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

Derivatives of Coumaran. V. Synthesis of 4-Hydroxycoumaran-3-one

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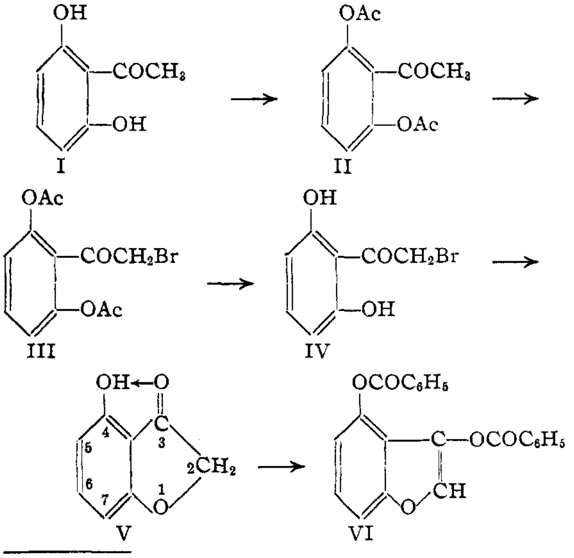
The synthesis of many substituted coumaranones has been accomplished by the reaction of phenols with α-halo acid chlorides[1] or with α-halonitriles.[2] These methods have proven useful for the synthesis of coumaranones with hydroxyl groups in the 6- and 7-positions. This paper reports the synthesis and properties of 4-hydroxycoumaran-3-one (V).

Acetylation of 2,6-dihydroxyacetophenone[3] (I) yielded the diacetoxy derivative (II).[4] When this 2,6-diacetoxyacetophenone was treated with bromine in carbon disulfide solution, substitution took place in the side chain giving an 80% yield of the monobromo compound (III). If 2,6-dihydroxyacetophenone is brominated without acetylation nuclear substitution takes place as well as side chain halogenation and a mixture is produced. If acetic acid is used instead of carbon bisulfide, a dibromo derivative is produced. Kröhnke[5] has pointed out that monohalo ketones are in equilibrium with dihalo ketones.

Hydrolysis of the 2,6-diacetoxy-α-bromoacetophenone with dilute hydrobromic acid yielded the 2,6-dihydroxy-α-bromoacetophenone (IV) which underwent ring closure upon treatment with sodium acetate to produce 4-hydroxycoumaran-3-one (V). Benzoylation by the Schotten–Bauman method yielded the dibenzoate, (VI). This is analogous to the oxygen acetylation of coumaran-3-ones previously reported.[6]



The physical properties of 4-hydroxycoumaran-3-one (V) are quite different from those of other monohydroxycoumaranones. It began to sublime at 85° and melted at 120°. 6-Hydroxycoumaran-3-one[7] melts at 243° and the 7-hydroxy isomer[8] at 184°. The 4-hydroxy isomer is also more soluble than the others. This suggests that the hydroxyl group is chelated with the carbonyl group as shown in Formula V. The chelated conjugated system in this structure is in agreement with the suggestion of Mills and Nixon[9] that the two carbon atoms common to the benzene ring and a five-membered ring are joined by a single bond.

Experimental

2,6-Diacetoxyacetophenone.[10]—A solution of 15 g. of 2,6-dihydroxyacetophenone[11] and 45 cc. of acetic anhydride was refluxed for five hours; then, while still hot, it was poured into ice water. A greenish oil separated which upon standing crystallized. The crude compound was recrystallized twice from isoamyl alcohol to give 19 g. of white platelets melting at 60° (corr.).

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.10. Found: C, 60.99; H, 5.47.

2,6-Diacetoxy-α-bromoacetophenone.—Four grams of 2,6-diacetoxyacetophenone was dissolved in 75 cc. of carbon disulfide and 2.8 g. of bromine dissolved in 25 cc. of carbon disulfide was added dropwise with stirring. The addition took one hour and sometimes heating was required to initiate the reaction. The reaction went to completion at room temperature. The carbon disulfide was then removed from the reaction mixture by distillation and the resulting crude brominated compound was twice recrystallized from isopropyl alcohol to give 4.3 g. (80%) of white crystals, m. p. 112° (corr.).

Anal. Calcd. for $C_{12}H_{11}O_5Br$: C, 45.71; H, 3.49; Br, 25.43. Found: C, 45.71; H, 3.60; Br, 25.30.

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(1) Auwers and Pohl, *Ann.*, **405**, 243, 294 (1914).

(2) Hoesch, *Ber.*, **48**, 1122 (1915).

(3) Baker, *J. Chem. Soc.*, 1953 (1934).

(4) Dattatraya, Balkrishna, Limaye and Gorind, *J. Ind. Chem. Soc.*, **12**, 788 (1935).

(5) Kröhnke, *Ber.*, **69**, 921–935 (1936).

(6) Shriner and Anderson, THIS JOURNAL, **60**, 1418 (1938).

(7) Brüll and Friedlaender, *Ber.*, **30**, 297 (1897).

(8) Mostmann and Tambor, *ibid.*, **49**, 1261 (1916).

(9) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(10) Dattatraya, Balkrishna, Limaye and Gorind, *J. Ind. Chem. Soc.*, **12**, 788 (1935), prepared this compound, but reported that they had to distil the above at 180° and 10 mm. and inferred that they had an oil. No mention of a solid was made by these authors although their compound analyzed correctly for C and H.

(11) This compound was prepared by modification of Baker's[3] method developed by Alfred Russell of the University of North Carolina. The details will be published by him.

2,6-Diacetoxy-α,α-dibromoacetophenone.—Four grams of 2,6-diacetoxyacetophenone was dissolved in 50 cc. of glacial acetic acid and 5.6 g. of bromine dissolve in 25 cc. of glacial acetic acid was added dropwise with stirring. The addition took one hour and sometimes heating was required to initiate the reaction which then continued to completion at room temperature. The reaction mixture was then poured into ice water with stirring and the crude brominated compound separated in greenish crystals. These were filtered and twice recrystallized from isopropyl alcohol to give 5.3 g. of white crystals which melted at 113° (corr.).

Anal. Calcd. for $C_{12}H_{10}O_5Br_2$: C, 36.54; H, 2.53; Br, 40.50. Found: C, 36.79; H, 2.66; Br, 39.82.

Both of the above halogen compounds gave an active halogen test by first heating with alcoholic sodium ethoxide solution, then testing the resulting solution after acidification with silver nitrate.

2,6-Dihydroxy-α-bromoacetophenone.—A mixture of 3 g. of 2,6-diacetoxy-α-bromoacetophenone, 80 cc. of 60% ethanol, 20 cc. of hydrobromic acid (40%) and 1 mg. of sodium hydrosulfite was refluxed for one hour. The solvent was then distilled at 30° and 30 mm. pressure to leave yellow platelets which were recrystallized twice from benzene to give a yield of 1.6 g. It melted at 143° (corr). This compound gave a green ferric chloride test.

Anal. Calcd. for $C_8H_7O_3Br$: C, 41.55; H, 3.03. Found: C, 41.84; H, 2.99.

4-Hydroxycoumaran-3-one.—A solution of 1 g. of 2,6-dihydroxy-α-bromoacetophenone, 1 g. of sodium acetate trihydrate, 1 mg. of sodium hydrosulfite and 50 cc. of ethanol was refluxed for one hour. Twenty cubic centimeters of water was added and 30 cc. of ethanol was distilled from the reaction mixture. The resulting solution was allowed to cool and placed in a refrigerator overnight. Brown crystals separated and were filtered and recrystallized twice from high boiling petroleum ether to give 0.4 g. of brown granular crystals. This compound began subliming at 85° and finally melted at 120° (corr.). It gave a violet ferric chloride test for phenols.

Anal. Calcd. for $C_8H_6O_3$: C, 64.00; H, 4.00. Found: C, 64.21; H, 4.17.

In this last reaction a few milligrams of sodium hydrosulfite was added to the reaction mixture to minimize oxidation of the rather unstable 2,6-dihydroxy-α-bromoacetophenone.

3,4-Dibenzoxybenzofuran.—A solution of 0.5 g. of 4-hydroxycoumaran-3-one, 1 g. of benzoyl chloride, 1 g. of sodium carbonate, 10 cc. of water and 15 cc. of acetone was warmed gently for thrity minutes, then poured into ice water. The benzoylated compound separated and was filtered. It was recrystallized from ethyl acetate to give 1.0 g. of colorless needles; m. p. 183° (corr.).

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 73.74; H, 3.91. Found: C, 73.47; H, 4.03.

Summary

4-Hydroxycoumaran-3-one has been synthesized by the following sequence: 2,6-dihydroxyacetophenone $\longrightarrow$ 2,6-diacetoxyacetophenone $\longrightarrow$ 2,6-diacetoxy-α-bromoacetophenone $\longrightarrow$ 2,6-dihydroxy-α-bromoacetophenone $\longrightarrow$ 4-hydroxycoumaran-3-one. The low melting point and tendency to sublime exhibited by this compound indicate that the hydroxyl group is probably chelated with the carbonyl group.

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Electrical Properties of Solids. IV.* The Influence of Thermal History on Polyvinyl Chloride Plastics

BY RAYMOND M. FUOSS

I. Introduction.—Plastics containing polyvinyl chloride have two characteristics which sharply differentiate them from most of the systems ordinarily studied by physico-chemical methods: the electrical properties of a given sample depend on the method of preparing the sample[1] and, after preparation, the properties of a given sample change with time. Obviously the influence of the corresponding variables must be eliminated before any correlation between properties and chemical composition and structure is attempted. The most important item in the preparation of the sample is the thermal history; two samples of the same composition with identical thermal histories will give results which check as precisely as might be desired (assuming that trivial variables, such as those due to surface effects and humidity, are eliminated).[2]

The changes with time are of at least two kinds: (1) a slow decrease of dielectric constant, amounting to several per cent., while the density remains constant and (2) a slow increase of d. c. conductance, which in turn induces an increase in dielectric constant and a. c. absorption. These two effects combine to produce a minimum in the dielectric constant–time curve.

It is the purpose of this paper to present and

(*) Paper III, THIS JOURNAL, **60**, 456 (1938).

(1) Fuoss, *Trans. Electrochem. Soc.*, **74**, 91 (1938).

(2) Fuoss, THIS JOURNAL, **59**, 1703 (1937).