61 g. (63%) of light yellow liquid, b.p. 100–102° (0.35 mm.), was obtained.

*Anal.* Calcd. for $C_9H_7NO_2S$: C, 55.94; H, 3.65; S, 16.59. Found: C, 56.02; H, 3.81; S, 16.25.

**Methyl 1-Aziridinylthiocarbamoylanthranilate (V).**—To 18.1 g. (0.10 mole) of IV in 50 ml. of ether was added dropwise, with efficient stirring and ice-bath cooling, 4.5 g. (0.105 mole) of freshly distilled ethyleneimine (b.p. 55–56°). The temperature was kept at 25–30°. A crystalline solid separated during the addition; this was collected and air-dried. The yield was 21 g. (94%) m.p. 88.5–89.5°. An analytical sample was prepared by reprecipitation from methylene chloride with *n*-hexane. The melting point was unchanged.

*Anal.* Calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; S, 13.57. Found: C, 55.69; H, 5.39; S, 13.59.

**Rearrangement of V to 2,3-Dihydrothiazolo[2,3-*b*]quinazolin-5-one (I).**—Two grams of V was refluxed for 0.5 hr. in 10 ml. of concentrated hydrochloric acid. The yellow solution was cooled and added with cooling to 30 ml. of 10% aqueous sodium hydroxide. The pale yellow product was collected and recrystallized from 100 ml. of water. The yield of colorless needles, m.p. 156–157°, was 0.3 g. (16%). The infrared spectrum and mixed melting point of the product were identical to I prepared from III and ethylene bromide.

## A New One-Step Synthesis of Substituted Coumarins

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In a recent publication[2] we have shown that esters and carboxylic acids would react with pyrone phenols in the presence of trifluoroacetic acid. In adapting the method to benzenoid phenols we were of the opinion that flavones would have been formed; however, in every case cited in this report only coumarins were obtained.

Experiments on a large number of phenols with β-keto esters in the presence of trifluoroacetic acid has made very evident certain limitations of the reaction. Phenol, catechol, 4,6-dichlororesorcinol, cresols and hydroquinone all failed to give the reaction. It is quite apparent from the experimental results that a compound must have nucleophilic substituent groups distributed around the periphery of the ring in such a manner that the β-keto ester may displace a ring proton activated by the COMBINED *ortho* effect of one of the nucleophilic groups and the *para* effect of the other nucleophilic group. One of these groups must be phenolic. An alkyl group is not strong enough, when there are only two substituents on the ring, to furnish the needed activation; however, when an alkyl group is one of three activating groups, as in the case of orcinol, distributed alternately around the ring it does appear to have some activating effect.

Situation of the hydroxyls or other nucleophilic groups 1,3 from each other in order to obtain the combined *ortho* and *para* activating effects, never results in an attack by the ester in the position between the groups. Blocking of the position between the groups with a methyl, as in the case of 2-methylresorcinol, or with a hydroxyl, as in the case of pyrogallol, enhances the reactivity of the phenol, rather than inhibits the reaction. Blocking one of the positions *para* to the groups, as in the case of 4-chlororesorcinol, results in lowered yields and blocking both positions *para* to the nucleophilic groups, as in the case of 2,6-dichlororesorcinol, completely inhibits an attack by the β-keto ester.

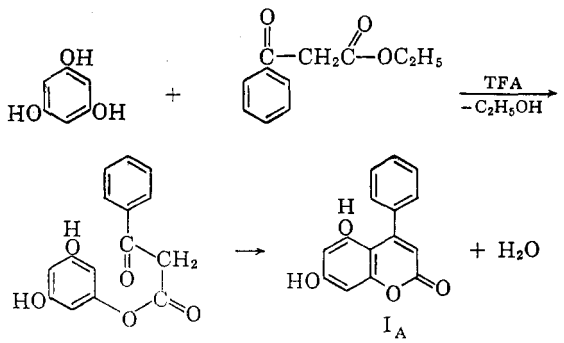
The physical properties of the coumarins produced by the series are described in Table I and the probable course of the reaction for their formation is depicted in Chart I using compound $I_A$ as the example.

Coumarins, as a rule, give three major absorption maxima in the region of 200–350 mμ. All of the coumarins listed in Table II show this characteristic behavior except $I_K$ which gives its third maximum beyond 350. The infrared absorption bands on all the coumarins (Table III) are either characteristic or give expected values as dictated by the nature and number of their substituents.

Compound $I_I$ is the only substance of the series which was not converted into the anhydrous condition due to the fact that it was completely soluble in benzene and prolonged refluxing of the substance caused the formation of dark impurities. The observed fluorescence pattern of the coumarins agrees with the observations made by Elderfield.[3]

The acetates of all the hydroxycoumarins are given in Table IV as members of the $II_{A-J}$ series.

Not included among the list of the coumarins synthesized are 4-methyl-5,7-dihydroxycoumarin




$I_A$

CHART I

(1) The person to whom all communications concerning this contribution should be directed.

(2) L. L. Woods, *J. Org. Chem.*, **27**, 696 (1962).

(3) R. C. Elderfield, "Heterocyclic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 193.

TABLE I
COUMARINS

| No. | Phenol used | Ester used | Crude yield, % | Reflux time, hr. | M.p., °C. | Empirical formula | Calcd. Carbon | Calcd. Hydrogen | Found Carbon | Found Hydrogen | Calcd. Chlorine | Found Chlorine |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $I_A$ | Phloroglucinol | Ethyl benzoylacetate | 85 | 2 | 246–247[a] | $C_{15}H_{10}O_4$ | 70.86 | 3.96 | 70.85 | 4.10 | | |
| $I_B$ | 2-Methylresorcinol | Ethyl benzoylacetate | 100 | 0.5 | 285 | $C_{16}H_{12}O_3$ | 76.17 | 4.79 | 75.94 | 4.95 | | |
| $I_C$ | 2-Methylresorcinol | Ethyl acetoacetate | 100 | 0.25 | 265–266 | $C_{11}H_{10}O_3$ | 69.44 | 5.29 | 69.47 | 5.13 | | |
| $I_D$ | Resorcinol | Ethyl benzoylacetate | 86 | 20 | 256.5–257 | $C_{15}H_{10}O_3$ | 75.62 | 4.23 | 75.43 | 4.19 | | |
| $I_E$ | Resorcinol | Ethyl acetoacetate | 91 | 20 | 194–195[b] | $C_{10}H_8O_3$ | 68.17 | 4.57 | 68.11 | 4.58 | | |
| $I_F$ | Orcinol | Ethyl benzoylacetate | 30 | 20 | 226 | $C_{16}H_{12}O_3$ | 76.17 | 4.79 | 75.94 | 4.73 | | |
| $I_G$ | 4-Chlororesorcinol | Ethyl benzoylacetate | 66 | 20 | 281[c] | $C_{15}H_9ClO_3$ | 66.06 | 3.32 | 65.91 | 3.51 | 13.00 | 13.28 |
| $I_H$ | 4-Chlororesorcinol | Ethyl acetoacetate | 57 | 20 | 285–286 | $C_{10}H_8ClO_3$ | 56.75 | 3.81 | 56.89 | 3.65 | 16.75 | 16.56 |
| $I_I$ | Pyrogallol | Ethyl benzoylacetate | 80 | 5 | 195–197 | $C_{15}H_{10}O\cdot H_2O$ | 66.17 | 4.44 | 66.11 | 4.50 | | |
| $I_J$ | 2-Methylresorcinol | Chloroethyl acetoacetate | 100 | 0.5 | 285.5–286.5 | $C_{11}H_9ClO_4$ | 58.81 | 4.03 | 58.73 | 3.97 | 15.78 | 15.73 |
| $I_K$ | 3-Hydroxydiphenyl amine | Ethyl benzoylacetate | 100 | 3 | 184–185 | $C_{21}H_{15}NO_2$ | 80.49 | 4.82 | 80.21 | 4.79 | | |

Nitrogen—Calcd.: 4.47; Found: 4.52

[a] M.p. lit.,[6] 235–237° from hydrogen iodide treatment of ether and would be expected to be lower than a very pure sample. [b] M.p. lit.,[7] 185–186°; however, a sample of β-methylumbelliferone (Eastman White Label) recrystallized once by our method, m.p. 194°. A mixture m.p. with the authentic sample, m.p. 194–194.5°. [c] M.p. lit.,[8] 280°.

from the reaction of phloroglucinol with ethyl acetate, a compound which has been prepared previously[4] but for which no melting point is given,

TABLE II
ULTRAVIOLET ABSORPTION AND FLUORESCENCE DATA[a]

| Coumarin used | Absorption maxima range 200–350 mμ | Fluorescence |
|---|---|---|
| $I_A$[b] | 225.5, 259.5, 336 | None |
| $I_B$ | 220, 244, 332.5 | Greenish yellow |
| $I_C$ | 221, 254, 324 | Pale blue |
| $I_D$ | 237, 257, 330 | None |
| $I_E$ | 221, 251, 322.5 | Blue-strong |
| $I_F$ | 222, 256, 329 | None |
| $I_G$ | 228, 259, 334.5 | None |
| $I_H$ | 226, 291, 328 | Blue-strong |
| $I_I$ | 224, 261.5, 322 | None |
| $I_J$ | 223, 258, 333 | Green-pale |
| $I_K$ | 218, 274, beyond 350 | Blue-green in ethylacetate |
| Coumarin | 218, 274.5, 310.5 | None |

[a] Spectra were determined on a Bausch and Lomb-505 in spectro grade methanol; fluorescence was ascertained on water–alcohol mixtures. [b] Compound $I_A$ gives a violet coloration with 1% solution of tetracyanoethylene in ethyl acetate.

and 4,5,7-trihydroxycoumarin from the reaction of phloroglucinol with diethyl malonate. These two compounds gave poor analyses but their acetates gave excellent analyses. 4,5,7-Trihydroxycoumarin has been synthesized previously by Sonn[5] who describes an inconsistency in the melting point, an inconsistency encountered, also, in our work.

TABLE III
SIGNIFICANT INFRARED ABSORPTION BANDS[a] IN CM.$^{-1}$ FROM KBr PELLET

$I_A$—3155, 1613, 1590-B, 1543-SH, 1361, 1290, 1233, 1140, 1074
$I_B$—3322, 1681, 1587, 1553, 1351, 1299, 1085
$I_C$—3195, 1678, 1603, 1567, 1377, 1361, 1330, 1087
$I_D$—3413, 3067, 1681, 1582, 1437, 1372, 1261, 1235, 1148, 1105
$I_E$—3448-SH, 3077-VB, 1667, 1592, 1385, 1267, 1156, 1130, 1066
$I_F$—3125, 1678, 1613, 1587, 1502, 1412, 1372, 1333, 1279, 1235, 1200, 1160, 1086
$I_G$—3145, 1692, 1613, 1587-SH, 1538, 1441, 1414, 1377, 1250-B, 1218, 1185, 1145
$I_H$—3077, 1667, 1592, 1383, 1359, 1266, 1220, 1157
$I_I$—3125-VB, 1600-B, 1493, 1403, 1292, 1160-B, 1040, 1008
$I_J$—3226, 1686, 1600, 1548, 1493, 1370, 1342, 1300, 1096
$I_K$—3289, 1686, 1618, 1592, 1493, 1376, 1344, 1239, 1121, 855, 840

[a] B, broad; VB, very broad; SH, shoulder.

(4) S. M. Sethna, *J. Univ. Bombay*, **9**, pt. 2, 104 (1940) [*Chem. Abstr.*, **35**, 6948 (1941)].

(5) A. Sonn, *Ber.*, **50**, 1292 (1917).

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

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

**Acknowledgment.**—The authors express their gratitude to the Robert A. Welch Foundation for support of this project.

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(7) H. Von Pechmann and C. Duisberg, *Ber.*, **16**, 2122 (1883).

(8) D. Chakravarti and B. Ghosh, *J. Indian Chem. Soc.*, **12**, 622 (1935).

(9) Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and all melting points were taken in duplicate on paired Fisher-Johns melting point blocks.

## 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 $\lambda_{max}^{Nujol}$ 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.

(1) K. V. Steiner and E. Sorkin, *Helv. Chem. Acta*, **35**, 2486 (1952).

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

(3) O. Jacobsen, *Ber.*, **11**, 2054 (1879).

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

(5) G. Powell and F. R. Johnsen, "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, New York, 1949, p. 449.

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