57.0° (ethanol)}. The compound was identical with an authentic sample prepared by the N-methylation of actinodaphnine VI with 37% formalin and $NaBH_4$ in methanol solution. With excess of ethereal diazomethane it afforded dicentrine, mp and mmp 166–167°.

Registry No.—IV, 16408-75-6; V, 16408-76-7; XVII, 16408-77-8; XVIII, 16408-78-9.

Acknowledgments.—The authors are grateful to Dr. S. R. Johns and Dr. J. A. Lamberton, C. S. I. R. O., Melbourne, Australia, for authentic samples of cassythine (cassyfiline) and cassythidine; to Dr. H. R. Arthur, University of Hong Kong, for a sample of neolitsine; to Dr. R. H. F. Manske, Dominion Rubber Co., Guelph, Ontario, for a sample of dicentrine; and to Professor M. Tomita, Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan, for samples of launobine and actinodaphnine. We are also indebted to Dr. D. C. deJongh of Wayne State University for mass spectral determinations and to Mr. O. Ribeiro of the Ministry of Agriculture, Brazil, for preparation of an alcoholic extract of the plant.

Coumarins. V. The Acid-Catalyzed Reaction of Phenols with β-Oxonitriles[1]

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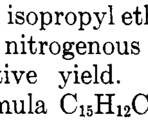
Received December 11, 1967

Benzoylacetonitrile (Ia) and acetoacetonitrile (Ib) were found to undergo carbon–carbon condensation with phenols providing a new route to coumarins, whereas carbon–oxygen condensation occurred with α-ethylacetoacetonitrile (Ic). The aluminum chloride catalyzed reaction of *meta*- and *para*-substituted phenols with Ia in the presence of dry hydrogen chloride yielded the corresponding iminocoumarins II and/or coumarins IV. Phenol as well as *o*-cresol gave predominantly β-(*p*-hydroxyphenyl)cinnamonitriles V. In contrast, Ib reacts with phenols in polyphosphoric acid or its ethyl ester to furnish 4-methylcoumarins in appreciable yields. The oxonitrile Ic on treatment with phenols in the presence of aluminum chloride and hydrogen chloride gave rise to both *cis*- and *trans*-β-aryloxy-α-ethylcrotononitriles VIIa and b in good yields. Mechanisms to account for the results are proposed.

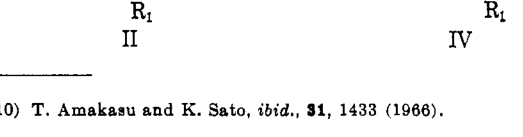
Previous papers in this series have demonstrated that anhydrous aluminum chloride, accompanied by dry hydrogen chloride, is an efficient reagent for nuclear addition reactions of phenols to α,β-unsaturated nitriles[3] and to 3-butenenitrile.[4] These studies have now been extended to β-oxonitriles. Whereas coumarins may be obtained by the acid-promoted condensation of phenols with β-keto esters (the von Pechmann reaction), little is known of a similar reaction with β-oxonitriles. It has been shown that benzoylacetonitriles condense with polyhydric phenols, such as resorcinol, in the presence of concentrated sulfuric acid to give the corresponding coumarins.[5,6] Mentzer and coworkers[7] have reported that the same acid-catalyzed reaction of resorcinol with α-aryl-β-ketonitriles yields 3-aryl-4-alkyl-7-hydroxycoumarins; no yields are given. While the reaction of the more active phenols, such as phloroglucinol, with 2-phenylacetoacetonitrile in trifluoroacetic acid is claimed[8] to give isoflavone in excellent yields, Cook and coworkers,[9] more recently, have noted that under identical conditions resorcinol reacts with α-(*p*-methoxyphenyl)acetoacetonitrile to provide the corresponding coumarin, which may be also secured by use of hydrogen fluoride as the condensation catalyst. No method of preparing coumarins by the acid-catalyzed reaction of phenols with aliphatic β-oxonitriles, such as acetoacetonitrile and its ethyl derivative, has yet appeared in the literature.

We have examined the condensation of phenols with β-oxonitriles Ia–c using anhydrous aluminum chloride, polyphosphoric acid (PPA), or its ethyl ester (PPE).[10]



Ia, R_1 = Ph; R_2 = H
b, R_1 = CH_3; R_2 = H
c, R_1 = CH_3; R_2 = C_2H_5

When equimolar amounts of resorcinol and benzoylacetonitrile (Ia) were treated with 2 equiv of anhydrous aluminum chloride in isopropyl ether saturated with dry hydrogen chloride, a nitrogenous product was obtained in nearly quantitative yield. The analytical data agreed with the formula $C_{15}H_{12}ClNO_2$, which is in accord with the structure of the coumarin derivative IIa



II IV

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[1] This investigation was supported mainly by Asahi Glass Co., Ltd., for which we are grateful.

[2] To whom inquiries should be directed: Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Ohka-machi, Minami-ku, Yokohama, Japan.

[3] Part I: K. Sato, T. Amakasu, and S. Abe, *J. Org. Chem.*, **29**, 2971 (1964).

[4] Part IV: T. Amakasu, *Bull. Chem. Soc. Jap.*, **41**, 451 (1968).

[5] (a) B. N. Ghosh, *J. Chem. Soc.*, **109**, 105 (1916); (b) G. Bargellini and G. Forti-Forli, *Gazz. Chim. Ital.*, **41**, 747 (1911); (c) A. Sonn, *Chem. Ber.*, **51**, 821, 1829 (1918).

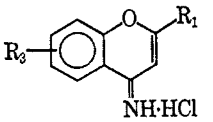
[6] W. Baker, *J. Chem. Soc.*, **127**, 2349 (1925).

[7] C. Mentzer, P. Gley, D. Molho, and D. Billet, *Bull. Soc. Chim. Fr.*, **5**, 13, 271 (1946).

[8] L. L. Wood and J. Sapp, *Texas J. Sci.*, **16**, 383 (1964); *Chem. Abstr.*, **62**, 6454 (1965).

[9] C. E. Cook, R. C. Corley, and M. E. Wall, *J. Org. Chem.*, **30**, 4114 (1965).

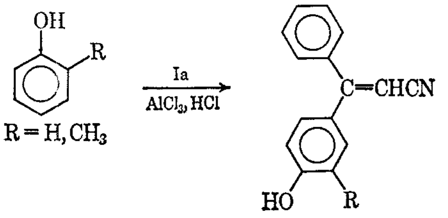
[10] T. Amakasu and K. Sato, *ibid.*, **31**, 1433 (1966).



III

or the isomeric flavone III (R_1 = Ph; R_3 = 7-OH). When heated with water or dilute hydrochloric acid the salt IIa underwent readily hydrolysis to 4-phenylumbelliferone (IVa, R_3 = 7-OH), which on treatment with hot acetic anhydride was quantitatively converted into the acetate IVi (R_3 = 7-AcO). Resorcinol monomethyl ether behaved analogously when treated with Ia under the same conditions and gave the corresponding coumarin IVb as well as IIb.

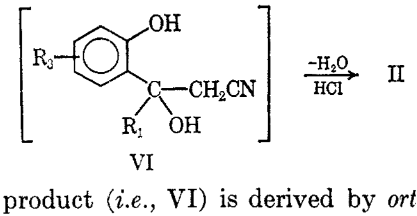
In contrast, under such similar conditions as described above (procedure A, see Experimental Section) cresols failed to react with Ia. However, when Ia was treated with excess *m*-cresol without an inert solvent in the presence of aluminum chloride and excess dry hydrogen chloride, the iminocoumarin salt IIc was obtained; with *p*-cresol, 6-methyl-4-phenylcoumarin (IVd) was directly isolated in 30% yield. On the other hand, phenol on a similar treatment with Ia underwent intermolecular dehydration at the *para* position leading to β-(*p*-hydroxyphenyl)cinnamonitrile (Va). The reaction also proceeded smoothly with *o*-cresol to furnish Vb in 60% yield. The results, along with the elemental analysis and the infrared spectra, confirm the structure V for the β-arylcinnamonitriles.



Va, R = H
b, R = CH_3

Although acetoacetonitrile (Ib) will readily polymerize in the cold on treatment with aluminum chloride, it was found to undergo such a condensation as Ia yielding the corresponding coumarins IV (R_1 = CH_3), when treated with phenols in PPA or PPE. Resorcinol and its monomethyl ether react with Ib in PPE at 110–145° to furnish 4-methylumbelliferone (IVe) and its methyl ether (IVf), respectively, in good yields. Coumarins of type IV (R = CH_3) could also be prepared by the PPA-catalyzed condensation of cresols at 75–90°, but even under these conditions phenol failed to react with Ib.

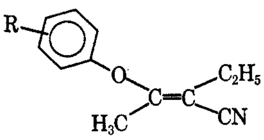
The results, summarized in Table I, suggest that the reactions proceed through addition of phenols to β-oxonitriles as indicated below. In those cases where the



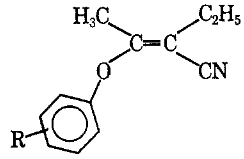
VI

addition product (*i.e.*, VI) is derived by *ortho* nuclear addition, dehydration of VI would be followed[11] by intramolecular cyclization to an iminocoumarin II. The ultraviolet data of coumarins IV (Table I) may distinguish[12] clearly between coumarins IV and chromones.

When 5 equiv of *p*-cresol was warmed with ethylacetoacetonitrile (Ic) in the presence of 2.2 equiv of aluminum chloride and excess of dry hydrogen chloride, a liquid, bp 119° (3 mm), and white crystals, mp 51–52°, were obtained. Both of the products were shown by elemental analyses to have the identical formula $C_{13}H_{15}NO$, which is in accord with the crotononitrile structure VIIa and VIIb (R = 4-CH_3). Their infrared

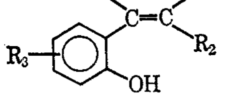


VIIa



VIIb

spectra showed cyano and conjugated olefin absorptions, respectively, at 2170–2200 and 1635–1641 cm⁻¹ in addition to enolic ether bands at 1209–1255 cm⁻¹. Neither one of the spectra contained absorptions attributable to potential hydroxyl groups (see Experimental Section). This definitely excludes the possibility of structures such as VIII and reveals that VIIa and VIIb are geometrical



VIII

isomers. In addition, the ultraviolet spectrum of the former showed a strong absorption at 283 mμ (ε 1200) as well as a very weak band at 332 mμ (ε 12) while that of the latter indicated the lack of a weak absorption in high region. Finally, the nmr spectra clearly distinguish between the two isomers, the most significant feature being the appearance of the β-methyl proton signal of VIIa, at lower field. In the crotononitriles, as previous workers[13] have reported, the *cis*-methyl protons are at lower field by 0.15 ppm than those *trans* to the nitrile group. The same situation, adequately explained on the basis of diamagnetic anisotropic shielding[13] due to the nitrile triple bond, exists in the present case where the β-methyl protons in the former lie 0.22 ppm below those in the latter. Thus, we conclude that the *cis*-crotononitrile structure VIIa must be assigned to the former and the *trans* isomer VIIb to the latter.

It is noteworthy that phenol similarly yields isomers VIIa and VIIb (R = H), whereas only the *cis* compound VIIa (R = 2-CH_3) is formed from *o*-cresol. The following discussion is presented to account for the stereochemical course of the reaction listed in Table II.

It is suggested that the most likely pathway for the formation of the vinyl ethers VIIa,b involves an addition–elimination mechanism. Anhydrous aluminum chloride is believed to coordinate not only with a cyano[14]

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[11] (a) A. Robertson, R. B. Waters, and E. T. Jones, *J. Chem. Soc.*, 1681 (1932); (b) S. Z. Ahmad and R. D. Desai, *Proc. Indian Acad. Sci.*, **6A**, 6 (1937).

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[14] (a) W. Gruber and F. Traub, *Monatsh.*, **77**, 414 (1947); (b) J. C. Westfahl and T. L. Gresham, *J. Amer. Chem. Soc.*, **76**, 1076 (1954); (c) A. D. Grebenyuk and I. P. Tsukervanik, *J. Gen. Chem. USSR*, **25**, 269 (1955).

TABLE I
THE ACID-CATALYZED REACTION OF PHENOLS WITH β-OXONITRILES Ia AND Ib

Phenol	Oxo-nitrile	Procedure[a]	Reaction temp, °C	Time, hr	Product composition, % II	IV	V
Resorcinol	Ia	A	50–60	5	94		
Resorcinol monomethyl ether	Ia	A	60–65	5	20	10	
m-Cresol	Ia	A′	70–75	5	41		
p-Cresol	Ia	A′	70–75	3		30	
o-Cresol	Ia	A′	70–75	1			60
Phenol	Ia	A′	70–75	7			43
Resorcinol	Ib	B	110–115	5		80	
Resorcinol monomethyl ether	Ib	B	140–145	5		70	
m-Cresol	Ib	C	70–80	1.5		10	
p-Cresol	Ib	C	90–95	1.5		20	

Compd[b] IV	R_1	R_3	Recrystn solvent[c]	Mp, °C Obsd	Lit	Infrared, cm^{-1} C=O	Ultraviolet λ_{max} mμ (ε)[m]
a	Ph	7-OH	A	249–250	245[d] 256.5–257[e]	1690	241 (10,500)[n] 259 ± 3 (7,700)[o] 375 (11,500)
b	Ph	7-OCH_3	A	110.5–111	110[f]	1725	233 ± 3 (12,600)[o] 259 ± 1 (8,000) 331 (12,900)
c	Ph	7-CH_3	B	97	96[g]	1740	290 (12,000)
d	Ph	6-CH_3	B	135	131[h]	1740	284 (14,700)
e	CH_3	7-OH	B	185	185[i]	1680	222 (14,000)[n,p] 254 ± 2 (2,300)[o] 326 (12,700)
f	CH_3	7-OCH_3	A	158.5–159	159[j]	1730	222 (16,400) 252 ± 2 (2,300)[o] 324 (13,900)
g	CH_3	7-CH_3	A	132	132[k]	1700	222 (19,500)[q] 282 (10,500) 319 (900)
h	CH_3	6-CH_3	B	151	150[l]	1710	218 (24,000)[q] 276 (11,500) 324 (5,700)

[a] See Experimental Section. [b] See Experimental Section for the characterization data of II and V. [c] A, ethanol; B, aqueous ethanol. [d] See ref 5c. [e] L. L. Wood and J. Sapp, *J. Org. Chem.*, **27**, 3703 (1962). [f] R. Robinson and M. R. Turner, *J. Chem. Soc.*, **113**, 859 (1918) [g] See ref 11a. [h] A. Robertson and W. F. Sandrock, *ibid.*, 1180 (1932). [i] D. Chakravarti and C. B. Bera, *J. Indian Chem. Soc.*, **21**, 109 (1944). [j] H. von Pechmann and C. Duisberg, *Chem. Ber.*, **16**, 2119 (1883). [k] K. Fries and W. Klostermann, *ibid.*, **39**, 871 (1906). [l] K. Fries and W. Kostermann, *Ann. Chem.*, **362**, 1 (1908). [m] The spectra were measured at concentration of 6–6.2 mg/l. of Spectrograde ethanol. [n] See ref 12c. [o] Flat. [p] See ref 12b. [q] See ref 12a.

TABLE II
THE ALUMINUM CHLORIDE CATALYZED CONDENSATION OF PHENOLS WITH α-ETHYLACETOACETONITRILE (Ic)[a]

No.	Phenol	Total yield, %	Product composition, mole fraction VIIa	VIIb	Bp (mm), °C VIIa	VIIb
1	Phenol	60	0.75	0.25	107 (1)	125 (1)
2	*o*-Cresol	33	1		113 (2)	
3	*p*-Cresol	70	0.75	0.25	119 (3)	140 (3)

No.	$n^{20}D$ VIIa	VIIb	d^{20} VIIa	VIIb	C, % Calcd	C, % Found VIIa	VIIb	H, % Calcd	H, % Found VIIa	VIIb
1	1.5355	1.5378	1.0439	1.0577	76.97	77.66	76.84	7.00	6.61	6.95
2	1.5365		1.0250		77.58	77.22		7.51	7.51	
3	1.5341	*b*	1.0069	*b*	77.58	77.70	77.30	7.51	7.36	7.24

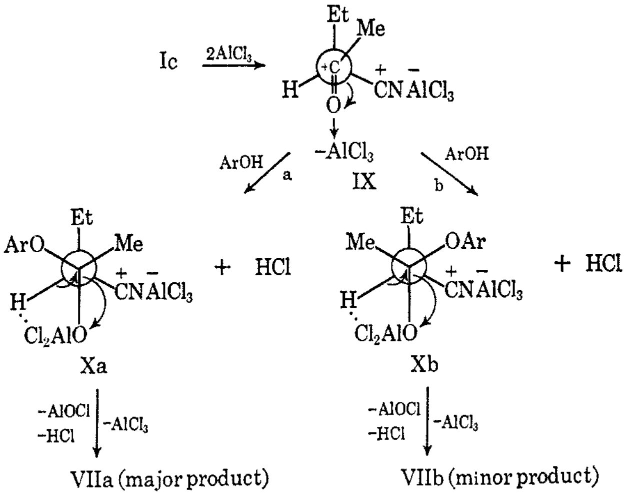
[a] The reaction was carried out at 40–50° for 4 hr according to the procedure A′; see Experimental Section. [b] Mp 51–52°, recrystallized from ligroin.

group but also with the carbonyl group[15] of a ketone. The observation that use of at least two molecular proportions of aluminum chloride is required in order to obtain good yield of VIIa,b supports this suggestion. The mechanism for the steric course of the reaction presented in Scheme I can account for the results (Table II).

Treatment of Ic with aluminum chloride might provide the complex IX containing two electrophilic centers, of which the one with less steric interference appears to be the carbonyl carbon rather than the cyano carbon. The subsequent addition reaction of phenol with IX may take place *via* two routes a and b (Scheme I) where the incoming nucleophile (ArO:) is expected to attack preferentially on the side near the α hydrogen, leading to hemiketal complex Xa rather than on the side adjacent to the more bulky nitrile

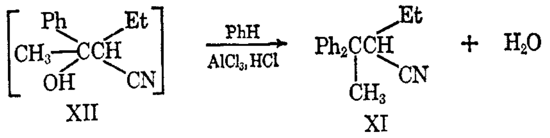
(15) (a) C. Mentzer, D. Molho, and D. Xuong, *Bull. Soc. Chim. Fr.*, **15**, 263 (1948); (b) J. Colonge and L. Pichat, *ibid.*, **16**, 177 (1949); (c) M. H. Dilke, D. D. Eley, and M. G. Cheppard, *Trans. Faraday Soc.*, **46**, 261 (1950); (d) J. Broome and B. R. Brown, *Chem. Ind.*, (London), 1307 (1956).

SCHEME I



group, which would result in the formation of the isomeric complex Xb. The intermediates Xa and Xb could then undergo "*cis* elimination," to form VIIa as major product and VIIb as minor product. The data in Table II, except in the case of *o*-cresol, are consistent with this view. This exception, probably attributable to the presence of the methyl substituent at a position *ortho* to the hydroxyl group, suggests that steric constraint is operative.

On the other hand, condensation of benzene with Ic in a similar manner readily resulted in formation of the saturated nitrile XI, which could arise by formation of XII followed by reaction with a second mole of benzene.



The enol content of α-substituted β-oxonitrile Ic was shown by means of nmr spectra to be negligible whereas the enol content in Ia and Ib is about 11[16] and 38%,[17] respectively. In contrast with their enolization character, it is of potential interest to note that Ic may predominantly undergo the carbon–oxygen condensation reaction with phenols to the vinyl ethers VIIa and b while the electrophilic attack by either Ia or b on their nuclei brings about the condensation which can provide a new route to the synthesis of coumarins.

Experimental Section

All melting points, determined on a Shimadzu Type MM-2 micro hot stage, and boiling points are uncorrected. Infrared and ultraviolet spectra were recorded, respectively, on a Hitachi Model EPI-S2 and a Hitachi Model EPS-3T spectrophotometers. The nmr spectra were taken in deuteriochloroform or carbon tetrachloride on a Varian A-60 and JEOL Model JNM 4H-100 instruments with tetramethylsilane as an internal standard.

Materials.—Benzoylacetonitrile (Ia) was prepared from ω-bromoacetophenone and potassium cyanide according to the procedure of Shriner and Fuson.[18] Monoetherification of resorcinol with dimethyl sulfate was carried out by the method of Kinugawa and coworkers.[19] α-Ethylacetoacetonitrile (Ic) was obtained by the sodium-induced dimerization of acetonitrile followed by ethylation with ethyl bromide.[20] The nmr spectrum of Ic showed a triplet at τ 8.97 (CH_3 of ethyl group), a multiplet centered at 8.20 (CH_2), and a singlet at 7.63 (CH_3 of acetyl group), but no singlet due to an enolic proton at lower field. Other materials were obtained from commercial sources.

Acetoacetonitrile (Ib).—This material was prepared by a simplification of the procedure of Dahn and Hauth[17] as follows. *t*-Butyl α-cyanoacetoacetate (21.6 g, 0.118 mol), prepared by acetylation of *t*-butyl cyanoacetate[21] anion with acetyl chloride, was refluxed in 260 ml of benzene for several hours. To this mixture was then added dropwise a solution of *p*-toluenesulfonic acid (1 g) in 75 ml of benzene. After the mixture was heated under refluxing until the generated crystals disappeared (about 3 hr); removal of the solvent followed by fractional distillation gave 8.4 g (84%) of Ib, bp 47–50° (0.5 mm), the infrared spectrum of which was identical with that of the authentic sample.[17]

The Acid-Catalyzed Reaction of Phenols with β-Oxonitriles. General Procedure A.—To a stirred suspension of anhydrous aluminum chloride (0.1 mol) in isopropyl ether (15 ml) was added dropwise at 20–30° a solution of the phenol (0.05 mol) and Ia (0.05 mol) in the solvent (60 ml). The mixture, into which dry hydrogen chloride was continuously passed, was gradually heated and kept under the conditions presented in Table I. Then the resulting mixture was chilled and poured over water containing crushed ice and concentrated hydrochloric acid. After it was stirred for 0.5 hr, filtration and drying gave the crude product II, which was purified by recrystallization from an appropriate solvent. Substitution of isopropyl ether for such an inert solvent as *sym*-tetrachloroethane afforded a lower yield of II. The alternative procedure of adding the catalyst to a stirred solution of the phenol and Ia in the solvent provided the same results as have been presented above. Analytical data for the hitherto unknown compound II are individually described below. The coumarin IV[22] was isolated by concentration of the aqueous layer followed by extraction with ether. Removal of the solvent from the separated organic layer resulted in recovery of the starting materials.

Procedure A'.—The procedure involves no use of such an inert solvent as described above. Finely powdered anhydrous aluminum chloride (0.1–0.11 mol) was added slowly to a vigorously stirred mixture of the phenol (0.25 mol) and I (0.05 mol) at 5–10°. Dry hydrogen chloride was passed into the viscous slurry, which then was heated in a steam or oil bath and kept under the conditions shown in Table I. Unless otherwise specified, the subsequent work-up followed the above procedure.

Coumarins IIc, IVc, and IVd were isolated by means of the following work-up 1, while crotononitriles VIIa and b were isolated by work-up 2.

Work-Up 1.—After treatment of the resulting mixture with cold water, the organic layer was separated. The aqueous layer was extracted with ether, which was then combined with the separated organic materials. Filtration gave a crystals mass, which was recrystallized from such a solvent as anhydrous ethanol–ether to provide IIc. Saturation of the filtrate with dry hydrogen chloride afforded additional amount of IIc. A small amount of IV was obtained by concentration of the aqueous layer followed by extraction with ether. *p*-Cresol yielded the corresponding crude II, mp 112–113°, the infrared spectrum of which showed the absorptions due to functional groups. Attempts, however, to isolate the pure product by repeated recrystallization were unsuccessful, leading to IVd.

Work-Up 2.—The compounds VIIa and VIIb were isolated by this procedure. Such an extract as shown above was washed with dilute sodium hydroxide solution and water and dried over anhydrous magnesium sulfate. After removal of the solvent, the residual oil was fractionated by distillation to give the products VIIa and b. Results with individual compounds are presented in Table II. Infrared spectra of compounds VIIa and VIIb

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[16] F. Arndt, L. Loewe, and R. Ginkök, *Rev. Fac. Sci. Univ. Istanbul Ser. A*, **11**, 147 (1946); *Chem. Abstr.*, **41**, 3760 (1947).

[17] H. Dahn and H. Hauth, *Helv. Chim. Acta*, **42**, 1214 (1959); **47**, 1424 (1964).

[18] R. L. Shriner and R. C. Fuson, "Preparation of Organic Intermediates," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 98.

[19] J. Kinugawa, M. Ochiai, and H. Yamamoto, *Yakugaku Zasshi*, **79**, 931 (1959); *Chem. Abstr.*, **54**, 497 (1960).

[20] E. Mohr, *J. Prakt. Chem.*, **90**, 189 (1914).

[21] R. E. Ireland and M. Chaykovsky, *Org. Syn.*, **41**, p 5 (1961).

[22] The formation of IV along with II would presumably depend upon the individual stability of II to the contact time with aqueous solution during workup.

are summarized as follows:[23] VIIa (R = H), $\nu_{\max}^{\text{film}}$ 2230 (A), 1648 (B), 1596, 1490 (C), 1257, 1220 (D), and 930, 760, 700 cm^{-1} (E); VIIb (R = H), $\nu_{\max}^{\text{film}}$ 2220 (A), 1647 (B), 1594, 1490 (C), 1250, 1210 (D), and 940, 759, 696 cm^{-1} (E); VIIa (R = 2-CH$_3$), $\nu_{\max}^{\text{film}}$ 2250 (A), 1650 (B), 1590, 1496 (C), 1262, 1237 (D), and 930, 780, 752 cm^{-1} (E); VIIa (R = 4-CH$_3$), $\nu_{\max}^{\text{film}}$ 2200 (A), 1635 (B), 1600, 1498 (C), 1255, 1223 (D), and 930, 832, 819 cm^{-1} (E); $\lambda_{\max}^{\text{EtOH}}$ 238 mμ (ϵ 1200)[23] and 322 (12); VIIb (R = 4-CH$_3$), $\nu_{\max}^{\text{KBr}}$ 2170 (A), 1641 (B), 1604, 1504 (C), 1220, 1209 (D), and 940, 829, 820 cm^{-1} (E); $\lambda_{\max}^{\text{EtOH}}$ 241 mμ (ϵ 1500).

The nmr spectrum of VIIa (R = 4-CH$_3$) showed a triplet at τ 8.83 (J = 7.2 cps, methyl protons of ethyl group), singlets at 7.95 (β-methyl protons) and 7.65 (aromatic methyl protons), and two doublets at 3.11 and 2.80 (J = 9.0 cps, aromatic protons) while that of VIIb (R = 4-CH$_3$) exhibited the corresponding peaks at τ 8.83 (J = 6.6), 8.17 and 7.71, and 3.16 and 2.91 (J = 8.4 cps).

Procedure B.—A solution of 0.05 mol of the phenol and 0.05–0.06 mol of acetoacetonitrile (Ib) in 52 g of PPE was stirred and heated under the conditions shown in Table I. In the case of resorcinol, the resulting mixture was decomposed with cold water and extracted with such a solvent as ethyl acetate or ether. After the extract was washed with water and dried over magnesium sulfate, removal of the solvent gave a mass of crystals (7 g, 80%). Recrystallization from aqueous ethanol afforded 4-methylumbelliferone (IVe), mp 185°. On the other hand, the mixture from resorcinol monomethyl ether obtained as described above on treatment with cold water and filtration gave a crude solid (11 g), mp 136–142°, which was recrystallized from ethanol to give 6.7 g (70%) of white crystals (IVf): mp 158.5–159°; $\nu_{\max}^{\text{KBr}}$ 1730 (C=O), 1625, 1610, 1510 (C=C), 1287, 1265, 1213, 1070 (C-O-C), and 858 cm^{-1} (aromatic).

Procedure C.—A mixture of 0.05 mol of the phenol, 0.05–0.06 mol of Ib, and 60 g of PPA was heated with mechanical stirring under the conditions given in Table I. The mixture was poured onto an ice–water slurry (200–300 ml), stirred vigorously for 0.5 hr, and filtered. Purification was effected by recryrstallization from an appropriate solvent. The filtrate was saturated with ammonium sulfate and extracted with ether. After drying, the ether was evaporated *in vacuo* and the residue was recrystallized from the appropriate solvent (Table I).

2-Imino-4-phenylumbelliferone Hydrogen Chloride (IIa).—This compound was prepared by means of the procedure A. Recrystallization from acetic acid or ethanol gave the pure compound IIa: mp 222–223°; $\nu_{\max}^{\text{KBr}}$ 3000 (N-H), 1670 (C=N), and 1560 cm^{-1} (δ N-H).

Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.81; H, 4.43. Found: C, 66.04; H, 4.46.

Methyl Ether of IIa (IIb).—The compound IIb was synthesized together with IVb by means of the procedure A. Recrystallization from ethanol afforded the analytical sample: mp 201.5–202°; $\nu_{\max}^{\text{KBr}}$ 2900 (N-H), 1675 (C=N), and 1550 cm^{-1} (δ N-H).

Anal. Calcd for $C_{16}H_{14}ClNO_2$: C, 66.79; H, 4.87. Found: C, 66.96; H, 4.99.

2-Imino-7-methyl-4-phenylcoumarin Hydrogen Chloride (IIc).—The crude salt IIc was prepared, through work-up 1, by using the procedure A′. Attempts to isolate the analytical sample by repeated recrystallization from such an anhydrous solvent as ethanol-ether failed although the infrared spectrum showed $\nu_{\max}^{\text{KBr}}$ 2850 (N-H), 1670 (C=N), and 1550 cm^{-1} (δ N-H); the melting point was 205–210°. Attempted recrystallization from such an aqueous solvent as aqueous ethanol provided quantitatively IVc.

β-(*p*-Hydroxyphenyl)cinnamonitrile (Va).—This compound was prepared by means of the procedure A′. The reaction was carried out under the conditions presented in Table I, using 28.2 g (0.3 mol) of phenol and 10 g (0.06 mol) of Ia. After the extract was shaken with 1 *N* sodium hydroxide solution, concentration of the separated alkaline layer followed by filtration gave 7.3 g of white crystals, which were presumed to be the sodium salt of Va. A solution of the crystals in 20 ml of water was acidified with hydrochloric acid. The precipitate (5.7 g, 43%) was filtered and washed with water. Recrystallization from aqueous ethanol afforded white crystals (needles): mp 162°; $\nu_{\max}^{\text{KBr}}$ 3350 (OH), 2250 (CN), 1620 (alkenic C=C), 1595, 1520 (aromatic C=C), 1260 (C-O), 840, 805 (*para* substituted), and 775, 700 cm^{-1} (aromatic).

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01. Found: C, 81.21; H, 4.97.

Compound IV was not found in the ethereal layer.

β-(4-Hydroxy-3-methylphenyl)cinnamonitrile (Vb).—The procedure for the preparation of Va was followed using the same molar ratios of the reagents and the conditions listed in Table I. Acidification of the sodium salt of Vb with hydrochloric acid afforded crude Vb (10.8 g) which was recrystallized from aqueous acetic acid: mp 135°; $\nu_{\max}^{\text{KBr}}$ 3380 (O-H), 2250 (CN), 1615 (alkenic C=C), 1570, 1515 (aromatic C=C), 1280 (C-O), 1120, 830, 805 (1,2,4 trisubstituted), and 780, 700 cm^{-1} (monosubstituted).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57. Found: C, 81.96; H, 5.56.

α-Ethyl-β,β-methylphenylhydrocinnamonitrile (XI).—This compound was prepared according to the procedure A′ using 0.5–0.7 mol of benzene, 0.1 mol of Ic, and 0.22 mol of anhydrous aluminum chloride. The reaction was carried out in the presence of dry hydrogen chloride at 40–50° for 5 hr. After the resulting mixture was treated with ice–water, the separated aqueous layer extracted with benzene and organic solution were combined. Removal of benzene followed by fractional distillation furnished 11.7 (47%) of a yellow viscous oil after recovery of Ic (40%): bp 159° (3 mm); n^{20}D 1.5774; $\nu_{\max}^{\text{film}}$ 3070, 3020 (C-H), 2260 (CN), 1609, 1500 (C=C), 1453, 1390 (C-H deformation), and 1033, 765, 705 cm^{-1} (aromatic).

Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68. Found: C, 86.62; H, 7.59.

Conversion of II into IV.—Compound IIa (0.6 g) in 6 ml of water was heated on a steam bath for 3 hr. Upon cooling to room temperature, the solution was filtered to give 0.5 g (95%) of IVa, mp 246–247°. One recrystallization from ethanol gave pure material, mp 249–250° (lit.[5c] 245°). Use of dilute hydrochloric acid smoothly effected partial hydrolysis. Its methyl ether IIb as well as IIc even upon heating with aqueous ethanol for a few minutes was converted into the corresponding coumarin IVb.

7-Acetoxy-4-phenylcoumarin (IVi).—A mixture of IVa (0.6 g) and acetic anhydride (1.2 g) was refluxed for 0.5 hr and was poured into cold water (10 ml). The precipitate was filtered and washed thoroughly with water. The crude product, 0.6 g, was recrystallized from aqueous ethanol to provide 0.3 g of white crystals: mp 120–121° (lit.[24] 120°); $\nu_{\max}^{\text{KBr}}$ 1765 (C=O of acetate), 1730 (C=O of lactone), 1620 (C=C), 1268, 1205, 1142, 1110 (C-O-C), and 868, 820, 780, 710 cm^{-1} (aromatic); $\lambda_{\max}^{\text{EtOH}}$ 286 mμ (ϵ 13,300, flat).

Registry No.—IIa, 16299-16-4; IIb, 16299-17-5; IIc, 16299-18-6; IVa, 2555-30-8; IVb, 2555-31-9; IVc, 7758-71-6; IVd, 16299-22-2; IVe, 90-33-5; IVf, 2555-28-4; IVg, 14002-90-5; IVh, 14002-89-2; IVi, 16299-27-7; Va, 16281-90-6; Vb, 16299-28-8; VIIa (R = H), 16299-29-9; VIIb (R = H), 16299-30-2; VIIa (R = 2-CH$_3$), 16299-31-3; VIIa (R = 4-CH$_3$), 16299-32-4; VIIb (R = 4-CH$_3$), 16299-33-5; XI, 16299-34-6.

Acknowledgment.—The authors wish to express their gratitude to Mrs. N. Monte, T. Takahashi, S. Tokita, and T. Itakura for capable technical assistance in these experiments.

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[23] The absorptions, A, B, C, D, and E are due to CN, alkenic C=C aromatic C=C, conjugated C-O-C bands, and aromatic C-H deformations, respectively. The ultraviolet spectra were determined at concentration of 1.5 × 10^{-3} mol/l.

[24] H. von Pechmann and E. Hanke, *Chem. Ber.*, **34**, 354 (1901).