[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Rearrangement of 2-Acetyl- and 2-Benzoylcoumarone Oxime *p*-Toluenesulfonates

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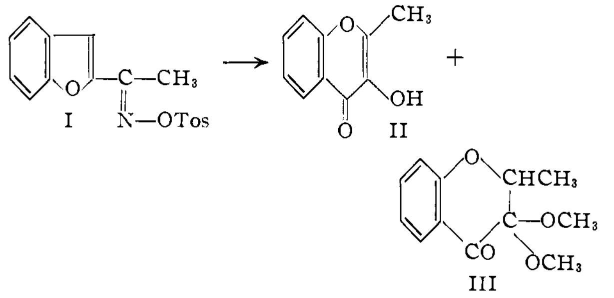
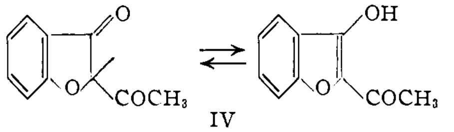
The reported rearrangement of the tosylate of 2-acetylcoumarone oxime to 2-methylchromonol-3 has been confirmed. A structure for the "acetal" formed in the reaction has been proposed. The rearrangement of 2-benzoylcoumarone oxime tosylate yields flavonol and 2-benzoylcoumaranone-3. New syntheses have been described for 2-acylcoumaronones; and 3-acetylcoumaranone-2 has been described for the first time, correcting an earlier report of its preparation by Pfeiffer and Enders.

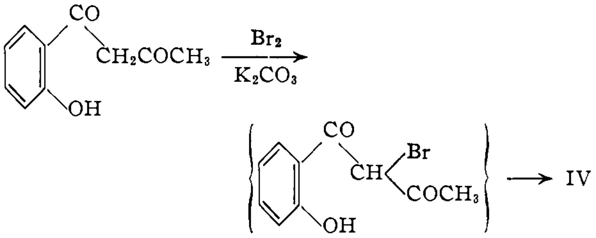
The reported formation of 2-methyl-3-hydroxychromone (II) from the tosyl derivative of 2-acetylcoumarone oxime (I)[1] was of considerable interest, since it suggests a new method of synthesis of 3-chromonols, a class of compounds for which convenient synthetic methods are not abundant.[2] There were, however, reasons for the re-examination of this transformation: the route proposed[1] for the rearrangement was highly unlikely, and because of this and a synthesis of II that was not unambiguous, it was regarded as possible that the so-called chromonol was in fact the coumaranone IV. Moreover, the properties of another product of the reaction were not in accord with the structure (III) assigned to it.[3]


I II III

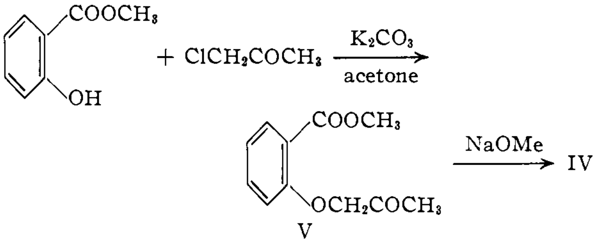

IV

Since II and IV are isomeric, would be expected to have properties qualitatively similar and were previously unknown substances, the synthesis of II by Vargha, *et al.*, could not be regarded as a structure proof of the compound in question. There is ample analogy for the formation of 2-acylcoumaranones as well as chromonols by the reaction of ω-halo-*o*-hydroxyacetophenones under conditions similar to those used by Vargha for the preparation of II from 2-bromoacetylphenol.[4] It was necessary, therefore, to synthesize II and IV by methods that left no doubt as to their structures.

2-Acetylcoumaranone (IV) was prepared in two ways. The most convenient synthesis consisted in the bromination of 2-acetoacetylphenol (V) in chloroform in the presence of potassium carbonate

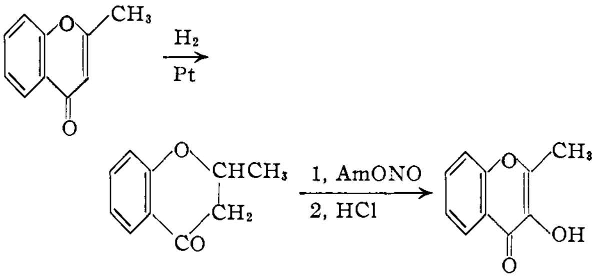


In another synthesis it was planned to prepare V by the alkylation of methyl salicylate with chloroacetone, and to cyclize V to IV under the conditions of the Dieckmann condensation


V

It was found that the product of the reaction of methyl salicylate with chloroacetone in the presence of potassium carbonate was IV; presumably the ring closure of V proceeded under the conditions of the first stage of the reaction. Since the formation of IV under these conditions is ambiguous,[5] the route from 2-acetoacetylphenol was used and was found to lead to the same compound.

2-Acetylcoumaranone-3 was not identical with the compound obtained from the oxime tosylate I, indicating that the chromonol II is indeed the


II

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[1] L. Vargha, J. Ramonczai and J. Bathory, THIS JOURNAL, **71**, 2652 (1949).

[2] See S. Wawzonek in R. C. Elderfield, "Heterocyclic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1951.

[3] In addition to II and the compound formulated as III, isocoumaranone, the expected ultimate product of a conventional Beckmann rearrangement also was formed.

[4] For example, J. Allan and R. Robinson, *J. Chem. Soc.*, **125**, 2192 (1924); G. H. Jones, J. B. D. McKenzie, A. Robertson and W. B. Whalley, *ibid.*, **562**, (1949); W. Baker, *ibid.*, 1381 (1933); 1370 (1940); K. von Auwers, *Ber.*, **43**, 2192 (1910); **45**, 976 (1912); **47**, 3292 (1914).

[5] Since V was not isolated, the possibility existed that the reaction had taken a course different from that anticipated; and among the possible alternative routes is one which could have led to the formation of the chromonol II.

product of the rearrangement. This was established by the synthesis of II by the following route, which is a modification of the long-known flavonol synthesis of Kostanecki.[2] The chromonol II prepared in this way was identical with the product of the rearrangement of I.

A final confirmation of the structures of II and IV was obtained by a comparison of the absorption spectra of the chromonol, the acetylcoumaranone, their respective acetates, chromone and 2-acetylcoumarone (Table I). It is apparent that, when the auxochromic effects of the hydroxyl groups of II and IV are destroyed by acetylation, the spectra of the resulting acetates resemble closely those of the chromone and coumarone, respectively.

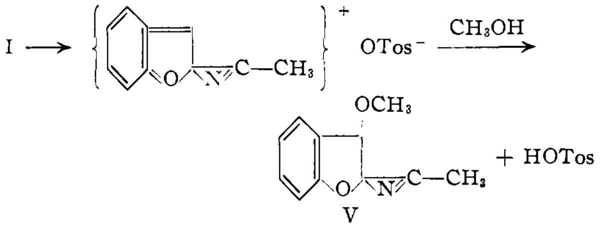
TABLE I

ABSORPTION SPECTRA OF II, IV AND RELATED COMPOUNDS

Compound, R	$\lambda_{\max}$	log ϵ	$\lambda_{\min.}$	log ϵ	$\lambda_{\max}$	log ϵ
			2-Acetyl-3-R-coumarone			
OH	307	4.30	262	3.42	236	3.93
OAc	297	4.24	247	3.40	231	3.94
H	295	4.31	246	3.17	230sh	3.80
					225	3.85
			2-Methyl-3-R-chromone			
OH	318	3.94	293	3.64	281	3.75
			262	3.59		
OAc	301	3.90	279	3.51		
H	298	3.84	276	3.47		

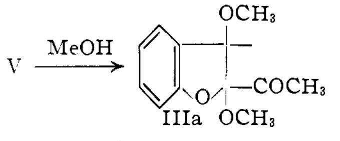
Following the demonstration that the chromonol, and not the acetylcoumaranone, is indeed formed from I, it was necessary to re-examine the formulation of the rearrangement of I, and to study the "acetal" III which is one of the products of the rearrangement.

It appeared at once that the initial change undergone by I was probably allied to the Neber reaction,[6] and involved a displacement of the solvated tosyloxy anion by the 2,3-double bond of the coumarone ring:

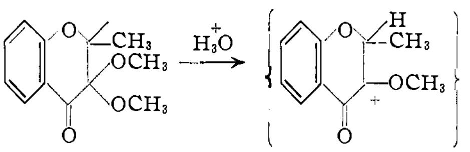


V

The subsequent transformation of the intermediate V is discussed in the sequel, but it was regarded as possible that one of the products of its methanolysis was the "acetal" of the structure IIIa



It was soon found that III cannot represent the structure of this compound. That it was the acetal III appeared unlikely at the outset, since it is very stable to boiling aqueous acid, an observation of Vargha's that was confirmed in the present study. (It should be remarked, however, that even a compound such as III could possess a high degree of acid stability since the expected course of hydrolysis, through a step III → VI would involve a transition through a carbonium ion which, despite its stabilization by the resonance contribution of the ether oxygen, has the carbonyl group in the energetically very unfavorable position adjacent to the carbonium carbon atom.)

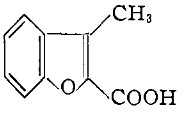


III VI

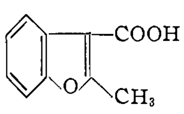
The absorption spectrum of the "acetal" was found to bear a very close resemblance to that of *o*-cresol, and lacked the intense absorption band at $\lambda_{\max}$ 306 mμ that characterizes *o*-methoxyacetophenone, and that III should possess. Indeed, the absorption spectrum was quite in accord with what would be expected for the coumarane derivative IIIa. To these results was added the observation that the oxime of the "acetal" showed an absorption spectrum almost identical with that of the "acetal" itself. It is clear from these observations that the carbonyl group of the "acetal" is isolated from the aromatic nucleus.

Attempts to demonstrate the presence of an acetyl group failed: the "acetal" did not give iodoform, nor did it form a benzal derivative. Attempts to degrade it to a recognizable product by reduction with lithium aluminum hydride and subsequent hydrolysis were unsuccessful. These experiments strongly suggested that the "acetal" did not possess structure IIIa, but gave no clue to its nature.

When the "acetal" was heated with 48% hydrobromic acid, there was formed a crystalline acid, $C_{10}H_8O_3$, m.p. 189–190°. The compound possessed one C-methyl group, and titrated sharply as a monobasic acid. It could be regarded only as one of the following two compounds (VII and VIII)



VII



VIII

The acid VII has been reported[7–9] to have m.p. 188–189°. A sample of VII, prepared by the method of Tanaka,[9] melted at 188–189° but strongly depressed the melting point of the acid derived from the acetal.

That the degradation product had the structure VIII appeared to be ruled out by the fact that the acid VIII was reported by Pfeiffer and Enders[10] to have m.p. 135–136°. Since the absorption spectrum of the new acid resembled that of coumarone itself (and was markedly different from that of VII), it appeared that our degradation product

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(6) P. W. Neber and co-workers, *Ann.*, **449**, 109 (1926); **467**, 52 (1926); **493**, 281 (1932); **515**, 283 (1935); **526**, 277 (1936). See also D. J. Cram and M. J. Hatch, THIS JOURNAL, **75**, 33, 38 (1953).

(7) A. Hantzsch, *Ber.*, **19**, 1292 (1886).

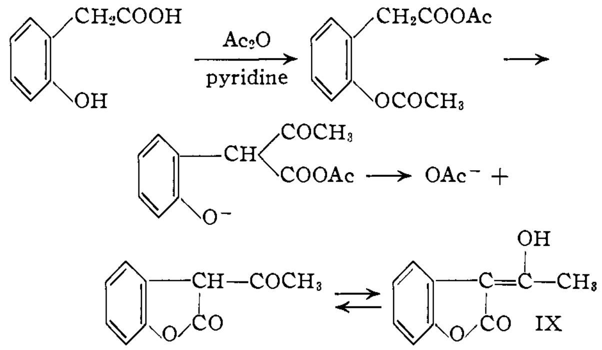
(8) F. Peters and H. Simonis, *ibid.*, **41**, 832 (1908).

(9) S. Tanaka, THIS JOURNAL, **73**, 872 (1951).

(10) P. Pfeiffer and E. Enders, *Ber.*, **84**, 247 (1951).

was indeed VIII and that the compound described by Pfeiffer and Enders possessed another structure.

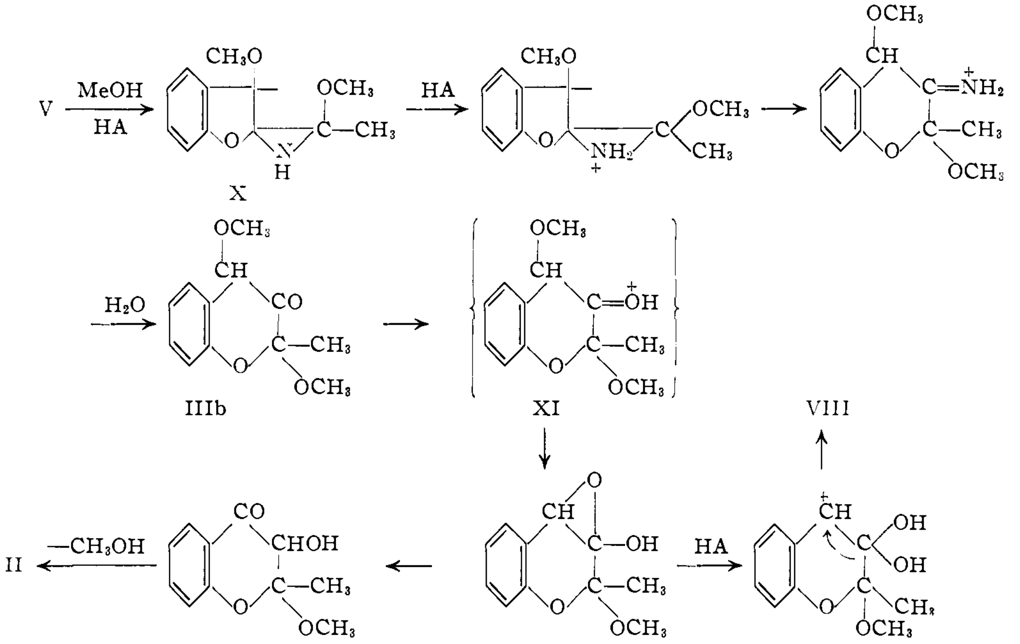
When *o*-hydroxyphenylacetic acid was treated with acetic anhydride and pyridine according to the directions of Pfeiffer and Enders, the bicarbonate-soluble "acid" described by these workers (m.p. 133–134°) was obtained. It was found to give a deep blue color with ferric chloride, and thus could not be VIII. The compound is undoubtedly 3-acetylisocoumaranone (IX), formed in the following way[11]



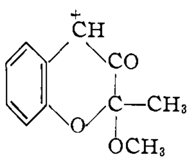
The so-called[10] "methyl ester of VIII" is the methyl ether of IX; and a compound, isolated by Pfeiffer and Enders, and formulated as *o*-acetoxyphenylacetic anhydride, is actually the acetate of IX.

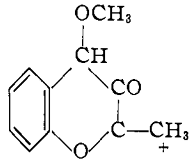
The acid VIII was synthesized by carbonation of the 3-lithium derivative of 2-methylcoumarone. It melted at 189–190° and was found to be identical with the degradation product of the "acetal."

The foregoing information makes it possible to formulate the rearrangement of the oxime tosylate I in such a way as to account for the products formed in the reaction and to provide the basis for assigning a structure IIIb to the "acetal." It appears that the initial stage of the reaction, leading to V, is as formulated above. The subsequent steps can now be written as



While alternative routes for the transformation of IIIb into II and VIII, depending upon alternative protonation steps, can be written, the above sequence is suggested because the position of the carbonyl group alpha to both the benzyl-ether-type of methoxy group and the acetal methoxyl group makes less attractive an initial stage that proceeds by way of XII or XIII


XII


XIII

It is probable that II and VIII are formed from a common intermediate, since the known stability of chromones in strong acids makes it very unlikely that II, initially formed, rearranges into VIII.

With the elucidation of the transformation of I and the establishment of the identity of the chromonol, it became of interest to examine the behavior of the tosylate of 2-benzoylcoumarone oxime, the rearrangement of which would be expected to yield flavonol.

The tosyl derivative XV of 2-benzoylcoumarone oxime (XIV) was found to be extremely unstable. It could be recrystallized by dilution of its cold ethanol solution with water, but when warmed in ethanol it was rapidly transformed into rearrangement products. The transformation of XV led chiefly to products resulting from a Beckmann rearrangement, and these were derivatives of coumarone-2-carboxylic acid, rather than, as in the case of I, of 2-aminocoumarone (leading ultimately to coumaranone-2). This indicates that the

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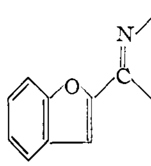
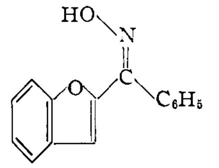
(11) Since it is unlikely that the rearrangement of the acetyl group to the α-carbon atom of the acetic acid occurs in the free acid or its anion, the preliminary formation of the mixed anhydride is postulated to account for the necessary activation of the methylene group.

oximes from which I and XV were derived had the following configurations (XVI and XIV)

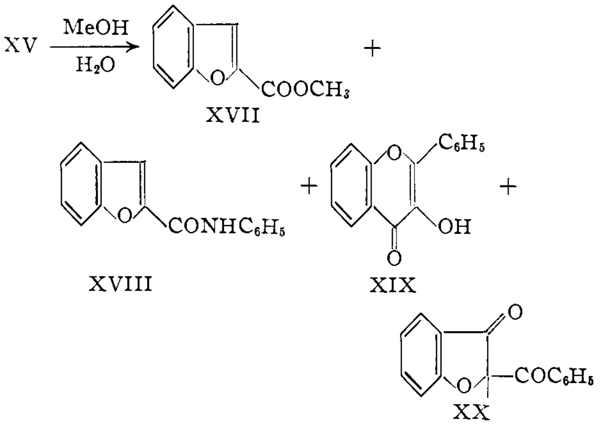


XVI



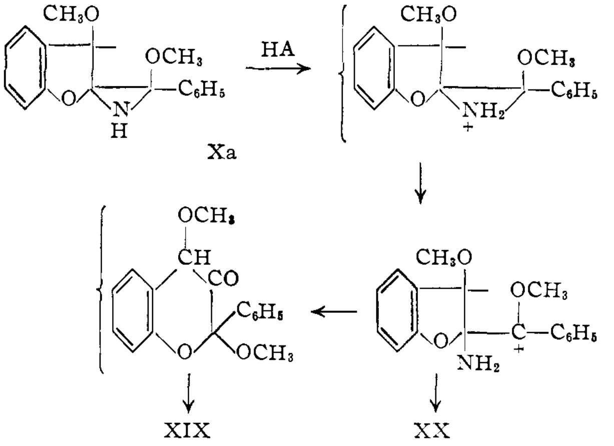
XIV

The rearrangement of XV (in aqueous methanol) yielded methyl coumarilate (XVII), coumarilanilide (XVIII), flavonol (XIX) (in about 10% yield) and 2-benzoylcoumaranone-3 (XX)



None of the product corresponding to the acetal IIIb was isolated.

The formation of 2-benzoylcoumaranone (XX) is of particular interest since it offers strong support to the proposed course of the rearrangement *via* the coumarane derivatives V and X. The formation of both XIX and XX can be accounted for by alternative courses for the solvolysis of Xa



Experimental

Melting points are uncorrected.

2-Acetylcoumarone oxime *p*-toluenesulfonate (I) was prepared and allowed to react in methanol according to the directions of Vargha, *et al.*[1] The chromonol II, m.p. 179–181°, and the "acetal" IIIb, b.p. 122–127° (4 mm.), $n^{25}\text{D}$ 1.5142, were isolated in yields reported.

2-Acetylcoumaranone (IIa). (A).—A mixture of 100 ml. of dry acetone, 75 g. of anhydrous potassium carbonate, 50 g. of methyl salicylate and 30.5 g. of chloroacetone was heated on the steam-bath for 5 hours. The cooled mixture was diluted with water and extracted thrice with ether, and the aqueous phase acidified. A crystalline solid (8.0 g.) precipitated. After recrystallization from ligroin and dilute ethanol, the product melted at 90–91°. It gave an olive-green ferric chloride color, dissolved in dilute sodium bicarbonate solution, gave a copper complex when its ether solution was treated with copper acetate, and formed a blood-red 2,4-dinitrophenylhydrazone.

(B).—A solution of 2.0 g. of *o*-hydroxybenzoylacetone in 200 ml. of chloroform containing 2 g. of potassium carbonate was cooled to 0°, and a solution of 1.8 g. of bromine in 40 ml. of chloroform was added dropwise with stirring. After addition was complete, the colorless mixture was kept at 0° for 30 minutes and then refluxed for one hour. The filtered solution was extracted with 5% sodium carbonate and the aqueous extract acidified. 2-Acetylcoumaranone (0.81 g.) separated as colorless crystals, m.p. 90–92°. It was identical with the product described above (A).

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.59. Found: C, 68.07; H, 4.55.

The **acetate** of IIa was prepared with the use of acetic anhydride and pyridine. The compound melted at 86–87°; it gave no color with ferric chloride.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.04; H, 4.62. Found: C, 66.14; H, 4.88.

2-Methylchromanol (II).—2-Methylchromone (3.1 g.) (prepared by acid-catalyzed ring closure of *o*-hydroxybenzoyl acetone) was dissolved in 30 ml. of thiophene-free benzene and hydrogenated at atmospheric pressure in the presence of 3.1 g. of palladium–calcium carbonate catalyst. After 22 hours, 72% of the theoretical amount (for one mole) of hydrogen had been absorbed. The filtered solution was evaporated and the residual oil dissolved in a mixture of 60 ml. of absolute ethanol, 6 ml. of acetic acid and 6 g. of Girard reagent T. This solution was refluxed for one hour, cooled, treated with 250 ml. of ice-cold water containing 3.6 g. of sodium carbonate, and the resulting solution extracted with four portions of ether. The aqueous solution was made 0.5 *N* in hydrochloric acid and allowed to stand at room temperature for one hour. Ether extraction yielded 1.74 g. of 2-methylchromanone. The compound, not purified further, showed absorption maxima at 251 and 321 mμ, minima at 232 and 275 mμ (log ε 3.95, 3.50, 3.48 and 2.45 in the order given).

To a solution of 0.74 g. of 2-methylchromanone in 35 ml. of boiling 95% alcohol was added, alternately and with shaking, portions of a total of 4.0 ml. of amyl nitrite and 20 ml. of concentrated hydrochloric acid. The resulting solution was allowed to stand for two hours, at the end of which time 100 ml. of water was added. On cooling, 0.52 g. of 2-methylchromonol separated. The compound melted at 178–180° and the mixed m.p. with the product of the rearrangement of I was 179–181°. Both compounds gave identical violet-blue ferric chloride colors.

The chromanone could be converted into the chromonol by nitrosation with amyl nitrite under alkaline conditions (potassium amyloxide), followed by acid hydrolysis of the isonitroso derivative. The yield was poorer than in the case of the nitrosation under acid conditions.

The **"Acetal"** IIIb was quite stable to acid hydrolysis, as reported by Vargha, *et al.*[1] When 240 mg. of the compound in a mixture of 10 ml. of alcohol and 10 ml. of 2 *N* sulfuric acid was refluxed for two hours, no chromonol could be isolated from the reaction mixture. When the same amounts of reactants were refluxed for three days, the solution on cooling deposited 60 mg. of the chromonol (identified by mixed m.p. and ferric chloride color).

The "acetal" gave no iodoform with sodium hypoiodite nor bromoform with sodium hypobromite. Attempts to form a piperonal, *p*-nitrobenzal or *p*-chlorobenzal derivative led to no crystalline product.

2-Methylcoumarone-3-carboxylic Acid (VIII).—A solution of 0.50 g. of the "acetal" in 15 ml. of 48% hydrobromic acid was heated at 120° for 1 hour. To the cooled solution was added 100 ml. of water and the mixture extracted with ether. The ether extract was shaken with 1 *N* sodium hydroxide and the basic solution filtered and acidified. The colorless solid that separated (m.p. 176–183°, 0.13 g.) was recrystallized from dilute ethanol, after which it melted at 190–191°.

The compound gave no ferric chloride color. A Kuhn-Roth determination showed 0.97 C-methyl group per mole cule (for mol. wt. 176). A mixture of VIII (m.p. 190–191°) and 3-methylcoumarilic acid[9] (m.p. 188–189°) melted at 146–160°.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.17; H, 4,59; neut. equiv., 176. Found: C, 68.05; H, 4.18; neut. equiv., 178 ± 2.

Reaction between *o*-Hydroxyphenylacetic Acid and Acetic Anhydride. 3-Acetylcoumaranone-2 (IX).—A solution of 1.5 g. of *o*-hydroxyphenylacetic acid and 4 ml. of acetic anhydride in 30 ml. of dry pyridine was warmed on the steam-bath for 30 minutes. The cooled mixture was diluted with dilute aqueous hydrochloric acid and cooled in ice. The solid (0.95 g.) that separated was dissolved in sodium bicarbonate solution, and the solution decolorized with Norite. Acidification of the filtered solution yielded 0.65 g. of a colorless solid which was purified by recrystallization from dilute ethanol. The compound melted at 133–134°, and gave a deep blue color with ferric chloride (reported[10] m.p. 135–136°).

The methyl ether of IX was prepared by treatment of an ether solution of IX with ethereal diazomethane. The compound had m.p. 125–126° (reported[10] 129.5–130°).

The acetate of IX was prepared by the action of acetic anhydride and sodium acetate (with heating for two hours). The product had m.p. 114–116°. Pfeiffer and Enders[10] report m.p. 118–119° for a compound isolated from the reaction of *o*-hydroxyphenylacetic acid, acetic anhydride and pyridine.

Anal, Calcd. for *o*-acetoxyphenylacetic anhydride,[10] $C_{20}H_{18}O_7$: C, 64.86; H, 4.90. Calcd. for acetate of IX, $C_{12}H_{10}O_4$: C, 66.04; H, 4.63. Found (Pfeiffer and Enders): C, 65.17, 64.96; H, 4.88, 4.62. Found (this work): C, 65.94; H, 4.56.

Attempt to Prepare IX. Self-condensation of Isocoumaranone in Ethyl Acetate.—An attempt was made to acylate isocoumaranone with ethyl acetate by the agency of sodium hydride.

A solution of 0.53 g. of isocoumaranone in 10 ml. of dry ethyl acetate was treated with 0.10 g. of sodium hydride. The mixture was refluxed for one hour, cooled and treated with 20 ml. of dilute hydrochloric acid. Ether was added and the layers separated. Sodium bicarbonate extraction of the ether layer, followed by acidification of the aqueous extract, yielded 0.30 g. of a colorless compound, m.p. 155–156°. The compound gave a deep blue ferric chloride color. From its behavior and composition it is probably 3-*o*-hydroxyphenylacetylisocoumaranone, formed by self-condensation of isocoumaranone.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.52. Found: C, 71.47; H, 4.78.

2-Methylcoumarone-3-carboxylic Acid (VIII).—Thirteen grams of 2-methylcoumarone[12] was converted to 2-methyl-3-bromocoumarone by the procedure described by Normant.[13] The product had b.p. 100–104° (6 mm.), $n^{20}D$ 1.5870 (reported[13] b.p. 123° (13.5 mm.), $n^{19}D$ 1.5832).

To 8 ml. of a 0.32 *M* solution of butyllithium in 15 ml. of cold (−78°) ether was added an ether solution (10 ml.) of 0.50 g. of 2-methyl-3-bromocoumarone. After two minutes, an excess of Dry Ice was added and the mixture allowed to warm to room temperature. Water was added and the ether layer separated and washed twice with sodium bicarbonate solution. The aqueous extract was acidified and the precipitate collected. It melted at 189–190°, and the mixed m.p. with the degradation product from the "acetal" (m.p. 190–191°) was 190–191°.

2-Benzoylcoumarone oxime (XIV) was prepared by the treatment of 20 g. of 2-benzoylcoumarone[14] with 18.8 g. of hydroxylamine hydrochloride and 50.5 g. of potassium hydroxide in dilute ethanol (refluxed for two hours). The oxime, which separated when the reaction mixture was diluted with water and cooled, was recrystallized from dilute acetic acid. The yield of pure material, m.p. 128–129.5°, was 18.2 g.

Anal. Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.68. Found: C, 75.99; H, 4.43.

2-Benzoylcoumarone Oxime *p*-Toluenesulfonate (XV).—A mixture of 0.46 g. of tosyl chloride, 0.50 g. of the oxime XIV and 1 ml. of dry pyridine was allowed to stand at 0° for one hour. After the addition of ether, the solution was washed thrice with dilute sulfuric acid, twice with 2 *N* sodium hydroxide and twice with water. The ether solution was dried over magnesium sulfate and the ether removed *in vacuo* at room temperature. The oily residue was dissolved in alcohol and water added until crystallization occurred. After three recrystallizations in this manner, the product had m.p. 109–110°.

Anal. Calcd. for $C_{22}H_{17}O_4NS$: C, 67.48; H, 4.38. Found: C, 67.35; H, 4.25.

In another experiment, when an attempt was made to recrystallize 14.35 g. of the crude tosylate (m.p. 102–105°) from hot aqueous ethanol, the solid that separated on cooling melted at 151–154°. This was shown to be coumarilanilide by its hydrolysis to coumarilic acid and aniline.

The aqueous alcoholic mother liquor was extracted with ether and the ether washed with dilute sodium hydroxide. Acidification of the alkaline solution yielded 0.33 g. of flavonol, m.p. 167–168°. The mixed m.p. with an authentic sample (m.p. 167–168°) was 167–168°.

Rearrangement of XV in Aqueous Methanol.—The crude tosyl derivative prepared from 10 g. of the oxime XIV and 9.2 g. of tosyl chloride in 20 ml. of dry pyridine was obtained in ether solution as described above. After the addition of 200 ml. of 80% aqueous methanol, the ether was removed by distillation through a Vigreux column and the residual solution refluxed for two hours. The cooled solution was extracted thoroughly with ether.

The ether solution was washed with 5% sodium bicarbonate solution. Acidification of the extract yielded 40 mg. of a solid, m.p. 72–77°, which gave an olive-green ferric chloride color. After recrystallization from dilute ethanol, the compound melted at 78–80°. A mixture of this substance with authentic **2-benzoylcoumaranone (XX)** (m.p. 79–80°) melted at 77–79°.

The remaining ether solution was extracted with dilute sodium hydroxide solution. Acidification of the alkaline extract yielded 1.1 g. of **flavonol**, m.p. 166–167° after one recrystallization from ethanol.

The residual ether solution of neutral products was dried and evaporated. The 9.0 g. of residual material partly crystallized on standing, and upon recrystallization from ethanol yielded 2.05 g. of coumarilanilide, m.p. 155–156°. The ethanol mother liquor was extracted with ether to give a final 250 ml. of ether solution.

A 50-ml. aliquot of this solution was evaporated to leave 1.15 g. of a residual oil. This gave a qualitative test for an ester, and upon saponification yielded 0.27 g. of coumarilic acid, m.p. and mixed m.p. 190–191°. The residue from another 50-ml. aliquot was distilled at 6 mm. The material boiling below 190° (0.30 g.) crystallized in the receiver, and after recrystallization from dilute ethanol melted at 51–52°. Methyl coumarilate is reported[15] to melt at 54–55°. No other compound could be isolated from the remaining ether solution.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.59. Found: C, 68.03; H, 4.38.

2-Benzoylcoumaranone (XX).—A mixture of 0.65 g. of *o*-hydroxydibenzoylmethane and 0.8 g. of dry potassium carbonate in 50 ml. of chloroform was treated with a solution of 0.44 g. of bromine in 10 ml. of chloroform, with stirring and cooling (0°). After the addition was completed, the mixture was refluxed for one hour, cooled, and washed with 1 *N* sodium hydroxide. The aqueous solution was acidified, yielding 0.37 g. of product, m.p. 79–80° after recrystallization from dilute ethanol. The compound gave an olive-green color with ferric chloride.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.67; H, 4.03.

Absorption spectra were measured with a Cary recording spectrophotometer (model 11 PMS), solvent 95% ethanol.

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[12] L. Claisen, *Ann.*, **418**, 69 (1910).

[13] H. Normant, *Bull. soc. chim.*, **12**, 609 (1945).

[14] R. Stoermer, C. W. Chydenius and E. Schinn, *Ber.*, **57**, 77 (1924).

[15] C. F. Koelsch and C. R. Stephens, Jr., THIS JOURNAL, **72**, 2209 (1950).