

When the addition was complete, the reaction mixture was stirred for 1 hr at room temperature, and the solvent was then evaporated by passing a stream of nitrogen gas over the mixture. The remaining yellow solid weighed 2.8 g (100%), mp 197°. A mixture melting point with authentic perbromide salt VIII was not depressed.

Reaction of 2-Chlorotetramethylguanidine with Benzoyl Chloride.—To a solution of 7.5 g (0.05 mole) of 2-chlorotetramethylguanidine in 250 ml of ether was added a solution of 7.0 g (0.05 mole) of benzoyl chloride in 100 ml of ether over a period of 1 hr while maintaining the temperature at -5 to 0° . The mixture was allowed to stand overnight, with stirring, at room temperature. The precipitated hygroscopic white solid was filtered quickly under a nitrogen atmosphere, washed thoroughly with ether and dried in a vacuum desiccator: yield 14.2 g (98%) of 1-chloro-1-benzoyltetramethylguanidinium chloride, mp 175–

185° dec. Tests showed the salt to be a strong oxidizing reagent. The extreme hygroscopicity of the chloride salt precluded the preparation of an analytical sample.

Conversion of 1-chloro-1-benzoyltetramethylguanidinium chloride to 2-benzoyltetramethylguanidine hydrochloride was effected by crystallization of the former compound from wet acetonitrile-ether: yield 8.4 g (66%), mp 207–211° dec. An analytical sample was prepared by another crystallization from acetonitrile-ether: mp 215–218° dec.

Anal. Calcd for $C_{12}H_{18}ClN_3O$: C, 56.36; H, 7.09; Cl, 13.86. Found: C, 56.51; H, 7.22; Cl, 13.96.

An infrared spectrum showed absorption bands consistent with the assigned structure. A mixture melting point determination with an authentic sample prepared by the reaction of tetramethylguanidine and benzoyl chloride showed no depression of melting point of either sample.

Coumarins. II. The Acid-Catalyzed Reaction of Phenols with Simple α,β -Unsaturated Acids¹

TAKESHI AMAKASU² AND KIKUMASA SATO

Chemical Laboratory, Seimi Chemical Company, Ltd., Chigasaki, Kanagawa, Japan, and the Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama, Japan

Received October 8, 1965

The reaction of excess phenols with crotonic acid, in the presence of 2 equiv of anhydrous aluminum chloride, yielded 4-methyldihydrocoumarins. In contrast, 2-hydroxycrotonophenones were obtained in appreciable yields by aluminum chloride catalyzed reaction of equimolar amounts of phenols and crotonic acid in tetrachloroethane solution. Resorcinol reacts smoothly with acrylic acid in ethyl ester of polyphosphoric acid (PPE) at 90–95° to furnish a good yield of dihydroumbelliferone along with the corresponding melilotic acid, while the similar reaction with crotonic acid gives 3-hydroxyphenylcrotonate. The PPE-catalyzed reaction of less reactive phenols with these acids gave several kinds of products at higher temperature.

An earlier paper in this series³ described a direct method of preparing several dihydrocoumarins by the reaction of phenols with α,β -unsaturated nitriles in the presence of anhydrous aluminum chloride and dry hydrogen chloride. These studies have now been extended to simple α,β -unsaturated acids and their esters. While the acid-catalyzed reactions of phenols with more than five-membered α,β -unsaturated acids, such as cinnamic acid or β,β -dimethylacrylic acid, have been extensively studied,^{4,5} little is known of similar reactions with simple α,β -unsaturated acids and their derivatives.

It has been shown that crotonoyl chloride reacts with resorcinol in the presence of aluminum chloride to give 7-hydroxy-2-methylchromanone⁶ and that crotonic acid condenses with phenols in hydrofluoric acid solution to furnish 2-methylchromanones in good

yields.⁷ Recently Miyano and Matsui have reported that reaction of resorcinol with crotonic acid in the presence of zinc chloride gives 7-hydroxy-2-methylchromanone.⁸ No method of preparing simple dihydrocoumarins by the reaction of phenols with acrylic acid and with crotonic acid has yet appeared in the literature. The ring positions in the phenols are said to be unreactive toward crotonic acid in the presence of hydrochloric acid.^{4g}

We have now examined the reaction of phenols with simple α,β -unsaturated acids, such as acrylic acid, using anhydrous aluminum chloride or the ethyl ester of polyphosphoric acid (PPE). It has been found that the aluminum chloride catalyzed reaction of equimolar amount of phenols and crotonic acid gives the 2-hydroxycrotonophenones (II, $R_2 = CH_3$); the structures follow from the infrared spectra (Table I), which showed strongly hydrogen bonded OH bands at 3200–3300 cm^{-1} and carbonyl bands at 1640–1665 cm^{-1} . With excess phenol, mainly 4-methyldihydrocoumarins (I, $R_2 = CH_3$) (Table II), identical in properties with those previously reported,³ were obtained. Phenols, except for resorcinol, react with acrylic acid and with crotonic acid in PPE solution to give ethyl esters III and phenyl esters IV as main products, with very small amounts of 2-methylchromanones (V) and Michael addition products (VI) (Table III).

Although sulfuric acid, pyrophosphoric acid, 85% syrupy phosphoric acid, and a mixture of the phosphoric acid and pyrophosphoric acid were effective, optimum results were obtained with aluminum chloride or PPE. Heating periods over 5 hr did not afford

(1) This investigation was supported mainly by Asahi Glass Co. for which we are grateful.

(2) To whom inquiries should be directed at the Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama, Japan.

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

(4) Syntheses of dihydrocoumarins have been reported in the following references: (a) L. I. Smith and L. J. Spillane, *J. Am. Chem. Soc.*, **65**, 282 (1943); (b) H. A. Offe and W. Barkow, *Chem. Ber.*, **80**, 464 (1947); (c) J. D. M. Simpson and S. S. Israelstem, *J. S. African Chem. Inst.*, **2**, 165 (1949); (d) A. Lespagnol, J. Schmitt, and P. Brunand, *Bull. Soc. Chim. France*, **82** (1951); (e) W. Baker, R. F. Curtis, and J. F. W. McOmri, *J. Chem. Soc.*, 76 (1951); (f) N. G. p.H. Buu-Hoi, H. Le Bihan, F. Binon, and P. Ma P. Maleyran, *J. Org. Chem.*, **17**, 1122 (1952); (g) J. D. Simpson and H. Stephen, *J. Chem. Soc.*, 1382 (1956); (h) J. Colonge, E. Le Sech, and R. Marey, *Bull. Soc. Chim. France*, 776 (1957).

(5) Syntheses of chromanones have been described in the following references: (a) W. John and P. Günther, U. S. Patent 2,274,449 (1942); (b) H. A. Offe and W. Barkow, *Chem. Ber.*, **80**, 458 (1947); (c) A. R. Alertson, *Acta Polytech. Scand. Ser.*, **13**, No. 10, 1 (1961).

(6) J. H. Richards, R. Robertson, and W. Barkow, *J. Chem. Soc.*, 1610 (1948).

(7) O. Dann, G. Volz, and O. Huber, *Ann.*, **587**, 16 (1954).

(8) M. Miyano and M. Matsui, *Bull. Chem. Soc. Japan*, **31**, 397 (1958).

TABLE I
ANALYTICAL CHARACTERISTICS OF 2-HYDROXYCROTONOPHENONES (II)

R	Bp (mm) or mp, °C		2,4-DNP Mp, °C	Infrared cm ⁻¹		C, %		H, %	
	Obsd	Lit		O—H	C=O	Calcd	Found	Calcd	Found
H	77-78 (0.3)	140 (10) ^a	255-256 ^b	3250	1665	74.05	73.56	6.22	6.28
CH ₃	54-55 ^c	65-66 ^d	260 ^e	3200	1660	74.96	75.05	6.86	7.06
Cl	116-117 ^f	112 ^g	220-221	3300	1640	61.08	60.97	4.61	4.67

^a A. B. Sen and V. S. Misra, *J. Indian Chem. Soc.*, **26**, 339 (1949). ^b The semicarbazone had mp 177°. ^c Recrystallization solvent is petroleum ether. ^d K. von Auwers and E. Lammerhirt, *Ann.*, **431**, 1 (1920). Sen, *et al.*,^e reported bp 160° (10 mm) but no melting point for 2-hydroxy-5-methylcrotonophenone. ^e The semicarbazone had mp 209-210°. ^f Recrystallization solvent is ethanol. ^g A. B. Sen and S. S. Parmar, *J. Indian Chem. Soc.*, **30**, 720 (1953).

TABLE II
THE ALUMINUM CHLORIDE CATALYZED REACTION OF PHENOLS
WITH CROTONIC ACID

Compd R	Molar ratios ^a	Reaction temp, °C	Product composition, %	
			I	II
H	A	120-125	23	
H	B	140-145		10 ^b
CH ₃	A	130-135	22	
CH ₃	B	140-145		56
Cl	A	140-145	20	
Cl	B	130-135		31

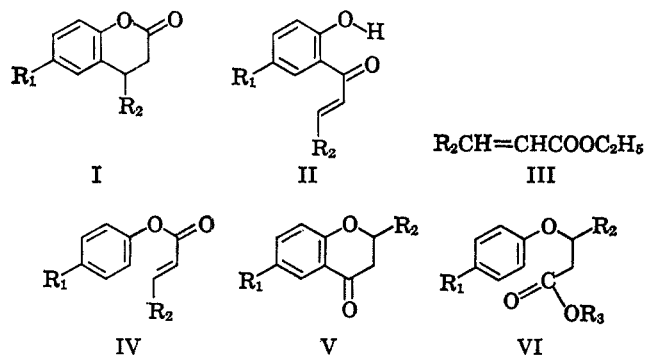
^a In A, the phenol:acid:AlCl₃ ratios were 2:1:2; in B, they were 1:1:2. Solvent used is *sym*-tetrachloroethane. ^b The yield of the isomer, 2-methylchromanone, was 10%.

TABLE III
THE PPE-CATALYZED REACTION OF PHENOLS WITH
 α,β -UNSATURATED ACIDS

Compd R ₁	R ₂	Reaction ^a temp, °C	Product composition, %				
			III ^b	IV	V	VI, R ₃ = H	VI R ₃ = Et
H	H	130-135	28	17		3	3
CH ₃	H	120-125	32	19		6	5
Cl	H	150-155	24	15		3	
OCH ₃	H	120-125	25	25		4	
H	CH ₃	150-155	24	31	1		1
CH ₃	CH ₃	150-170	56	9	5		2
Cl	CH ₃	165-175	89	11	1		2
OCH ₃	CH ₃	160-185	46	10	6		2

^a The phenol-acid molar ratios were 1:1.25 and the PPE quantity used was 195 g/mole of the phenol. ^b Yield based on the acid.

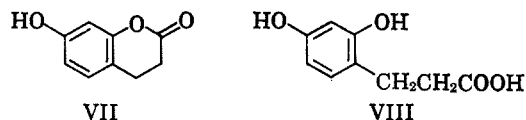
increased yields. Dihydrocoumarins I (R₂ = H) and 2-hydroxyacrylophenones II (R₂ = H) could not be obtained when the less reactive phenols were treated with acrylic acid in the presence of aluminum chloride or PPE. The data, summarized in Tables II and III, indicate the scope of these procedures.



R₁ = H, CH₃, Cl, OCH₃; R₂ = H, CH₃; R₃ = H, C₂H₅

Whereas a small amount of 2-methylchromanones (V, R₂ = CH₃) could be obtained by the PPE-catalyzed reaction of phenols with crotonic acid, none of the corresponding chromanones (V, R₂ = H) were obtained by the similar reaction with acrylic acid. In contrast to these results, it is interesting to note that β -phenoxybutyric acids (VI, R₂ = CH₃, R₃ = H) could not be isolated from the reaction with crotonic acid in PPE solution, while a similar reaction with acrylic acid gave β -phenoxypropionic acids (VI, R₂ = R₃ = H) in poor yields.

When resorcinol was treated with acrylic acid at a lower temperature in the presence of PPE, which has recently been reported to be an effective reagent for intramolecular dehydration reactions and to be less acidic than polyphosphoric acid,⁹ the lactone VII was obtained (58%), accompanied by the acid VIII in 23% yield. On the other hand, only the ester, *m*-hydroxyphenyl crotonate, is obtained, in 18.5% yield on treatment of resorcinol with crotonic acid in excess PPE solution at 90-95° for 8 hr.



In order to explain the results in Table II, the mechanism suggested by Groggins¹⁰ can be applied to the behavior of crotonic acid toward aluminum chloride, and the need for at least two molecular proportions of aluminum chloride may be elucidated as shown in Scheme I.

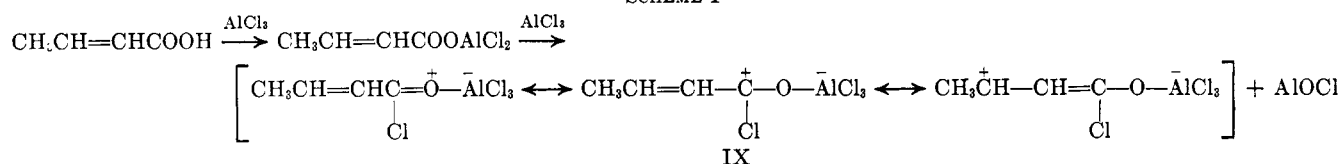
The liberation of hydrogen chloride observed on cold treatment of crotonic acid with aluminum chloride results from the first step, in which the aluminum chloride salt of the acid may be formed. At the high temperature shown in Table II, the salt presumably interacts with the second mole of the catalyst to provide the ionic resonance complex IX containing two electrophilic centers (second step). The data in Table II are consistent with this view.

From the results described above, the intermolecular reaction of phenols and the α,β -unsaturated acids was found to have the inconvenient complication that it may not be directed efficiently to a particular product. The esters IV have not yet been found to undergo intramolecular addition to dihydrocoumarins I, although the aluminum chloride catalyzed cyclization of

(9) T. Mukaiyama and T. Hata, *Bull. Chem. Soc. Japan*, **34**, 99 (1961).

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

SCHEME I



phenyl β,β -dialkylacrylates or cinnamates has been shown to give dihydrocoumarins.¹¹

Experimental Section¹²

Materials.—PPE was prepared by the procedure of Mukaiyama and Hata⁹ from phosphorus pentoxide (2 moles) and ethanol (5 moles). Other materials were obtained from commercial sources.

4-Methyldihydrocoumarins (I). General Procedure.—To a stirred suspension of anhydrous aluminum chloride (0.4 mole) in *sym*-tetrachloroethane (40 ml) was added dropwise at 15–20° a solution of the phenol (0.4 mole) and crotonic acid (0.2 mole) in *sym*-tetrachloroethane (40 ml) over a period of 0.5 hr, during which hydrogen chloride was evolved vigorously. The mixture was gradually heated in oil bath and kept for 5 hr at the temperature shown in Table II; thereafter the mixture was chilled and poured over water containing crushed ice and concentrated hydrochloric acid. The organic layer was separated from the aqueous layer, which then was shaken with chloroform. The extract was combined with the separated organic material and then was washed with saturated sodium bicarbonate solution and water. After it was dried over anhydrous magnesium sulfate and the solvents were removed, the residue was distilled under reduced pressure to give the crude lactone I (containing the phenol as a contaminant). The analytical sample was prepared by cold treatment of the crude product with dilute sodium hydroxide solution followed by distillation, recrystallization, or vapor phase chromatographic fractionation. The infrared spectra of the 4-methyldihydrocoumarins were identical with those reported previously.³ The dihydrocoumarins were also obtained in lower yields by passing dry hydrogen chloride through reaction mixture of the phenol (1 mole), the acid (0.2 mole), and anhydrous aluminum chloride (0.4 mole) at 120–145° for 5 hr.

2-Hydroxycrotonophenones (II).—These compounds were prepared by adding dropwise a solution of 0.2 mole of the phenol and 0.2 mole of crotonic acid dissolved in 60–110 ml of *sym*-tetrachloroethane to a suspension of 0.4 mole of anhydrous aluminum chloride in 50 ml of *sym*-tetrachloroethane, followed by treatment of the reaction mixture according to the procedure already described.

The reaction of phenol (37.6 g, 0.4 mole) with crotonic acid (34.4 g, 0.4 mole) under the condition described above gave 13.5 g of a yellow oil consisting of 2-hydroxycrotonophenone and 2-methylchromanone. An ethereal solution of the mixture was treated with 3 *N* sodium hydroxide to provide a pale yellow solid, which was collected by filtration. 2-Hydroxycrotonophenone (5.9 g, 10%) was isolated from the solid after treatment with hydrochloric acid followed by extraction and distillation. The filtrate was extracted with ether and the ethereal extract was washed with water and dried over magnesium sulfate. After removal of ether, the residue was fractionated by vacuum distillation to give 6 g (10%) of 2-methylchromanone, bp 82–84° (1 mm), which crystallized after standing for a few weeks: mp 31–32° (lit.¹³ 32°); $\nu_{\text{max}}^{\text{film}}$ 1690 (ketone C=O), 1610 (aromatic C=C), and 765 cm^{-1} (*ortho*-disubstituted). The chromanone gave the 2,4-dinitrophenylhydrazone, mp 232–233° (lit.¹³ mp 236°).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.05; H, 6.22. Found: C, 74.05; H, 6.15. Results with individual compounds are shown in Table I.

3,4-Dihydroumbelliferone (VII) and 4-Hydroxymelilotic Acid (VIII).—A mixture of 22 g (0.2 mole) of resorcinol, 18 g (0.25

mole) of acrylic acid, and 52 g of PPE was stirred and held at 90–95° by warming on an oil bath for 7 hr. The reaction mixture was poured over cold water and extracted with three 100-ml portions of ether. The ethereal solution was washed with saturated sodium bicarbonate and water. After it was dried over magnesium sulfate and the solvent was removed, the residue (19 g, 58%) was a mass of crystals, mp 115–120°. Attempts to obtain pure lactone VII from the residue by recrystallization failed. The solid was heated with water for 1 hr, thus causing the lactone to go gradually into solution, and then was allowed to stand. Hard crystals separated and were filtered. The recrystallization from water gave 4-hydroxymelilotic acid (VIII): mp 155° (lit.¹⁴ mp 165°); $\nu_{\text{max}}^{\text{KBr}}$ 3470, 3360 (phenolic O–H), 1705 (acid C=O), 1625, 1530 (aromatic C=C) and 840, 803 cm^{-1} (aromatic substitution peaks). The melilotic acid was readily soluble in dilute sodium carbonate and gave a positive ferric chloride test.

Anal. Calcd for $\text{C}_9\text{H}_8\text{O}_4$: C, 59.33; H, 5.53. Found: C, 59.02; H, 5.51.

The acid VIII (0.5 g) was heated on a Mantol heater at 160–170° for 2 hr. The melt which formed was allowed to cool and was extracted with ether. The ethereal solution was washed with sodium bicarbonate and water. After drying (MgSO_4) and removal of solvent the residual crystals (0.4 g) melted at 126–132°. The recrystallization from toluene provided dihydroumbelliferone: mp 132–133° (lit.¹⁴ 132–133°); $\nu_{\text{max}}^{\text{KBr}}$ 3350 (O–H), 1760, 1735 (doublet, lactone C=O), and 850, 815 cm^{-1} (aromatic). It showed a positive ferric chloride test.

Anal. Calcd for $\text{C}_9\text{H}_8\text{O}_3$: C, 68.85; H, 4.91. Found: C, 65.44; H, 4.80.

4-Hydroxymelilotic acid was also obtained in 1 and 22% yields, respectively, from the mother liquor and the alkaline solution by the usual procedure.

3-Hydroxyphenylcrotonate.—The procedure for the preparation of dihydroumbelliferone VII was followed using 55 g (0.5 mole) of resorcinol, 64.5 g (0.75 mole) of crotonic acid, and 105 g of PPE. The reaction was carried out at 90–95° for 8 hr. After removal of benzene, the residual oil was fractionated to give 16.5 g (18.5%) of a viscous oil: bp 135–137° (1 mm); $\nu_{\text{max}}^{\text{film}}$ 3430 (O–H), 1717 (ester C=O), 1660 (alkenic C=C), 1610, 1490 (aromatic C=C), and 990 cm^{-1} (*trans* C–H). It solidified and melted at 50–52°. The new compound, 3-hydroxyphenyl crotonate, was insoluble in sodium carbonate solution until the solution was heated, and when boiled with saturated sodium carbonate solution it was converted to the starting materials. The ester showed a positive ferric chloride test.

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_3$: C, 67.40; H, 5.66. Found: C, 67.06; H, 6.06.

PPE-Catalyzed Reaction of Phenols with α,β -Unsaturated Acids.—The procedure for the reaction of resorcinol was followed using the condition given in Table III. The ethereal extract was thoroughly washed with saturated sodium bicarbonate solution and water. The alkaline solution was stirred with carbon black, filtered, and acidified with hydrochloric acid. The phenoxypropionic acid (VI, $\text{R}_2 = \text{R}_3 = \text{H}$) which deposited was collected by filtration. The analytical sample was prepared by recrystallization from the appropriate solvent.

Fractional distillation of the extract gave the ester III and a mixture of IV, V, and VI ($\text{R}_3 = \text{Et}$) contaminated with the phenol and by-products that could not be identified. Each separation of products IV, V, and VI ($\text{R}_3 = \text{Et}$) was effected by vapor phase chromatography employing a Shimadzu Model GC-1B operated with a 2.25-m column packed with silicone oil (5%) on Diasolid M using a condition described in Table IV. The retention times are also shown in Table IV. Quantitative determinations were made to estimate the areas under the curves by multiplying the height of a peak by its half-width.

Analytical data for the hitherto unknown compounds VI ($\text{R}_2 = \text{CH}_3$) are described in Table V, and the physical properties

(11) J. Colonge and R. Chambard, *Compt. Rend.*, **233**, 1464 (1951).

(12) All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Hitachi Model EPI-S2 spectrophotometer.

(13) G. W. K. Cavill, F. M. Dean, A. Mc Gookin, B. M. Marshall, and A. Robertson, *J. Chem. Soc.*, 4579 (1954).

(14) W. D. Langley and R. Adams, *J. Am. Chem. Soc.*, **44**, 2320 (1922).

of compounds V and VI ($R_2 = R_3 = H$) are summarized in Table VI.

TABLE IV

RETENTION TIMES OF COMPOUNDS IV, V, AND VI ($R_3 = Et$)

Compd		Column temp, °C	He carrier gas flow rate, cc/min	Retention times, min		
R_1	R_2			IV	V	VI
H	H	173	80	2.0	7.6	
CH ₃	H	195	100	1.6	5.0	
Cl	H	173	80	4.4		
OCH ₃	H	173	80	5.7		
H	CH ₃	173	80	4.2	6.0	8.0
CH ₃	CH ₃	173	80	6.2	8.5	11.2
Cl	CH ₃	173	80	7.8	11.6	15.6
OCH ₃	CH ₃	195	100	4.7	5.8	7.8

TABLE V

ETHYL β -PHENOXYBUTYRATES (VI, $R_2 = CH_3$)

Compd R_1	Infrared cm^{-1}		C, %		H, %	
	C=O	C-H (aromatic)	Calcd	Found	Calcd	Found
H	1742	750, 690	69.21	69.35	7.74	7.68
CH ₃	1723	810	70.24	70.05	8.16	7.99
Cl	1740	825	59.41	59.39	6.19	6.15
OCH ₃	1740	825	65.53	65.31	7.61	7.30

TABLE VI

IDENTIFICATION OF PRODUCTS V ($R_2 = CH_3$) AND VI ($R_2 = R_3 = H$)

Compd R_1	Mp, °C		2,4-DNP, Mp, °C
	Obsd	Lit.	
V			
H	31-32	32 ^a	236-237 ^a
CH ₃	51-52	52-54 ^b	246-248
Cl	103-103.5	98-99 ^b	254-256
OCH ₃	63-64	65-67 ^b	235-236
VI			
H	95-95.5	98 ^c	
CH ₃	146.5	146 ^d	
Cl	135	138-139 ^d	
OCH ₃	110.5-111	109 ^e	

^a See ref 13. ^b See ref 7. ^c S. G. Powell, *J. Am. Chem. Soc.*, **45**, 2708 (1923). ^d D. Chakravarti and J. Dutta, *J. Indian Chem. Soc.*, **16**, 639 (1939). ^e J. Colonge and A. Guyot, *Bull. Soc. Chim. France*, 1228 (1957).

Acknowledgment.—The authors wish to express their gratitude to Mr. T. Itakura for capable technical assistance in these experiments and to Mr. M. Kimura for help in isolating products by means of gas chromatography. The authors are also indebted to Professor S. Abe for his kind advice and to Miss T. Hara for microanalyses.

Homolytic Autoxidative Decarboxylation of Aromatic Acids¹

W. H. STARNES, JR.

Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas

Received December 13, 1965

Aromatic carboxylic acids undergo homolytic decarboxylation in aromatic solvents at 125–200° in the presence of oxygen and large amounts of di-*t*-butyl peroxide or *t*-butyl hydroperoxide. Cobalt salts exert a strong catalytic effect on the reaction, and evidence that this effect results from direct oxidation of the substrate by cobalt(III) is presented. Decarboxylation of the aryloxy radicals thus formed gives aryl radicals, whose attack upon solvent affords biaryls in yields ranging up to 50%. Yields are much lower in the absence of cobalt, under which conditions the main course of the reaction is suggested to involve abstraction of hydrogen from the carboxyl group by peroxy and/or hydroxy radicals. The preferential entrapment of aryl radicals by solvent is discussed in terms of absolute rate constants calculated from literature data; these calculations suggest that the phenyl radical does not differ significantly from other carbon radicals in its rate of reaction with oxygen.

A puzzling phenomenon encountered in the liquid phase autoxidation of alkylaromatic compounds is the extraordinary inertness of substrates containing nuclear carboxyl groups. To cite a classic example, autoxidative conversion of *p*-toluic acid to terephthalic acid occurs to only a limited extent under conditions where autoxidation of *p*-xylene to *p*-toluic acid proceeds with ease.^{2,3} Although the electron-withdrawing properties of carboxyl undoubtedly retard the abstraction of

benzylic hydrogen by peroxy radicals, whose electrophilicity is well established,⁴ the idea that an electronic effect is the sole cause of the lowered reactivity seems to be vitiated by the observation that esters and certain other derivatives of alkylbenzoic acids autoxidize readily under conditions where the acids themselves are essentially inert.^{2a,c} Alternative explanations for the behavior of the acids need to be considered, and the present investigation was undertaken to test a particularly intriguing possibility, *viz.*, that the carboxyl group is intimately involved in the autoxidation chain. Thus, if homolytic abstraction of carboxyl hydrogen were to occur, loss of carbon dioxide would follow, and reaction of the resulting aryl radicals with oxygen might eventually lead to substances (phenols, phenoxy radicals) capable of acting as inhibitors. However, at the time our work was begun there was little evidence which could be cited in support of this sequence. The very strong acid O–H bond⁵ was known to be notoriously unreactive toward free radicals, and

(1) Presented in part at the 18th Southwest Regional Meeting of the American Chemical Society, Dallas, Texas, Dec., 1962. For a preliminary account, see W. H. Starnes, Jr., *J. Am. Chem. Soc.*, **84**, 2270 (1962).

(2) For discussion and documentation of the refractivity of alkylaromatic carboxylic acids toward autoxidation, see (a) W. G. Toland and E. L. Nimer, *Proceedings of the Fourth World Petroleum Congress*, Section IV, Carlo Colombo Publishers, Rome, 1955, p 39; (b) D. J. Loder, U. S. Patent 2,245,528 (1941); (c) I. E. Levine, U. S. Patent 2,653,165 (1953); (d) D. S. P. Roebuck, U. S. Patent 2,644,840 (1953).

(3) Readers who are familiar with this subject will recognize that these remarks are meant to apply only to "conventional" liquid phase autoxidation systems, *i.e.*, systems containing no components other than substrate, solvent, transition metal catalysts, and small amounts of a free radical initiator. Alkyl aromatic carboxylic acids are readily oxidized by certain modified autoxidation procedures which involve use of various "promoters" (*e.g.*, cooxidants, bromine compounds), and a number of commercial processes for producing aromatic polycarboxylic acids are based on such systems. Cf. W. G. Toland and S. J. Lapporte, *Ind. Eng. Chem. Annual Rev. Suppl.*, **68** (1963), and other reviews in this series.

(4) (a) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956); (b) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

(5) L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).