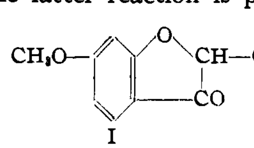
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

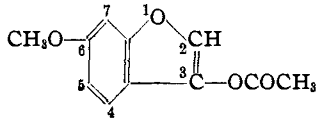
Derivatives of Coumaran. III. O-Acetylation of 6-Methoxycoumaran-3-one

BY R. L. SHRINER AND JOHN ANDERSON

In one of a series of experiments designed to cause aliphatic aldehydes and ketones to condense with 6-methoxycoumaran-3-one,[1] acetic anhydride was added as a reagent to take up the water formed in the reaction. A compound was isolated the analysis of which indicated that it was an acetyl derivative. The compound melted at 74–75°, however, whereas a previously recorded[2] melting point was 62°. It is evident that three acetyl derivatives are possible according to whether C-acylation (I), O-acylation (II) or acylation of the benzene ring (III) has taken place. The latter reaction is possible since the parent 6-methoxycoumaran-3-one is a resorcinol derivative and hence the 5-position should be substituted easily.



I



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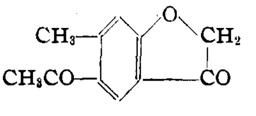
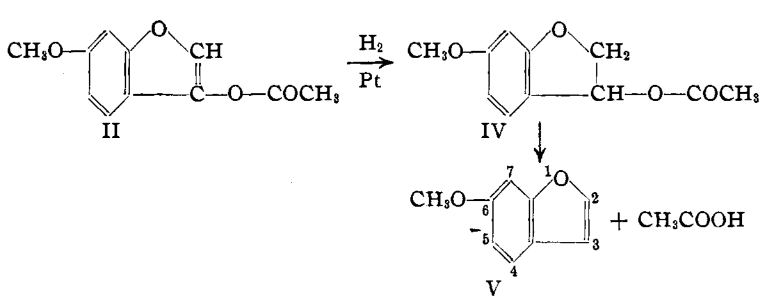


III

In the present work it has been shown that the compound melting at 74–75° produced by the action of acetic anhydride on 6-methoxycoumaran-3-one is the oxygen acetylated compound (II). Acid hydrolysis regenerated the parent coumaranone and an acetyl determination by the ester interchange method described by Phillips[3] gave the theoretical acetyl values. These observations eliminate the possibility of ring substitution, structure III, but do not distinguish between carbon (I) and oxygen (II) acylation since the product of one is a 1,3-diketone and of the other an ester. Both would be expected to hydrolyze in the presence of acids to yield acetic acid and the coumaranone.



Catalytic reduction[4] of the acetyl derivative (II) and subsequent distillation yielded acetic acid and 6-methoxybenzofuran[5] (V). The intermediate acetoxydihydrobenzofuran (IV) could not be isolated pure, since it lost acetic acid on distillation. Both the acetic acid and 6-methoxybenzofuran were isolated and identified by derivatives, the former as piperazonium diacetate[6] and the latter as the picrate previously described by Stoermer.[7] It is evident that neither structure I nor III could yield 6-methoxybenzofuran (V) and acetic acid and hence the acetylated coumaranone must be 3-acetoxy-6-methoxybenzofuran (II).

The formation of this acetyl derivative of the enol form is of interest since the parent coumaranone is entirely in the keto form. It gives no color with ferric chloride immediately. After the solution has stood several hours it turns red, indicating a slow tautomerization. Evidently the acetylation reaction shifted the equilibrium.

Experimental

3-Acetoxy-6-methoxybenzofuran.—A solution of 30 g. of 6-methoxycoumaran-3-one and 150 g. of acetic anhydride in 300 cc. of glacial acetic acid was heated to 100° for twenty-four hours. The reaction mixture was then poured into 2 liters of ice water. The product which separated was removed by filtration and recrystallized from ethanol. A 72% yield of light yellow plates was obtained. A second recrystallization from alcohol using Norite gave colorless crystals which melted at 74–75°. The mother liquors contained a mixture of unreacted coumaranone and the acetyl derivative. No compound melting at 62° could be isolated.[2]

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.08; H, 4.84. Found:

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[1] Shriner and Anderson, THIS JOURNAL, **60**, 1415 (1938).

[2] Sonn and Falkenheim, *Ber.*, **55B**, 2978 (1922). According to the numbering system in this paper the compound was denoted as O¹-acetyl-5-methoxy-(enol) coumaranone. The carbon atom attached to the benzene ring was numbered 1, and the oxygen 3. No proof of structure was given.

[3] Phillips, *Ind. Eng. Chem., Anal. Ed.*, **6**, 321 (1934).

[4] Roll and Adams, THIS JOURNAL, **53**, 3469 (1931).

[5] The revised numbering system adopted by *Chemical Abstracts* for use from 1937 onward makes the hetero-atom number 1. Accordingly benzofuran is numbered as shown in Formula V.

[6] Pollard, Adelson and Bain, THIS JOURNAL, **56**, 1759 (1934).

[7] Stoermer, *Ann.*, **312**, 335 (1900).

C, 64.02; H, 4.93. The percentage of acetyl groups was determined by the method of Phillips.[5] Calcd. for $C_{11}H_{10}O_4$: acetyl, 20.85. Found: acetyl, 21.30.

Acid Hydrolysis of 3-Acetoxy-6-methoxybenzofuran.—A solution of 0.5 g. of 3-acetoxy-6-methoxybenzofuran and 2 drops of concentrated sulfuric acid in 15 cc. of absolute ethanol was allowed to stand for three days with intermittent heating to boiling (3 times). At the end of this time, the solution was allowed to evaporate at room temperature until 0.2 g. of a crystalline substance was deposited. This substance melted at 108–110° but upon being recrystallized three times from ethanol melted at 118–119° and a mixed melting point with an authentic sample of 6-methoxycoumaran-3-one showed no depression.

Reduction of 3-Acetoxy-6-methoxybenzofuran.—A solution of 22 g. of 3-acetoxy-6-methoxybenzofuran in 70 cc. of absolute ethanol at 25° was reduced with hydrogen at a pressure of 2 to 3 atmospheres in the presence of 0.1 g. of platinum oxide catalyst. One mole of hydrogen was absorbed in two hours; the reduction mixture was then filtered and the solvent removed by distillation. The liquid residue distilled at 112° (10 mm.), but redistillation gave a main fraction boiling at 99–100° (10 mm.) with an appreciable forerun. The forerun proved to be mostly acetic acid and the main fraction proved to be 6-methoxybenzofuran which when purified by a third distillation gave the following constants: b. p. 99–100° (10 mm.), n^{25}_{D} 1.5620, d^{20}_{20} 1.1463; M_D calcd., 41.88; found, 41.76.

Anal. Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.53; H, 5.65.

The 6-methoxybenzofuran was further characterized as the picric acid addition compound which was prepared by allowing equimolar quantities of picric acid and 6-methoxybenzofuran to combine in alcoholic solution. Partial evaporation of the solvent at room temperature deposited the addition compound in large yellow needles which when recrystallized by taking up in alcohol and partially evaporating at room temperature gave yellow needles which melted at 64–65°, which is in agreement with the melting point given by Stoermer.[7]

A few drops of the forerun was treated on a watch glass with piperazine hexahydrate[6] and the salt which formed was recrystallized from *n*-butanol to give fine white needles which melted at 208°. A mixed melting point of this substance with an authentic sample of piperazonium diacetate showed no depression.

Test for the Enol Form of 6-Methoxycoumaran-3-one.—A dilute solution of 6-methoxycoumaran-3-one in 95% ethanol was treated with a few drops of 2% ferric chloride solution. The resulting solution was indistinguishable in color from a control solution until two hours had passed, when it appeared to be assuming a red tint. At the end of twelve hours the color had changed to deep red showing slow formation of the enol form.

Summary

Acetylation of 6-methoxycoumaran-3-one with acetic anhydride gave the acetyl derivative of the enol form. That this compound was the O-acetyl derivative was shown (a) by acid hydrolysis to regenerate the parent coumaranone and (b) by catalytic reduction to 3-acetoxy-6-methoxydihydrobenzofuran which lost acetic acid to produce 6-methoxybenzofuran.

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[CONTRIBUTION FROM THE EXPERIMENT STATION, HERCULES POWDER COMPANY]

The Resin Acids. The Action of Palladium on Abietic Acid

BY EDWIN R. LITTMANN

The recent publication of Fieser and Campbell[1] on dehydroabietic acid made it desirable to present our work on the behavior of abietic acid when treated with palladium. The action of palladium at high temperatures has been reported by Fleck and Palkin[2] and by the author,[3] and the present note discusses the preparation of the dehydroabietic acid of Fieser and Campbell by a different method and presents additional evidence on the disproportionation of abietic acid.

Investigations in this Laboratory on the action of a palladium catalyst on abietic acid and methyl abietate led to the isolation of dehydroabietic acid and its methyl ester which compounds appear to be identical with those reported by Fieser and Campbell and an acid which is probably tetrahydroabietic.

When methyl abietate was passed over a palladium catalyst, supported on activated alumina, at 230°, there was obtained on cooling a pasty mass of crystals which, after filtration, washing with methanol, and recrystallization from the same solvent, could be nitrated to give a dinitro derivative, corresponding by analysis to an ester of a dinitro acid of the dehydroabietic series. This nitro derivative was stable at its melting point and gave no tests for aliphatic nitro groups with aqueous alkali or sodium ethylate. On catalytic reduction in methanol solution over copper chromite, a diamino compound was obtained which could be diazotized

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[1] Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938).

[2] Fleck and Palkin, *ibid.*, **59**, 1593 (1937); **60**, 921 (1938).

[3] French Patent 801,470, May 23, 1936.