TABLE IV. ACETATES OF THE HYDROXYCOUMARINS OF I_{A-K} SERIES

No.	Coumarin used	M.p., °C.	Empirical formula	Calcd. Found Carbon	Hydrogen	Chlorine
II_A	4-Phenyl-5,7-dihydroxycoumarin	186.5–187	$C_{19}H_{14}O_6$	67.45	4.17	
				67.67	4.25	
II_B	4-Phenyl-7-hydroxy-8-methylcoumarin	188–188.5	$C_{18}H_{14}O_4$	73.45	4.79	
				73.17	4.50	
II_C	4,8-Dimethyl-7-hydroxycoumarin	138–139	$C_{13}H_{12}O_4$	67.23	5.20	
				67.16	5.36	
II_D	4-Phenyl-7-hydroxycoumarin	124–125	$C_{17}H_{12}O_4$	72.85	4.31	
				72.93	4.40	
II_E	4-Methyl-7-hydroxycoumarin	153–154[a]	$C_{12}H_{10}O_4$	66.05	4.61	
				66.20	4.57	
II_F	4-Phenyl-5-hydroxy-7-methylcoumarin	154–155	$C_{18}H_{14}O_4$	73.45	4.79	
				73.58	4.78	
II_G	4-Phenyl-6-chloro-7-hydroxycoumarin	169–170[b]	$C_{17}H_{11}ClO_4$	64.87	3.52	11.26
				64.90	3.70	11.13
II_H	4-Methyl-6-chloro-7-hydroxycoumarin	168–169	$C_{12}H_9ClO_4$	57.04	3.59	14.03
				56.91	3.43	14.02
II_I	4-Phenyl-7,8-dihydroxycoumarin	125–126	$C_{19}H_{14}O_6$	67.45	4.17	
				67.44	4.16	
II_J	3-Chloro-4,8-dimethyl-7-hydroxycoumarin	192	$C_{13}H_{11}ClO_4$	58.54	4.15	13.29
				58.63	4.30	13.14

[a] M.p. lit.,[7] 150°. [b] M.p. lit.,[8] 168°.

Experimental[9]

Synthesis of the Coumarin.—A mixture consisting of 0.1 mole of phenol, 0.1 mole of the β-keto ester, and 25 ml. of trifluoroacetic acid was refluxed for different periods of time (see Table I). At the termination of the reflux period the mixture was poured into about 300 ml. of cold water. The precipitate was filtered, with suction, and the solid was dried in air to give the crude yields given in Table I. The compounds were freed of water by dehydrating them in benzene in a reflux assembly fitted with a Dean and Stark water take-off. The dry compounds were purified by taking them up in dry ethyl acetate, filtering, and then precipitating them with heptane. This process was repeated a second or third time until a uniform product with a constant melting point was obtained.

Preparation of Coumarin Acetates.—The acetates of the coumarins were prepared in the usual manner from acetic anhydride, poured into water, chilled, filtered, and dried in air. The compounds were purified by recrystallizing them twice from boiling heptane. Compound II_J was recrystallized first from ethanol, then from heptane.

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A Practical Oxidation of Nitromesitylene

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3,5-Dimethyl-4-nitrobenzaldehyde.—Previously 3,5-dimethyl-4-nitrobenzaldehyde was available only in very low yield by chromyl chloride oxidation of nitromesitylene.[1] In this case, the isomeric aldehyde, 2-nitro-3,5-dimethylbenzaldehyde, and sizeable amounts of the higher oxidized acids were formed in addition to the desired compound.

We have adopted a similar procedure used in oxidizing p-nitrotoluene[2] to p-nitrobenzaldehyde for our purpose of preparing the 4-nitro-3,5-dimethylbenzaldehyde from nitromesitylene. This procedure involves oxidation by chromium trioxide in glacial acetic acid and acetic anhydride at salt–ice-bath temperatures. Higher temperatures cause undesirable oxidation.

With this procedure, we found preferential oxidation of the methyl group *para* to the nitro group. From our data (see Experimental) it seems apparent that the isomeric compound is not formed in any appreciable amount. It was also possible to isolate minute amounts of 4-nitro-3,5-dimethylbenzoic acid.[3]

The diacetate obtained from the oxidation was easily converted in excellent yields to 4-nitro-3,5-dimethylbenzaldehyde by hydrolysis with dilute sulfuric acid.[2]

Experimental

Nitromesitylene[4] was prepared.[5] The infrared spectrum[6] gave bands at $\lambda^{\text{Nujol}}_{\text{max}}$ 6.60 (nitro NO_2) and 7.35 μ (nitro NO_2).

Diacetate of 4-Nitro-3,5-dimethylbenzaldehyde.—In a 150-ml. flask, cooled to −5 to 0°, was added 38 g. of glacial acetic acid and 41 g. of acetic anhydride, and 4 g. of nitromesitylene. This solution was stirred vigorously.

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(2) S. V. Lieberman and R. Conner, "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, New York, 1959, p. 441.

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(4) The authors would like to thank Mr. Robert Temple for preparing this compound.

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(6) Infrared spectra were done with a Perkin-Elmer Model 137 Infracord.

To this solution, 5.6 ml. of concentrated sulfuric acid was added slowly; then 6.72 g. of chromium trioxide (U.S.P.) was added slowly, so that there was no rise in temperature. The addition took about 45 to 60 min. After an additional stirring of 10 min., the contents were poured into 400 ml. of ice water. The solid material was filtered off and washed with cold water until the washings were colorless. The product was suspended in 35 ml. of cold 5% solution of sodium bicarbonate and stirred. After thoroughly mixing, the solid was collected on a filter and washed with cold water. The product was dried in a vacuum desiccator. The crude yield was 3.10 g. (72.6%), and the melting point was 123–125°. From the reaction mixture, some unreacted starting material can be recovered.

The crude product can be used without further purification. When recrystallized from aqueous ethanol, the diacetate melted at 126°.[7]

The infrared spectrum gave bands at $\lambda_{\max}^{\text{Nujol}}$ 5.72 (acetate C=O), 6.58 (nitro NO_2), 7.32 (nitro NO_2), and 8.10 μ (acetate C—O).

Anal. Calcd. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.37. Found: C, 55.79; H, 5.38.

The sodium bicarbonate solution was acidified and upon extraction with ether yielded 0.35 g. of 4-nitro-3,5-dimethylbenzoic acid; the melting point of which was 223°.[3]

The infrared spectrum was typical of aromatic carboxylic acids with broad O—H absorption and a strong carbonyl peak at 5.92 μ (Nujol mull).

4-Nitro-3,5-dimethylbenzaldehyde.—To 3 ml. of water and 0.2 ml. of concentrated sulfuric acid in 3 ml. of ethanol, was added 1 g. of diacetate. This mixture was refluxed for 2.5 hr. (shorter times lead to incomplete hydrolysis). The solution was filtered hot and chilled in an ice bath. Sometimes the product would oil out and it was necessary to extract the organic material with ether and recrystallize from aqueous ethanol. Concentration of the mother liquor yields additional product, both of which melted sharply at 50.0–50.5°, while the literature value is 42–44°.[1] The two crops of crystals gave 0.69 g. of aldehyde. The semicarbozone was prepared and it melted at 209–210°. The literature value is 210–211°.[1]

The infrared spectrum gave bands at $\lambda_{\max}^{\text{Nujol}}$ 3.66 (carbonyl H—C=O), and 5.87 μ (carbonyl C=O).

The 2,4-dinitrophenylhydrazine was prepared which decomposed at 256–258°.

Anal. Calcd. for $C_{15}H_{13}N_5O_6$: N, 19.49. Found: N, 19.28.

The retention time of the 4-nitro-3,5-dimethylbenzaldehyde on a Perkin-Elmer 154-D vapor phase fractometer was 7.88 min. No other peaks were obtained. The conditions were the following: column pressure 20, flow rate 8.5, carrier gas He, temperature 170°, voltage 7.8, and the column used was a Perkin-Elmer O type.

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[7] All melting points were taken on a Hershberg melting point apparatus and are corrected.

Studies of the Kolbe Electrolytic Synthesis. II. The Preparation of Trialkylacetic Esters and Acids[1]

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Methods for the preparation of trialkylacetic acids include carbonation of Grignard reagents,[2,3] alkylation of esters, ketones, and nitriles,[4–8] hydrogenation of alkenyldialkylacetic esters,[9,10] reaction of carbon monoxide under pressure or *in situ* with olefins, alcohols, alkyl chlorides, or esters,[11] oxidation of ketones and olefins,[12,13] and rearrangement of α-*t*-bromo ketones.[14] These methods often suffer from the disadvantages of involving multistep procedures, difficultly hydrolyzable intermediates, *e.g.* trialkylacetonitriles, and tedious purification processes.

In this paper, the Kolbe electrolysis of a mixture of a dialkylmalonic half ester and a monocarboxylic acid has been studied in order to see if it might offer a convenient alternative to the above methods.[15] There is only one previous report of such a synthesis, namely the preparation of ethyl triisoamylacetate from monoethyl diisoamylmalonate and isocaproic acid.[16] A few trialkylacetonitriles have also been prepared by co-electrolysis of dialkylcyanoacetic acids and fatty acids,[16,17] but the difficulty encountered in hydrolyzing the nitriles makes this method less attractive.

Table I, column 4 gives yields of a number of trialkylacetic esters prepared according to the Kolbe method. Boiling points, refractive indices, and densities are not reported since analyses indicated that transesterification occurred to a considerable extent in most cases. This has also been observed in the preparation of dialkyl- and tetraalkylsuccinic esters by the Kolbe method.[18] The yields of trialkylacetic esters are low or moderate,

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