B. **In the Presence of Hydrazine Hydrate.**—The procedure was essentially the same as above, except for the addition of 22 ml. of 80% hydrazine hydrate. The reaction product (7.8 g. which was distilled at 135–170° at 3 mm.) deposited 1.8 g. of solid substance identified as 10-ketoundecanoic acid by mixture melting point. The liquid fraction (6.0 g.) gave the *p*-bromophenacyl ester, m.p. 68.0–68.5°, which did not depress the melting point when admixed with an authentic sample of *p*-bromophenacyl undecanoate, m.p. 68.0–68.9° (lit.[23] m.p. 69°).

***cis*-15-Heptadecenoic Acid.**—The preparative method of 15-heptadecenoic acid from 15-heptadecenoic acid[1] was similar to that adopted in the preparation of VIII; thus, 11.0 g. of 15-heptadecenoic acid was converted to 10.5 g. (96%) of crude 15-heptadecynoic acid, m.p. 72–74°, which was recrystallized from *n*-pentane. The pure sample melted at 77.4–77.7° and depressed the melting point when admixed with VIII.

Anal. Calcd. for $C_{17}H_{30}O_2$: C, 76.68, H, 11.35. Found: C, 76.87; H, 11.43.

The *p*-bromophenacyl ester was prepared in the usual manner[24] and melted at 79.5–80.0° after recrystallizations from ethanol.

Anal. Calcd. for $C_{25}H_{35}BrO_3$: C, 64.79; H, 7.61. Found: C, 64.88; H, 7.66.

A sample of 15-heptadecynoic acid (1.76 g.) in a mixed solvent composed of 30 ml. of methanol and 50 ml. of ethanol was hydrogenated at atmospheric pressure over Lindlar catalyst.[10] After 188 ml. (calculated 161 ml.) of hydrogen was absorbed, usual work-up gave 1.68 g. of wax-like substance, m.p. 43–45°, which melted at 44.0–45.0° after two recrystallizations from *n*-hexane, ν_{max} (Nujol) 960 cm.$^{-1}$ (trace).

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 75.99; H, 12.01.

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(24) See ref. 14, p. 200.

Direct Synthesis of Dihydrocoumarin and Its Derivatives

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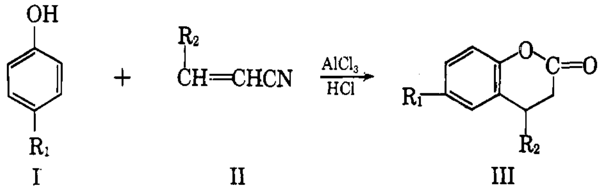
Reaction of acrylonitrile with phenol or the *para*-substituted phenols in the presence of anhydrous aluminum chloride and dry hydrogen chloride provided considerably good yields of dihydrocoumain or 6-substituted dihydrocoumarins in one step. It fails with phenols which are sufficiently deactivated by electron-attractive groups. Similarly reaction of crotononitrile with the *para*-substituted phenols gave the corresponding 4-methyldihydrocoumarin derivatives.

Dihydrocoumarins may be obtained by the catalytic hydrogenation of coumarins.[2] The carbon–carbon cyanoethylation of the more active phenols, such as resorcinol, is known to give dihydrocoumarin derivatives in the presence of anhydrous zinc chloride and dry hydrogen chloride.[3] Phenol itself does not react under these conditions, but, if a more active catalyst, anhydrous aluminium chloride, is used, a good yield of β-(*p*-hydroxyphenyl)propionitrile is obtained.[4] The addition of vinylidene cyanide to phenol in the presence of anhydrous aluminum chloride gives β-(*p*-hydroxyphenyl)-α-cyanopropionitrile and a trace of dihydrocoumarin.[5] The cyanoethylation of phenol by acrylonitrile gives β-(*p*-hydroxyphenyl)propionitrile and a small amount of dihydrocoumarin.[6] Recently Kost, *et al.*, have reported that the cyanoethylation of *p*-cresol by acrylonitrile gives β-(2-hydroxy-5-methylphenyl)propionitrile and a trace of 6-methyldihydrocoumarin.[7]

The authors have now found the following modified method of preparing dihydrocoumarins.



R_1 = –H, –CH_3, –OCH_3, –Cl
R_2 = –H, –CH_3

The reactions of nitrile II with phenol I were carried out at 120–145° in the presence of 1 mole of anhydrous aluminium chloride per mole of phenol I and an excess of dry hydrogen chloride. The data, summarized in Tables I and II, indicate the scope of these procedures.

These dihydrocoumarins were identified by their infrared spectra and microanalyses. The following compounds which were sufficiently deactivated by electron-attractive groups did not react: *p*-acetylaminophenol, methyl *p*-hydroxybenzoate, *p*-hydroxyacetophenone, *p*-phenol sulfonic acid, and *p*-nitrophenol.

The reactions of crotononitrile with phenols provided poor yields of 4-methyldihydrocoumarins. No *para* addition product was isolated from the reaction of crotononitrile with phenol. It was very difficult to isolate 4-methyldihydrocoumarins from crude products by repeated refractionation. This is probably because 4-methyldihydrocoumarins formed azeotropes with crotonamide. It was possible to isolate the pure products by gas chromatographing over silicon oil (D. C. 550).

Although several experiments were made under the described conditions, the reaction with crotononitrile produced a lower yield than with acrylonitrile. This result suggests the influence of steric hindrance and hyperconjugation.

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(1) On leave of absence from the Seimi Chemical Laboratory, Chigasaki, Japan, 1962–.

(2) P. L. De Benneville and R. Conner, *J. Am. Chem. Soc.*, **62**, 283 (1940); L. Palfray, *Bull. Soc. Chim.*, **7**, 401 (1940); C. L. Palfray, *J. Am. Chem. Soc.*, **63**, 3540 (1941); Y. Ito, H. Kitagawa, T. Hiramori, Y. Suzuki, and M. Yamagata, *J. Pharm. Soc. Japan*, **71**, 686 (1951); Y. Ito and H. Kitagawa, *J. Pharm. Soc. Japan*, **73**, 107 (1953); P. Maitte, *Ann. chim.* (Paris), **9**, 431 (1954); T. R. Ingle and B. V. Bride, *J. Univ. Bombay*, **23**[Pt. 3], *Sect. A*, No. 36, 33 (1954); F. Korte and K. H. Bückel, *Chem. Ber.*, **93**, 1025 (1960).

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TABLE I

SYNTHESES OF DIHYDROCOUMARINS

Compound	Products III		Phenols I		Nitriles II		AlCl$_3$, moles	Reaction temp., °C.	Reaction, hr.	Yield, %
	R$_1$	R$_2$	R$_1$	Moles	R$_2$	Moles				
1	H	H	H	1.3	H	3.9	1.3	105	3	10[a]
2	CH$_3$	H	CH$_3$	0.5	H	0.75	0.5	140–145	3	80
3[b]	OCH$_3$	H	OCH$_3$	0.5	H	0.75	0.5	120–125	3	36
4	Cl	H	Cl	1.0	H	1.5	1.0	135–140	6	30

Compound	M.p., °C. (uncor.)	Stretching vibration, $\nu_{C=O}$, cm.$^{-1}$	C, %		H, %	
			Calcd.	Found	Calcd.	Found
1	21–22	1780[c]	72.96	72.76	5.44	5.09
2	80–81[d]	1745	74.05	74.08	6.22	6.29
3[b]	46–47	1760	67.40	67.56	5.66	5.78
4	110–111[e]	1745	59.20	59.18	3.86	3.87

[a] The yield of *p*-cyanoethyl compound was 60%. [b] **3** is a new compound. [c] Johnston, *et. al.*,[6] report $\nu_{C=O}$ 1775 cm.$^{-1}$ for dihydrocoumarin. [d] Kost, *et. al.*,[7] report m.p. 79–79.5° for 6-methyldihydrocoumarin. [e] Westfahl, *et. al.*,[5] report m.p. 110–111° for 6-chlorodihydrocoumarin.

TABLE II

SYNTHESES OF 4-METHYLDIHYDROCOUMARINS

Compound	Products III		Phenols I		Nitriles II		AlCl$_3$, moles	Reaction temp., °C.	Reaction, hr.	Yield, %
	R$_1$	R$_2$	R$_1$	Moles	R$_2$	Moles				
5	H	CH$_3$	H	0.37	CH$_3$	0.37	0.18	130–135	4	4
6	CH$_3$	CH$_3$	CH$_3$	0.55	CH$_3$	0.37	0.37	140–145	5	10
7	OCH$_3$	CH$_3$	OCH$_3$	0.37	CH$_3$	0.37	0.18	120–125	5	17
8	Cl	CH$_3$	Cl	0.37	CH$_3$	0.37	0.18	140–145	5	8

Compound	B.p., °C., (mm. of Hg) (uncor.)	Stretching vibration, $\nu_{C=O}$, cm.$^{-1}$	C, %		H, %	
			Calcd.	Found	Calcd.	Found
5	97–98 (1)	1770	74.05	73.75	6.22	6.30
6	100–105 (5[a])	1770	74.97	75.10	6.86	6.82
7	140–142 (5[a])	1745	68.73	68.58	6.29	6.16
8	90–92 1[a,b]	1740	61.08	60.79	4.61	4.73

[a] These are new compounds. [b] M.p. 36.5–37.5°.

Experimental[8]

Typical Procedure.—Finely powdered anhydrous aluminum chloride (70.2 g., 0.5 mole, purity 95%) was added slowly to the mixture of distilled acrylonitrile (40.0 g., 0.75 mole) and *p*-cresol (54.1 g., 0.5 mole), which continued to be stirred vigorously at 10–15°. Dry hydrogen chloride was passed into an orange viscous slurry; then the slurry was gradually heated on a Mantol heater up to 80° until it turned into a fluid solution. The dark red reaction mixture, into which dry gas was continuously passed, was held at 140–145° for 3 hr.; thereafter the mixture was allowed to cool.

Before the mixture was solidified, it was poured over 350 g. of crushed ice containing 40 ml. of concentrated hydrochloric acid, and was vigorously stirred until the precipitated salt redissolved. The organic layer was separated, and the aqueous layer was extracted with three 70-ml. portions of ethylacetate, which were then combined with the separated organic material. The organic mixture was washed with 10% potassium chloride solution. After it was dried over anhydrous sodium sulfate and the solvent was removed, the residual oil was fractionated by distillation to give 64.9 g. (80% based on *p*-cresol) of 6-methyldihydrocoumarin, b.p. 115–118° (3 mm.), which soon crystallized. The crude product had m.p. 78–80° and was recrystallized from aqueous ethyl alcohol to provide a glistening white plate, m.p. 80–81°. The infrared spectrum showed a strong band, assignable to a carbonyl group of lactone, at 1745 cm.$^{-1}$.

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(8) Melting points and boiling points are uncorrected. Infrared spectra were recorded with a Hitachi Model EPI-S2 spectrophotometer.