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Coumarins. VII. The Acid-catalyzed Reaction of Aromatic Compounds with β-Chlorocarboxylic Acids[1]

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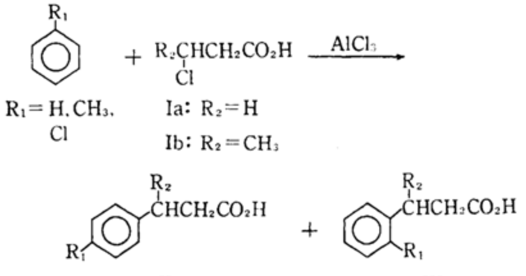
The aluminum chloride-catalyzed reaction of aromatic compounds, such as benzene and phenols, with β-chlorocarboxylic acids was investigated. Although the reactions of benzene, toluene, and chlorobenzene with β-chloropropionic acid were found to give the corresponding dihydrocinnamic acids in high yields, attempts to prepare dihydrocoumarin by a similar reaction of phenol were unsuccessful. Similarly, β-arylbutyric acids were obtained in good yields by means of the aluminum chloride-induced reaction of aromatic hydrocarbons with β-chlorobutyric acid (Ib). In contrast, phenols, such as phenol, *o*- and *m*-cresols, reacted with Ib under similar conditions to provide the corresponding β-(*p*-hydroxyphenyl)butyric acids in 22—60% yields, while a 51% yield of β-(5-hydroxy-2-methylphenyl)butyric acid was obtained upon a similar treatment of *p*-cresol with the acid Ib.

An earlier paper in this series[2] has demonstrated that the aluminum chloride-catalyzed reaction of phenols with crotonic acid gives 4-methydihydrocoumarins or their isomers and that dihydroumbelliferone is obtained by the reaction of resorcinol with acrylic acid in the presence of the ethyl ester of polyphosphoric acid. These studies have been extended to the corresponding β-chlorocarboxylic acids. Whereas the acid-catalyzed reactions of aromatic compounds with α,β-unsaturated acids have been extensively studied, little attention has been given to the similar reaction with β-chlorocarboxylic acids.

It has been shown[3] that the condensation of aromatic compounds, such as benzene, toluene, and chlorobenzene, with β-chlorocarboxylic acids, such as β-chloropropionic acid (Ia) and β-chlorobutyric acid (Ib), in the presence of aluminum chloride gives the corresponding indanones; no yields have been given, however. The aluminum chloride-catalyzed reactions of benzene with Ia[4] and with its ethyl ester[5] have previously been shown to provide dihydrocinnamic acid. Recently Dann and his coworkers[6] have reported that phenols condense with Ia in hydrofluoric acid to afford β-chloro-2-hydroxypropiophenones. No method of preparing dihydrocoumarins by the acid-catalyzed reaction of phenols with I has yet appeared in the literature.

In the present study we have examined the condensation of such aromatic compounds as phenols with Ia and Ib, using anhydrous aluminum chloride or boron trifluoride etherate.



II III

A convenient method of preparing dihydrocinnamic acid (II, $R_1=R_2=H$) was developed by the use of at least two molecular proportions of aluminum chloride for the reaction of benzene with Ia. Similarly, toluene reacted with Ia at 50—55°C for 5 hr to give a high-total yield of the corresponding

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[1] This investigation was presented at the 21 st Annual Meeting of the Chemical Society of Japan, Ohsaka, April, 1968; and was supported mainly by Asahi Glass Co., for which we are grateful. Part VI of this series: K. Sato, M. Ōhashi, T. Amakasu, and K. Takeda, This Bulletin, **42**, 2319 (1969).

[2] T. Amakasu and K. Sato *J. Org. Chem.*, **31**, 1433 (1966).

[3] I. G. Farbenindustrie Akt.-Ges., German Pat. 485309 (1929).

[4] K. Nagakubo, Y. Iwakura, K. Takei and T. Okada, *Nippon Kagaku Zassi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **78**, 1209 (1957).

[5] I. P. Tskervanic and I. V. Terent'eva, *Dokl. Akad. Nauk SSSR*, **50**, 257 (1945).

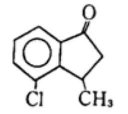
[6] O. Dann, G. Volz and O. Huber, *Ann.*, **587**, 16 (1954).

Table 1. The aluminum chloride-catalyzed reaction of aromatic compounds with β-chlorocarboxylic acids (Ia, b)

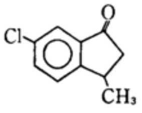
No.	Compound		Aromatic compound	I (mol)	$AlCl_3$ (mol)	Reaction		Total yield (%)	Product composition, mol fraction	
	R_1	R_2				temp,°C	hr		II	III
1	H	H	120 ml	0.2	0.42	55—60	5	84		
2	CH_3	H	500 ml	1	2	55—60	5	90	0.6	0.4
3	Cl	H	1 mol	0.2	0.5	70—75	7	52	0.6	0.4
4	H	CH_3	50 ml	0.1	0.25	55—60	6	70		
5	CH_3	CH_3	40 ml	0.1	0.25	55—60	5	41	0.31	0.69
6	Cl	CH_3	0.1 mol[a)]	0.1	0.3	50—55	5	33	b)	b)

a) The inert solvent used was *sym*-tetrachloroethane (50 m*l*).
b) Attempts to isolate the individual compounds were unsuccessful.

dihydrocinnamic acids, II and III (R_1=CH_3, R_2=H), in the same ratio as that of II to III (R_1=Cl, R_2=H). On the other hand, Ib, when treated with benzene in the presence of 2 equivalents of aluminum chloride at 65—70°C, furnished β-phenylbutyric acid (II, R_1=H, R_2=CH_3) in a 70% yield. Toluene behaved analogously when treated with Ib, giving the corresponding butyric acids, II and III (R_1=R_2=CH_3). While the reaction of chlorobenzene with Ib at 100°C gave the corresponding indanones, IVa (56%) and IVb (16%), under mild conditions a mixture of their precursors, II and III (R_1=Cl, R_2=CH_3), was obtained in a 33% yield. These results, summarized in Table 1, indicate the predominant alkylation rather than acylation of aromatic compounds with I; they also confirm, along with the infrared spectra and their physical properties, the II and III structures for the β-arylacids.

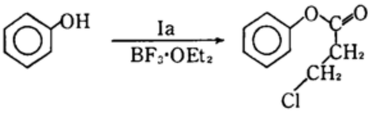


IVa



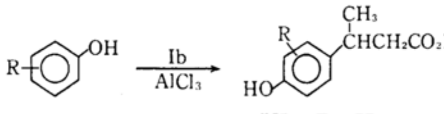
IVb

Although attempts to prepare dihydrocoumarin by extending the above results from Ia to phenol failed, phenyl β-chloropropionate (V) was obtained in a 26% yield when phenol was treated with Ia at 85—95°C for 4 hr in boron trifluoride etherate. The infrared spectrum was identical with that of an authentic sample of V.



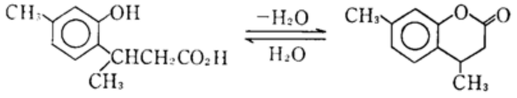
V

In contrast, when phenol was treated with Ib in the presence of 3 equivalents of anhydrous aluminum chloride in *sym*-tetrachloroethane, β-(4-hydroxyphenyl)butyric acid (VIa) was obtained in a 52% yield. The structure follows from the infrared spectrum, which clearly shows hydroxyl and acid C=O bands and an out-of-plane deformation of aromatic C–H at 3100, 1700, and 820 cm^{-1} respectively.



VIa, R=H
b, R=2-CH_3
c, R=3-CH_3

o-Cresol, when treated similarly with Ib, gave the corresponding butyric acid, VIc (22%). The new compound, VIc, was verified by a study of its infrared spectrum and by elemental analysis. With *m*-cresol white crystals, mp 123—124°C, were obtained. The analytical data agreed with the formula $C_{11}H_{14}O_3$, which is in accord with the structure of the *p*-alkylated product, VIb, and the *o*-isomer, VII.



VII VIII

The infrared spectrum exhibited hydroxyl and carbonyl absorptions at 3150 and 1690 cm^{-1} respectively, along with aromatic deformations (860, 820 cm^{-1}). This spectrum does not make it possible to distinguish clearly between VIb and VII. The compound VII, obtained by the hydrolysis of the corresponding dihydrocoumarin, VIII, is known[7)] to undergo an intramolecular dehydration cyclization to VIII. Accordingly, attempts to prepare VIII from the product resulted in the recovery of the starting material, VIb. Thus, it may be concluded that the product is β-(4-hydroxy-

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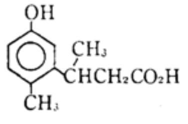
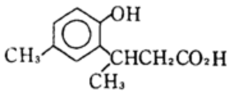
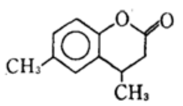
7) T. Nakabayashi, *Yakugaku Zasshi* (*J. Pharm. Soc. Japan*), **74**, 23 (1954).

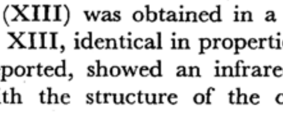
2-methylphenyl)butyric acid (VIb).

On the other hand, *p*-cresol behaved abnormally when similarly treated with Ib, giving crystals with a melting point of 111—112°C. The product was shown by elemental analysis to have the formula $C_{11}H_{14}O_3$, which is in accord with those of IX and X. The infrared spectrum showed hydroxy and acid C=O absorptions respectively at 3200 and 1710 cm^{-1}, in addition to an out-of-plane deformation of aromatic C–H at 860 and 800 cm^{-1}. The experimental fact that an attempt at cyclization to XI results in the recovery of the starting material may eliminate the possibility of such a structure as the *o*-alkylated product, X. Furthermore, in order to obtain evidence for the structure (IX), conversion to the indanone derivative XII was attempted. Compound IX, upon treatment in polyphosphoric acid (PPA) at 60—70°C for 1 hr, was converted into the corresponding indanone, XII, which gave its semicarbazone. The infrared spectrum of compound XII indicated the presence of a hydroxyl group (3300 cm^{-1}), a ketone carbonyl group (1675 cm^{-1}), and two adjacent hydrogen atoms of substituted benzene (820 cm^{-1}). Thus, the product, IX, was proved to be *β*-(5-hydroxy-2-methylphenyl)butyric acid.

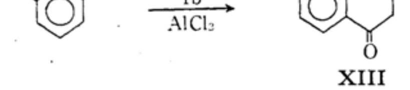

IX


X


XI

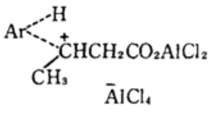

XII

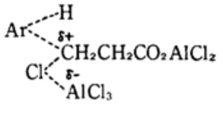
When resorcinol was similarly treated with Ib in the presence of 3.3 equivalents of aluminum chloride at 85—90°C for 5 hr, 7-hydroxy-2-methylchromanone (XIII) was obtained in a 34% yield. The product, XIII, identical in properties with that previously reported, showed an infrared spectrum consistent with the structure of the chromanone derivative.


XIII

From the results obtained in this experiment, the following conclusions can be reached. While *β*-chlorocarboxylic acid, Ib, reacts not only with aromatic hydrocarbons and chlorobenzene, but also with phenols (but not resorcinol) to give *β*-arylbutyric acids, the aluminum chloride-catalyzed reaction of Ia takes place only with aromatic compounds, except for the cases of phenols and their ethers. In addition, it should be noted that the formation ratios of II to III are remarkably different between the reaction of Ia and that of Ib (Table 1). These facts suggest that the transition state (*i. e.*, XIV) in the attack of the electrophilic *β*-carbon of Ib on an aromatic nucleus might differ from that of Ia (*i. e.*, XV).

Anhydrous aluminum chloride is believed, of course, to coordinate with a chloro group and not only with a carboxylic group[2,8] but also with the hydroxyl group[9] of a phenol. The observation that the use of at least two and three molecular proportions of aluminum chloride in the reaction of aromatic hydrocarbons and of phenols respectively are necessary in order to obtain good yields of the products (II, III and VI, IX) supports this suggestion. In addition, the liberation of hydrogen chloride observed on the cold treatment of I acids with aluminum chloride results from the first step, in which the aluminum salt of I may be formed.


XIV


XV

Experimental

All the melting points, determined on a Shimadzu Type MM-2 micro hot stage, and all the boiling points are uncorrected. The infrared spectra were recorded on a Hitachi Model EPI-S2 spectrophotometer, while gas chromatographic analysis were carried out on a Shimadzu Model GC-1C chromatograph.

Materials. *β*-Chloropropionic acid (Ia) (72.5%) was prepared by the addition of dry hydrogen chloride to acrylic acid at 10—20°C[10]; bp 101—103°C/12 mmHg; mp 38.5—40°C (from ligroin) (lit[10]) mp 40.5°C). *β*-Chlorobutyric acid (Ib) was obtained in a quantitative yield by the similar treatment of the dry gas with crotonic acid in ether at 0°C for three days; bp 111—112°C/20 mmHg (lit[11]) bp 98.5—99.5°C/12 mmHg). The other materials were obtained from commercial sources.

Dihydrocinnamic Acid (II, $R_1=R_2=H$). *Typical Procedure A*. Fine-powdered anhydrous aluminum chlo-

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8) a) P. H. Groggins and P. H. Nagel, *Ind. Eng. Chem.*, **26**, 1313, 1317 (1934); b) P. H. Gore, *Chem. Revs.*, **55**, 229 (1955); c) W. R. Edwards and E. C. Sibille, *J. Org. Chem.*, **28**, 674 (1963).

9) H. W. Johnston and F. J. Gross, *J. Org. Chem.*, **22**, 1264 (1957).

10) E. Linnermann, *Ann.*, **163**, 96 (1872).

11) A. M. Cloves, *ibid.*, **319**, 357 (1901).

ride (56.1 g, 0.42 mol) was added slowly to a solution of Ia (21.7 g, 0.2 mol) in 120 m*l* of benzene, after which stirring was vigorously continued. The mixture was gradually heated on an oil bath and kept under the conditions shown in Table 1. The resulting mixture was chilled and poured over water containing crushed ice and concentrated hydrochloric acid. The organic layer was separated from the aqueous layer, which was then shaken with benzene. The extract was combined with the separated organic material, and then washed with water. After the extract had been dried over anhydrous magnesium sulfate and the solvent had been removed, the residue was distilled under reduced pressure to afford 50.8 g (84%) of a colorless oil; bp 153—155°C/12 mmHg (lit[4]) bp 125—126°C/4 mmHg). It solidified after standing for some time. Recrystallization from ligroin gave the pure product; mp 48°C (lit[4]) mp 48—49°C): ν_{max}^{KBr} 1700 (C=O), 750, 700 cm^{-1} (mono-substituted).

The product (23 g) was heated in PPA (280 g) at 70°C for 1 hr. The subsequent treatment of the mixture according to the usual manner provided indanone (14.6 g, 70%); mp 38.5°C (from ligroin) (lit[12]) mp 40°C).

***p*- and *o*-Methyldihydrocinnamic Acids (II and III; $R_1=CH_3$, $R_2=H$).** The Procedure A shown above was followed, using the molar ratios of the reagents and the conditions listed in Table 1. The fractional recrystallization of the crude products (bp 140—143°C/3 mmHg, mp 50—80°C) from aqueous acetic acid (1 : 1.5, vol) and ligroin furnished II ($R_1=CH_3$, $R_2=H$); mp 115—116°C (lit[13]) mp 117°C); ν_{max}^{KBr} 1700 (C=O), 810 cm^{-1} (aromatic C–H).

The recrystallization-mother liquor was extracted with ether and dried. The removal of the ether, followed by fractional distillation, gave 59.2 g of III ($R_1=CH_3$, $R_2=H$), which was then recrystallized from 95% ethanol to afford the pure product; mp 100—102°C (lit[14]) mp 102°C); ν_{max}^{KBr} 1700 (C=O), 780 cm^{-1} (ortho-disubstituted).

***p*- and *o*-Chlorodihydrocinnamic Acids (II and III; $R_1=Cl$, $R_2=H$).** These compounds were prepared by means of Procedure A. The reaction was carried out under the conditions presented in Table 1. The resulting organic material, like that described above, was washed with diluted sodium hydroxide (50 m*l*×3). Acidification, followed by filtration, gave 8 g of the crude product, II. Recrystallization from water provided colorless crystals; mp 94—96°C (lit[15]) mp 91—93°C).

The filtrate was extracted with ether. Drying and the removal of the solvent afford 12 g of the crude compound, III, which was then recrystallized from aqueous ethanol to provide colorless crystals; mp 118—120°C (lit[16]) mp 123°C).

Found: C, 58.80; H, 5.19%. Calcd for C_9H_9ClO: C, 58.55; H, 4.91%.

Phenyl β-Chloropropionate (V). To a mixture of 9.4 g (0.1 mol) of phenol and 10.8 g (0.1 mol) of Ia, boron trifluoride etherate (21.3 g, 0.15 mol) was added, drop by drop. The mixture was stirred and heated on an oil bath at 85—95°C for 4 hr. The resulting mixture was poured onto an ice-water slurry. The organic layer was separated from the aqueous layer, which was shaken with ether. The extract was washed with water and with saturated sodium bicarbonate, and then dried over magnesium sulfate. The removal of the ether, followed by distillation, gave V (3.9 g, 26%) as a colorless oil; bp 94—95°C/2 mmHg (lit[17]) bp 132—135°C/12 mmHg); ν_{max}^{film} 1750 (ester, C=O), 750, 690 cm^{-1} (monosubstituted).

Found: C, 58.43; H, 5.10%. Calcd for $C_9H_9ClO_2$: C, 58.55; H, 4.91%.

β-Phenylbutyric Acid (II, $R_1=H$, $R_2=CH_3$). This compound was prepared according to Procedure A using the conditions shown in Table 1. The resulting extract was shaken with diluted sodium hydroxide, and the alkaline layer was acidified with hydrochloric acid. Extraction with ether, drying, and the subsequent removal of the solvent gave a crude oil, which was fractionated to yield the pure product (11.5 g, 70%); bp 145—148°C/5 mmHg (lit[18]) bp 168°C/17 mmHg). It solidified and was recrystallized from ligroin, providing the pure compound as colorless crystals; mp 35—36°C (lit[18]) mp 36—38.5°C); ν_{max}^{film} 1700 (C=O), 750, 690 cm^{-1} (aromatic C–H).

β-(*p*-Tolyl)butyric Acid (II, $R_1=R_2=CH_3$) and Its *o*-Isomer (III, $R_1=R_2=CH_3$). Procedure A was followed, using the molar ratios of the reagents and the conditions listed in Table 1. A mixture (7.3 g, 41%) of the compounds II and III was obtained, through such a workup as has been described above, from the resulting reaction mixture; bp 165—167°C/15 mmHg. It solidified after standing in an ice-box. Filtration gave the *p*-isomer (2.3 g), which was recrystallized from petroleum ether to afford the pure compound; mp 88—89°C (lit[19]) mp 91°C); ν_{max}^{KBr} 1700 (C=O), 810 cm^{-1} (*p*-substituted).

The filtrate was fractionated to give the *o*-isomer (5 g); bp 168—169°C/13 mmHg (lit[20]) bp 166—167.5°C/12 mmHg); ν_{max}^{film} 1700 (C=O), 780 cm^{-1} (*o*-substituted).

4-Chloro-3-methylindanone (IVa) and Its Isomer (IVb). These compounds were prepared according to Procedure A, using 40 m*l* of chlorobenzene, 12 g (0.1 mol) of Ib, and 33 g (0.25 mol) of aluminum chloride. The reaction was carried out at 100°C for 5 hr. The resulting mixture was treated such as has already been described, giving an organic material which was then shaken with an aqueous alkaline solution. After drying and the removal of the solvent, the residual oil was distilled to afford a mixture of IVa and IVb (13 g, 72%); bp 134—135°C/18 mmHg. A part of it solidified after standing at 0°C for a while. Filtration gave IVa (4.5 g), which was recrystallized from petroleum ether, providing the pure compound; mp 45—46°C (lit[3]) mp 47°C); ν_{max}^{KBr} 1705 (ketone C=O), 840, 790, 780 cm^{-1} (1,2,3-trisubstituted).

The product gave the semicarbazone; mp 220—223°C.

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12) K. von Auwers, *ibid.*, **415**, 160 (1918).

13) R. Huisgen and V. Vossius, *Monatsh. Chem.* **88**, 517 (1957).

14) C. Grundmann, *Chem. Ber*, **81**, 513 (1948).

15) T. F. Dankova, T. N. Bokova, N. A. Preobrazhenskii, A. E. Petrushchenks, I. A. Il'shtein and N. I. Shvetsov, *Zhur. Obshch. Khim.*, **21**, 787 (1951).

16) A. N. Nesmeyanov, R. Kh. Freidlina and N. A. Semenov, *Izvest. Akad. Nauk, SSSR, Otdel. Khim. Nauk*, **1955**, 993.

17) F. Mayer and L. v. Zütphen, *Ber.*, **57B**, 200 (1924).

18) D. H. Hey, J. Honeyman, D. H. Kohn and W. J. Peal, *J. Chem. Soc.*, **1953**, 2021.

19) T. Wagner-Jauregg and H. Hippchen, *Ber.*, **76B**, 694 (1943).

20) V. P. Gol'mov and C. Kun, *Zhur. Obshch. Khim.*, **29**, 3705 (1959).

Attempts to isolate the analytical sample, IVb, from the filtrate by repeated distillations failed; bp 136—140°C. Gas-chromatographic analysis showed the distillate (8.5 g) to consist of IVa (60%) and IVb (40%). The formation ratio of IVa to IVb is, accordingly, 0.78/0.22.

β-(*p*-Chlorophenyl)butyric Acid (II, R_1=Cl, R_2=CH_3) and Its *o*-Isomer III (R_1=Cl, R_2=CH_3). The procedure involves the use of an inert solvent such as *sym*-tetrachloroethane. Procedure A was followed, except for the use of such a solvent, using the molar ratio of the reagents and the conditions presented in Table 1. Fractional distillation gave a colorless oil (6.5 g, 33%), which was shown by means of gas-chromatographic analysis to be a mixture of the corresponding II and III. Attempts to isolate the individual compounds by a variety of means such as gas chromatography were unsuccessful; bp 170—173°C.

Found: C, 60.39; H, 5.81%. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.53%.

β-(*p*-Hydroxyphenyl)butyric Acid (VIa). *Typical Procedure B.* A solution of phenol (9.4 g) and Ib (12 g, 0.1 mol) in *sym*-tetrachloroethane (25 m*l*) was added, drop by drop, to a stirred suspension of anhydrous aluminum chloride (40 g, 0.3 mol) in the solvent (25 m*l*) at 0—5°C for 1 hr, after this period stirring was vigorously continued until the evolution of hydrogen chloride subsided. The mixture was then gradually heated on an oil bath and kept at 70—75°C for 6 hr; the resulting mixture was chilled and poured over an ice-water slurry (300 m*l*) containing concentrated hydrochloric acid (100 m*l*). The organic layer was separated from the aqueous layer, which was then shaken with three 100 m*l* portions of ether. The extract was combined with the separated organic material and then washed with a saturated sodium bicarbonate solution and water. After it had been acidified with hydrochloric acid and extracted with ether, the extract was dried over anhydrous magnesium sulfate. The removal of the solvent gave a viscous oil contaminated with the starting Ib, which could be removed by means of high-vacuum distillation. It solidified after standing in an ice-box for some time. Filtration, followed by recrystallization from benzene, provided VIa (9.4 g, 52%): mp 136—138°C (lit[21] mp 136°C); ν_{max}^{KBr} 3100 (OH), 1700 (C=O) and 820 cm^{-1} (*p*-disubstituted).

Found: C, 66.59; H, 6.94%. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%.

β-(4-Hydroxy-3-methylphenyl)butyric Acid (VIb). Procedure B for the preparation of VIa was followed, using 10.8 g (0.1 mol) of *o*-cresol, 12 g (0.1 mol) of Ib, 40 g (0.3 mol) of anhydrous aluminum chloride, and 50 m*l* of the solvent. The reaction was carried out at 70—75°C for 7 hr. VIb (4.2 g, 22%) was obtained as the product, through a work-up such as that shown above; mp 107—108°C (from benzene); ν_{max}^{KBr} 3400 (OH), 1680 (C=O) and 850, 800 cm^{-1} (1,3,4-trisubstituted).

Found: C, 67.71; H, 7.36%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

β-(4-Hydroxy-2-methylphenyl)butyric Acid (VIc). Compound VIc was prepared by means of Procedure B. The reaction was carried out under the same conditions as were shown in the preparation of VIb, using 5.4 g (0.05 mol) of *m*-cresol, 6 g (0.05 mol) of Ib, 20 g (0.15 mol) of aluminum chloride, and 25 m*l* of the solvent. When a viscous oil, obtained from the reaction mixture through the same work-up, was allowed to stand in an ice-box for two weeks, it solidified. Recrystallization from benzene afforded VIc (11 g, 60%): mp 123—124°C; ν_{max}^{KBr} 3150 (OH), 1690 (C=O), and 860, 820 cm^{-1} (1,2,4-trisubstituted).

Found: C, 67.80; H, 7.33%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

β-(5-Hydroxy-2-methylphenyl)butyric Acid (IX). This compound was prepared according to Procedure B, using 21.6 g (0.2 mol) of *p*-cresol, 24 g (0.2 mol) of Ib, 80 g (0.6 mol) of aluminum chloride, and 100 m*l* of the solvent. The reaction was carried out at 70—85°C for 7 hr. Recrystallization from benzene gave IX (19.8 g, 51%); mp 111—112°C; ν_{max}^{KBr} 3200 (OH), 1710 (C=O), 860, 800 cm^{-1} (1,2,5-trisubstituted).

Found: C, 67.77; H, 7.38%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

7-Hydroxy-3,4-dimethylindan-1-one (XII) A mixture of IX (3 g) and PPA (40 g) was stirred at 60—70°C for 1 hr, poured over cold water, and then extracted with ether. After it had been washed with a saturated sodium bicarbonate solution and with water, and dried over anhydrous magnesium sulfate, the solvent was removed to give a crude product; mp 35°C (lit[22] mp 53—54°C); ν_{max}^{KBr} 3300 (OH), 1675 (C=O) and 820 cm^{-1} (1,2,3,4-tetrasubstituted). The compound gave the semicarbazone; mp 203—205°C (from water) (lit[22] mp 217°C).

Found: C, 61.94; H, 6.67%. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.48%.

7-Hydroxy-2-methylchromanone (XIII). Procedure B was followed, using 11 g (0.1 mol) of resorcinol, 12 g (0.1 mol) of Ib, 45 g (0.33 mol) of aluminum chloride, and 50 m*l* of the solvent. The reaction was carried out at 85—90°C for 5 hr. The extract, obtained in the usual manner, was washed with a sodium hydroxide solution, and the alkaline layer was acidified with hydrochloric acid. Filtration, followed by recrystallization from water, afforded XIII (6 g, 34%); mp 174—176°C (lit[6] mp 175—176°C); ν_{max}^{KBr} 3100 (OH), 1600 (C=O), 850, 780 cm^{-1} (aromatic C–H). The compound gave the semicarbazone; mp 205—207°C (from aqueous ethanol).

Found: C, 66.90; H, 5.89%. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.50%.

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