[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,1-Dimethyl-6,7-methylenedioxytetralin[1]

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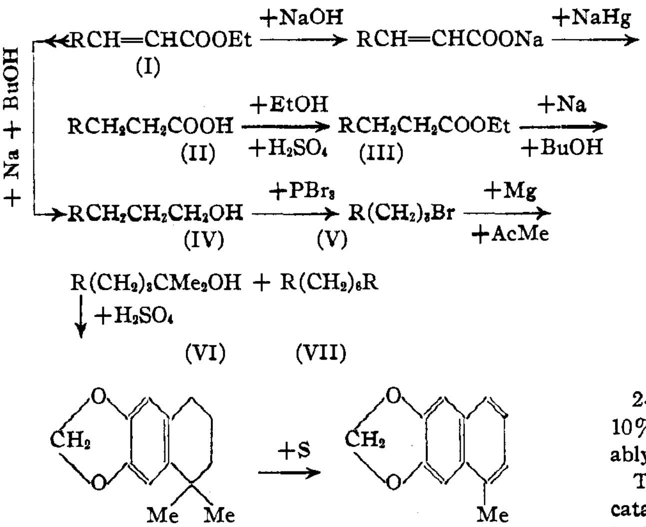
In continuation of our investigations in the ionene field,[2] and in the cyclodehydration of aromatic alcohols,[3] we have had occasion to synthesize a methylenedioxytetralin by the following steps, in which formulas R = $\mathrm{CH_2}\langle\overset{\mathrm{O}}{\underset{\mathrm{O}}{}}\rangle\mathrm{C_6H_3}$—



$$\mathrm{RCH{=}CHCOOEt\ (I)} \xrightarrow{+\mathrm{NaOH}} \mathrm{RCH{=}CHCOONa} \xrightarrow{+\mathrm{NaHg}}$$

$$\mathrm{RCH_2CH_2COOH\ (II)} \xrightarrow[+\mathrm{H_2SO_4}]{+\mathrm{EtOH}} \mathrm{RCH_2CH_2COOEt\ (III)} \xrightarrow[+\mathrm{BuOH}]{+\mathrm{Na}}$$

$$\mathrm{(I)} \xrightarrow{+\mathrm{Na} + \mathrm{BuOH}} \mathrm{RCH_2CH_2CH_2OH\ (IV)} \xrightarrow{+\mathrm{PBr_3}} \mathrm{R(CH_2)_3Br\ (V)} \xrightarrow[+\mathrm{AcMe}]{+\mathrm{Mg}}$$

$$\mathrm{R(CH_2)_3CMe_2OH\ (VI)} + \mathrm{R(CH_2)_6R\ (VII)}$$

$$\mathrm{(VI)} \xrightarrow{+\mathrm{H_2SO_4}} \mathrm{(VIII)} \xrightarrow{+\mathrm{S}} \mathrm{(IX)}$$

(VIII) (IX)

Experimental

Ethyl Piperonylacetate (III).—Ethyl piperonylideneacetate (I), prepared from piperonal and ethyl acetate, according to Hoering's directions,[4] was saponified by boiling with the calculated amount of 0.1 *N* sodium hydroxide. The solution was cooled quickly, to prevent the crystallization of the sodium salt, and a 10% excess of sodium amalgam was added slowly. When the reduction was complete, the mixture was filtered, the filtrate cooled with ice and acidified with hydrochloric acid. The precipitated piperonylacetic acid was washed, dried, and crystallized from ether, giving a colorless crystalline product, m. p. 87–90°, which did not decolorize a cooled 10% carbon tetrachloride solution of bromine; yield 75–80%.

Lorenz,[5] who prepared this acid by a similar method, differing only in certain details, gave its m. p. as 84°. Kaufmann and Radosević,[6] who obtained it by hydrolysis of its methylamide, also recorded the m. p. as 84°.

Warmed with absolute ethanol and a little sulfuric acid, the acid yielded the ethyl ester as a colorless transparent liquid, of pleasant odor, b. p. 184–185° at 14 mm., which did not decolorize a cooled 10% carbon tetrachloride solution of bromine; yield 83%.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.84; H, 6.35. Found: C, 64.94; H, 6.64.

2-Piperonylethanol (IV), prepared from the foregoing ester by reduction with sodium and *n*-butyl alcohol, formed a colorless viscous liquid, b. p. 170–172° at 8 mm., 182–183.5° at 14 mm., 184–186° at 16 mm., and 186–188° at 19 mm.; yield 87%. Cooled to −10°, it slowly congealed to a crystalline mass. When the temperature of this solid was permitted to rise slowly, it began to melt at 28° and was completely liquefied at 29°. The m. p. of 2-piperonylidene ethanol is given in the literature[7] as 78–78.8° (corr.). Hence the product cannot be the unsaturated alcohol.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.63; H, 6.72. Found: C, 66.30; H, 6.75.

2-Piperonylethanol immediately decolorized a cooled 10% carbon tetrachloride solution of bromine, presumably being promptly oxidized thereby.

This saturated alcohol has been reported[8] as one of the catalytic reduction products of piperonylidene acetaldehyde, although the b. p. recorded (149–150°, uncorr., at 6 mm.) was lower than that given above.

Phenylurethan, m. p. 98–99°.

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.20; H, 5.72. Found: C, 67.97; H, 5.83.

A more direct and shorter road to the same goal (IV), was the reduction of the ethyl piperonylideneacetate (I) by sodium and *n*-butyl alcohol, as follows:

A 3-necked 2-liter flask, equipped with mercury-sealed stirrer, a reflux condenser, and a dropping funnel, protected with calcium chloride guard tubes, and containing 37.8 g. of sodium and 100 cc. of dry toluene, was heated above the m. p. of the sodium and then allowed to cool during vigorous stirring, so as to obtain the sodium in a finely divided state. To this mixture, there was added, as rapidly as possible, a solution of 36.2 g. of the ester (I) in 100 cc. of *n*-butyl alcohol. There ensued a vigorous reaction, with much foaming. When this subsided, more (150 cc.) *n*-butyl alcohol was added, to dilute the mixture, to aid in keeping the alcoholate in solution, and to react with any unattacked sodium.

The mixture was hydrolyzed by addition of water, the oily layer separated from the aqueous alkaline one, the latter extracted twice with *n*-butyl alcohol and the extracts added to the oily layer. This was distilled at ordinary pressure, to remove the toluene and butyl alcohol, and then under reduced pressure, to isolate the

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[1] Presented in abstract before the Division of Organic Chemistry, at the New York meeting of the American Chemical Society, April 23, 1935.

[2] (a) Bogert and Fourman, THIS JOURNAL, **55**, 4670 (1933); (b) Bogert and Apfelbaum, *Science*, [N. S.], **79**, 280 (1934); (c) Bogert, Davidson and Apfelbaum, THIS JOURNAL, **56**, 959 (1934).

[3] (a) Bogert and Davidson, *ibid.*, **56**, 185 (1934); (b) Roblin, Davidson and Bogert, *ibid.*, **57**, 151 (1935).

[4] Hoering, *Ber.*, **40**, 2176 (1907).

[5] Lorenz, *ibid.*, **13**, 758 (1880).

[6] Kaufmann and Radosević, *ibid.*, **49**, 681 (1916).

[7] Bogert and Powell, THIS JOURNAL, **53**, 1609 (1931).

[8] Bogert and Powell, *ibid.*, **53**, 2757 (1931).

piperonylethanol (IV); b. p. 184–186° at 16 mm.; yield 62%.

From the aqueous alkaline layer there was obtained a small amount of piperonylideneacetic acid, $(CH_2O_2)C_6H_3CH{=}CHCOOH$, m. p. 237–238° (from acetic acid), agreeing with that in the literature.

Repeating the above experiment, with amyl in place of butyl alcohol, the results were much the same, except that the initial reaction was more vigorous, the yield somewhat lower (60%), and the by-product piperonylacetic acid, $(CH_2O_2)C_6H_3CH_2CH_2COOH$ (large, colorless crystals, m. p. 84°; m. p. in literature,[6] 84°).

In another series of experiments, replacing the toluene by xylene, the results were less satisfactory. The same alcohol (IV) was obtained and, as by-products, there were recovered both piperonylidene and piperonylacetic acids, in the ratio of 3:1. The former was reduced to the latter, in 80% yield, by sodium amalgam.[5]

1-Bromo-2-piperonylethane (V) could not be secured from the alcohol (IV) by the action of 48% aqueous hydrogen bromide, alone or with the addition of sulfuric acid, because of the decomposition which almost immediately ensued. It was obtained, however, by the following process.

The alcohol (28 g.), contained in a flask well protected from access of any moisture, was congealed in a freezing mixture and phosphorus tribromide (16 g.) added. After a few minutes' standing, the container was removed from the freezing mixture and allowed to come slowly to room temperature. The reaction began gradually, with evolution of hydrogen bromide, and accelerated considerably as the temperature approached that of the m. p. (28–29°) of the alcohol, so that some cooling occasionally was necessary at this point. The crude yellowish-brown product was poured into a mixture of dilute sodium bicarbonate solution and cracked ice, and the bromide (V) extracted with ether. The aqueous layer, containing some of the original alcohol as sodium alcoholate, was acidified and the alcohol recovered. The bromide obtained from the ether extracts, when freshly distilled and pure, was a colorless liquid, b. p. 163–165° at 7.5 mm., n^{25}_{D} 1.5599, but darkened rapidly on exposure to air and light; yield, 50–53%; original alcohol recovered, 20–25%.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: C, 49.38; H, 4.56. Found: C, 49.41; H, 4.87.

1,4-Dipiperonylbutane (VII).—The Grignard reagent was prepared by mixing 48.8 g. of the above bromide, 8 g. of magnesium, and 50 cc. of dry ether, and adding 100 cc. more of dry ether when the reaction was well started. A final warming for an hour completed the reaction. After cooling the mixture to −5°, 14 g. of acetone in an equal volume of dry ether was slowly stirred in, and the stirring continued for a further half hour. It was then poured upon ice acidulated with the calculated quantity of sulfuric acid, extracted with ether, the ether extract dried over anhydrous potassium carbonate and the ether evaporated. As the residue cooled, crystals began to separate, and this separation was greatly hastened by the addition of some 95% ethanol. These crystals were colorless and their m. p. remained constant at 77–78.5° after six crystallizations from alcohol; b. p. about 240° at 3 mm.; yield, about 28%. Their analysis, however, indicated retention of some of the solvent alcohol. They were therefore fused for an hour at 120° and a pressure of 7.2 mm. (m. p. then 78°), and analyzed again.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.58; H, 6.79. Found: C, 73.79; H, 6.65.

2-Methyl-4-piperonylbutanol-2 (VI).—The mother liquors from the crystallization of the dipiperonylbutane (VII) were freed of solvent and distilled at 2 mm. pressure. Two fractions were thus obtained. One boiled at 65–75° and had a safrole odor. The other, b. p. 150–160°, consisted of the nearly pure tertiary alcohol (VI); yield 32%. Purified by two rectifications, it boiled at 145–148° at 2 mm. pressure.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.23; H, 8.17. Found: C, 70.07; H, 8.50.

This alcohol was a very viscous pale yellowish liquid, which congealed to a glass, but did not crystallize, when cooled to −17°. No phenylurethan could be obtained from it, because phenyl isocyanate immediately withdrew the elements of water, with formation of carbanilide.

Attempts to isolate the olefin formed by this dehydration were not very successful, because the repeated rectifications to which it was subjected rearranged it to the tetralin, a change which takes place very easily, as shown by tests with potassium permanganate in acetone solution.

From the residue of the above distillation, more of the dipiperonylbutane was recovered.

1,1 - Dimethyl - 6,7 - methylenedioxytetralin (VIII).—Into 5 g. of vigorously stirred 85% sulfuric acid, there was dropped slowly 4 g. of the above alcohol (VI), maintaining the temperature at 10° or below. After all the alcohol had been added, the stirring was continued for thirty minutes. The mixture was poured upon ice, extracted with ether, to free it from insoluble tarry contaminants, the ether extract washed with dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate, the ether removed, and the residual liquid distilled twice over sodium. The tetralin was thus obtained as a colorless transparent liquid, of camphoraceous odor, b. p. 148–149° at 10 mm.; yield 70%.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89. Found: C, 76.38; H, 7.76.

1 - Methyl - 6,7 - methylenedioxynaphthalene (IX).—Fusion of the tetralin (VIII) with sulfur gave such small yields of the expected naphthalene derivative (IX) that it could be satisfactorily characterized only by its *picrate*, which melted at 134–136°.

Anal. Calcd. for $C_{18}H_{13}O_9N_3$: N, 10.12. Found: N, 9.91.

Summary

Starting with ethyl piperonylideneacetate, the 1,1-dimethyl-6,7-methylenedioxytetralin has been synthesized by a series of steps analogous to those used by Bogert, Davidson and Apfelbaum[2c] for the preparation of ionene.

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