently successful. The product, which was obtained in 70–80% yield, consisted of white needles, m.p. 277° (lit.[6] m.p. 277–278°). High pressure reductions using Raney nickel catalyst gave starting material or a mixture of products. Only starting material was isolated from the reduction at room temperature using aluminum amalgam.[6]

1,2-Dimethylhexahhyropyridazine-3,6-dione. A solution of 4.0 g. (0.034 mole) of dimethyl sulfate in 75 ml. of 50% ethanol was added with stirring over a period of 4 hr. to a refluxing solution of 2 g. (0.017 mole) of cyclic succinhydrazide in 60 ml. of 50% alcohol. The reaction mixture was maintained at a *p*H of 8–9 by the addition of small amounts of concentrated aqueous sodium hydroxide. At the end of the reaction time the alcohol was removed by distillation during which water was added to replace the alcohol. The remaining aqueous solution was extracted several times with chloroform and the combined extracts were dried over anhydrous sodium sulfate. The average yield of crude product after the evaporation of the solvent was 0.4 g. (16%). After recrystallization from a mixture of hexane and chloroform and 2 sublimations, the melting point of the purified compound was 104–105° (lit.[5] m.p. 104–105°). The compound was highly hygroscopic.

Alkylation of hexahydropyridazine-3,6-dione with ethyl iodide. The above alkylation was carried out substituting 5.3 g. (0.034 mole) of ethyl iodide in 30 ml. of ethanol for the dimethyl sulfate solution. After recrystallization from a mixture of hexane and chloroform and 2 sublimations, 0.3 g. (12%) of white crystals melting at 140–142° was obtained. The compound analyzed for 1-ethylhexahydropyridazine-3,6-dione.

Anal. Calcd. for $C_6H_{10}N_2O_2$: C, 50.70; H, 7.04. Found: C, 50.66; H, 7.10.

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IOWA CITY, IOWA

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[7] Melting points are uncorrected.

[8] H. H. Hatt, *Org. Syntheses*, **Coll. Vol. II**, 208 (1943).

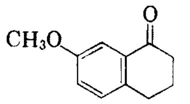
Polyphosphoric Acid–Catalyzed Reaction of Anisole with γ-Butyrolactone

HERBERT O. HOUSE AND RONALD J. MCCAULLY

Received December 15, 1958

The reaction of γ-substituted-γ-butyrolactones with benzene and alkyl-substituted benzenes in the presence of aluminum chloride has served to produce γ-aryl-γ-substituted butyric acids.[1,2] The comparable reaction of benzene with γ-butyrolactone in the presence of excess aluminum chloride afforded α-tetralone in one step.[3] These observations suggested that 7- (or 6-) alkoxy-1-tetralones might be prepared directly by the reaction of alkoxybenzenes with γ-butyrolactone in the presence of polyphosphoric acid.[4,5]

The reaction of anisole with γ-butyrolactone in the presence of polyphosphoric acid was found to yield neither of the expected tetralones I or II, but rather a hydroxy ketone which has infrared and ultraviolet spectra compatible with structure III. This structure was confirmed by oxidation of the product to form the keto acid IV.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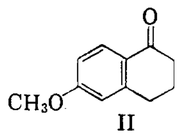
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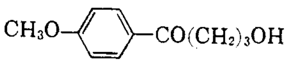
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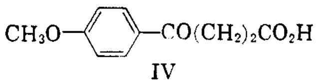
IV

EXPERIMENTAL[6]

γ-Hydroxy-p-methoxybutyrophenone (III). A mixture of 6.14 g. (0.0568 mole) of anisole and 4.876 g. (0.0568 mole) of

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(1) J. F. Eijkman, *Chem. Weekblad*, **1**, 421 (1904).

(2) D. D. Phillips, *J. Am. Chem. Soc.*, **77**, 3658 (1955).

(3) C. E. Olson and A. R. Bader, *Org. Syntheses*, **35**, 95 (1955).

(4) For a review of cyclizations effected in the presence of polyphosphoric acid, see F. D. Popp and W. E. McEwen, *Chem. Revs.*, **58**, 321 (1958).

(5) A successful intermolecular acylation of anisole reported by N. C. Deno and H. Chafetz [*J. Org. Chem.*, **19**, 2015 (1954)] may have involved a γ,γ-disubstituted butyrolactone as an intermediate.

γ-butyrolactone was added, with stirring, to 100 g. of polyphosphoric acid which have been heated to 50°. The resulting mixture was heated to 85–90° with stirring for 8 hr. and then poured onto ice and extracted with four portions of ether. The combined extracts were washed with sodium bicarbonate, dried over sodium sulfate, and concentrated. The residue, when cooled, solidified as yellow needles, m.p. 35–48°, yield 5.53 g. (50%). Recrystallization from an ether-hexane mixture and from ethanol afforded the pure hydroxy ketone as white needles, m.p. 48–49°. The infrared spectrum[7] of the product has bands at 3400 cm.$^{-1}$ (associated O—H) and 1670 cm.$^{-1}$ (conj. C=O); the ultraviolet spectrum[8] has maxima at 218 mμ (ε 10,300) and 272 mμ (ε 14,600).

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.88; H, 7.30.

A solution of 0.0518 g. (0.00027 mole) of the keto alcohol in 10 ml. of reagent acetone was cooled in a Dry Ice-acetone bath and treated, dropwise and with stirring, with a solution of 0.044 g. (0.00044 mole) of chromium trioxide and 0.15 ml. of concentrated sulfuric acid in 1.8 ml. of water. The mixture was allowed to warm to room temperature and stand over a 4-hr. period. The reaction mixture was concentrated, diluted with water, and extracted with ether. The ether solution was extracted with three 20-ml. portions of 5% aqueous sodium bicarbonate. Acidification of the combined bicarbonate extracts afforded 0.0329 g. (57%) of β-(*p*-methoxybenzoyl)propionic acid, m.p. 146–147°, which was identified by a mixed melting-point determination with an authentic sample. More vigorous oxidation of the keto alcohol with chromic acid in boiling acetic acid afforded *p*-anisic acid, identified by a mixed melting-point determination with an authentic sample, in 19% yield.

7-Methoxy-1-tetralone (I). β-(*p*-Methoxybenzoyl)propionic acid, m.p. 146–147° (lit.[9] 144.5–146.5°), was converted to γ-(*p*-methoxyphenyl)butyric acid, m.p. 60–60.8° (lit.[10] 61–62°) in 82% yield by low-pressure hydrogenolysis[10] in acetic acid solution at 65° in the presence of a 10% palladium-on-carbon catalyst and in 88% yield by high-pressure hydrogenolysis[11] of aqueous solution of the sodium salt of the acid at 200° in the presence of copper chromite catalyst. The reaction of 11.98 g. (0.0618 mole) of γ-(*p*-methoxyphenyl)-butyric acid with 150 g. of polyphosphoric acid at 90–93° for 15 min. followed by appropriate manipulations afforded 10.17 g. (93.5%) of 7-methoxy-1-tetralone, m.p. 56–62°. The pure tetralone, which crystallized from aqueous ethanol as pale yellow plates melting at 60.9–62° (lit.[9] 61–62.5°), has a band in the infrared[12] at 1685 cm.$^{-1}$ (conj. C=O) and exhibits ultraviolet[8] maxima at 222 mμ (ε 19,600), 253 mμ (ε 8900) and 323 mμ (ε 3100). The product formed a semicarbazone, m.p. 222–223.1° dec. (lit.[13] 224–226° dec.), in 72% yield and a crude 2,4-dinitrophenylhydrazone, m.p. 280–284°, in 99.5% yield. The pure *2,4-dinitrophenylhydrazone of 7-methoxy-1-tetralone* crystallized from ethyl acetate as red prisms, m.p. 285–286°. The ultraviolet spectrum[7] of the 2,4-dinitrophenylhydrazone has a maximum at 385 mμ (ε 31,400).

Anal. Calcd. for $C_{17}H_{16}N_4O_5$: C, 57.30; H, 4.53; N, 15.72. Found: C, 57.57; H, 4.39; N, 15.62.

The 2,4-dinitrophenylhydrazone of 6-methoxy-1-tetralone, m.p. 233–234° (lit.[14] 236–238°), has an ultraviolet[7] maximum at 396 mμ (ε 29,200).

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CAMBRIDGE 39, MASS.

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[6] The infrared spectra were determined with either a Baird, Model B, or a Perkin-Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

[7] Determined in chloroform solution.

[8] Determined in 95% ethanol solution.

[9] D. G. Thomas and A. H. Nathan, *J. Am. Chem. Soc.*, **70**, 331 (1948).

[10] E. C. Horning and D. B. Reisner, *J. Am. Chem. Soc.*, **71**, 1036 (1949).

[11] This procedure developed by L. F. Fieser and W. H. Daudt, *J. Am. Chem. Soc.*, **63**, 782 (1941), was found to be more convenient in the present study.

[12] Determined in carbon tetrachloride solution.

[13] A. Muller, M. Meszaros, M. Lempert-Sreter, and I. Szara, *J. Org. Chem.*, **16**, 1003 (1951).

[14] F. J. Villani, M. S. King, and D. Papa, *J. Org. Chem.*, **18**, 1578 (1953).

The Triterpenes of *Heliabravoa chende*[1]

MAURICE SHAMMA AND PAUL D. ROSENSTOCK

Received December 18, 1958

A sample of the water-insoluble, "nonglycosidic", extracts of the giant Mexican cactus *Heliabravoa chende* (formerly *Lemaireocereus chende*),[2] kindly supplied by Prof. Carl Djerassi, was investigated for triterpenes. The sample was composed mostly of neutral material (A), and a small fatty acid fraction (B) which gave a negative Liebermann-Burchard test. Saponification of the neutral material (A) with 15% methanolic potassium hydroxide yielded an acid fraction (C) and a neutral fraction (D).

The acidic fraction (C) which was crude and only partly crystalline was washed several times with hexane. The hexane-insoluble residue, which proved to be oleanolic acid (I), was purified as its methyl ester (II).

Chromatography of the neutral fraction (D) over alumina gave oleanolic aldehyde (III) followed by erythrodiol (IV).

The presence of oleanolic aldehyde in *Heliabravoa chende* deserves special attention since this is the first instance of this triterpene being found in nature. However, its 3-acetyl derivative (V) had previously been prepared by Ruzicka and Schellenberg via a Rosenmund reduction of oleanolic acid chloride acetate.[3] In our hands, crude oleanolic aldehyde was obtained as a yellowish solid, m.p. 112–186°, which could best be purified as the acetate. Oleanolic aldehyde was also reduced in very high yields by lithium aluminum hydride to erythrodiol.

An interesting aspect of the present study is that oleanolic aldehyde is one more pentacyclic triterpene which should be added to the impressive

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[1] This investigation was supported by a research grant (No. G5105) from the National Science Foundation.

[2] Helia Bravo and Don K. Cox, *Cactaceas Y Succulentas Mexicanas*, **3**, 3 (1958).

[3] L. Ruzicka and H. Schellenberg, *Helv. Chim. Acta*, **20**, 1553 (1937).