

*Anal.* Calcd. for  $C_6Cl_4O_2$ : C, 29.1; Cl, 57.3. Found: C, 28.93; Cl, 57.50.

Under the same reaction conditions as above, except that refluxing hexane was used as solvent (b.p. 68°), the reaction of fuming nitric acid with the phenol was violently fast, and the product was worked up right after the addition. By filtering the reaction product through a sintered-glass funnel, from 20 g. of pentachlorophenol used, there was isolated 2.8 g. (15.2%) of chloranil, m.p. 280–290°. From the filtrate which was treated with ice water, there was isolated 10.5 g. of red product, m.p. 118–119°. Infrared analysis indicated that this was tetrachloro-*o*-benzoquinone, 56.9% yield. No 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadiene was isolated or detected.

**Chloranil from 2,3,4,5,6-Pentachloro-4-pentachlorophenoxy-2,5-cyclohexadiene.**—To 2.0 g. of the cyclohexadiene there was added 4.0 ml. of fuming nitric acid. The solution turned red instantaneously and a yellow solid precipitated. This mixture was kept at room temperature overnight whereupon the red color of the solution disappeared. Excess of water was added to the reaction product and the mixture was filtered to give pure chloranil, m.p. 290°, wt., 1.1 g. or 59.2%.

**Acknowledgment.**—The author wishes to thank Dr. R. Dowbenko for stimulating discussion and suggestions and Drs. H. L. Gerhart, S. W. Gloyer, R. M. Christerson, and M. Wismer for continued interest and encouragement.

### Preparation of Mono- and Difluorobenzoic Acids and Their Vinyl Esters

H. HOPFF AND G. VALKANAS<sup>1</sup>

Laboratory of Organic Chemical Technology, Swiss Federal Institute of Technology, Zurich, Switzerland

Received February 21, 1962

All isomeric fluorobenzoic acids are known. Many methods may be used for their preparation, of which that from the amino acids<sup>2a,b,c</sup> and their esters,<sup>2d</sup> employing the Schiemann reaction, is the most common. The oxidation of fluorotoluenes with potassium permanganate and chromic acid is also reported, but has been found to lead predominantly to nuclear oxidation.<sup>3</sup> Nitric acid oxidation of fluorobenzyl chlorides is more satisfactory.<sup>4</sup>

Fluorotoluenes can be oxidized at high temperature under pressure with yields up to 95% with a 20% nitric acid solution to essentially pure carboxylic acids. The oxidation is carried out in an autoclave, and the nitric acid solution used is calculated to be 10% in excess in nitric acid. More concentrated solution or more excess nitric

acid causes nuclear oxidation and depresses the yield. The oxidation under the described conditions starts at 140–150°, but for a rapid and complete reaction, higher temperatures must be used. When the reaction is kept at 180–200°, or, better, at 190–195°, heating for three to four hours is sufficient. Since the oxidation is an exothermic reaction, care must be taken to keep below 200°. For better results, pressure is needed. Conditions at which a pressure of 930 p.s.i. was developed led to a 10% better yield than for 720 p.s.i.

Difluorotoluenes<sup>5</sup> are advantageously oxidized likewise, but with 15% nitric acid solution. The difluorobenzoic acids thus prepared are the 2,5-, 2,4-, and 3,4-difluorobenzoic acids, of which the 3,4-difluorobenzoic acid prepared by the iodoform reaction on the corresponding difluoroacetophenone is known.<sup>6</sup> As shown in Table I, smaller yields result in the case of oxidation of difluorotoluenes, although still in the region of 65–70%. It is characteristic that the melting points of fluoro- and difluorobenzoic acids are very close to that of benzoic acid except when fluorine is in the 4-position; however, 3,4-difluorobenzoic acid is no exception.

TABLE I

Benzoic acid	Yield, %	M.p., °C.
<i>p</i> -Fluoro-	96	181–182
<i>m</i> -Fluoro-	89	121–122
<i>o</i> -Fluoro-	82	120–121
2,5-Difluoro-	69	118–119
3,4-Difluoro-	70	119–120
2,4-Difluoro-	65	182–184

Preparation of the vinyl esters of the three mono-fluorobenzoic acids followed the transesterification method of Adelman.<sup>7</sup> Difficulty was encountered in finding an efficient inhibitor for the polymerization reaction during the transesterification. At a reaction temperature of 60°, hydroquinone was found inefficient, and low-molecular-weight polymers of polyvinyl acetate and polyvinyl fluoro-benzoate were formed. With traces of sulfur, however, the vinyl fluoro-benzoates were obtained free of polymeric impurities. The transesterification reaction proceeds slower with the *p*-fluorobenzoic acid.

TABLE II

Vinyl-benzoate	Yield, %	B.p., °C., 14 mm.	$n_D^{20}$
<i>p</i> -Fluoro-	82.5	78–79	1.4843
<i>m</i> -Fluoro-	89.0	80–81	1.4725
<i>o</i> -Fluoro-	84.2	89–89.5	1.5048

All three vinyl fluoro-benzoates prepared polymerize readily when treated with benzoyl peroxide.

(1) To whom inquiries should be addressed.

(2) (a) J. Pippy and F. Williams, *J. Chem. Soc.*, 1466 (1934); (b) E. D. Bergmann, J. Berkovic, and R. Ikan, *J. Am. Chem. Soc.*, **78**, 6039 (1956); (c) L. S. Fosdick and E. E. Campaigne, *ibid.*, **63**, 974 (1941); (d) E. Bennet and C. Niemann, *ibid.*, **72**, 1800 (1950).

(3) M. Slothouwer, *Rec. trav. chim.*, **33**, 325 (1914).

(4) I. Nazarov and A. Semenovskii, *Izv. Akad. Nauk. SSSR. Khim. Nauk.*, 1101 (1957); *Chem. Abstr.*, **52**, 6256d (1958).

(5) H. Hopff and G. Valkanas, unpublished work.

(6) J. Minor and C. Vanderwerf, *J. Org. Chem.*, **17**, 1429 (1952).

(7) B. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

For the same amount of catalyst, the *ortho* isomer polymerizes faster than the *meta* and *para* isomers. The esters of *o*-fluorobenzoic acid are known not to correlate in behavior with those the *m*- and *p*-isomers, as shown in the hydrolysis of ethyl *o*-fluorobenzoate.<sup>8</sup>

The *p*-fluorobenzoic acid is readily nitrated<sup>9</sup> to give 3-nitro-, 4-fluorobenzoic acid. In a sulfuric acid-nitric acid mixture, the nitration proceeded to 86% of mononitrated product, compared to 50% yield indicated in the literature.<sup>9</sup> The ethyl ester of this compound was converted to ethyl 4-fluoro-3-aminobenzoate.

### Experimental

**I. *p*-Fluorobenzoic Acid.**—In a stainless steel autoclave (0.5-l. capacity), 45 g. (0.408 mole) of *p*-fluorotoluene and 264 ml. of 20% nitric acid (0.848 mole in nitric acid) were introduced. The mixture was heated for 2 hr. to 190–195°, and maintained for 4 hr. at this temperature. A pressure of 1000 p.s.i. was developed. On opening of the autoclave, brown nitric oxides escaped. The oxidation product was found as precipitate on the bottom of the autoclave. The solid was dissolved in cold 5% sodium hydroxide solution, filtered, and acidified. The white *p*-fluorobenzoic acid was filtered, washed with cold water, and dried at 100°; yield 55 g., m.p. 181–182°.

If the oxidation is carried out in a glass-lined autoclave, the purification is unnecessary. The acid is collected by filtration in its crystalline form and, on being washed to uncolored washings, it is obtained almost analytically pure.

**II. *m*-Fluorobenzoic Acid.**—A 45-g. sample of *m*-fluorotoluene was oxidized with 264 ml. of 20% nitric acid solution as described for the *p*-fluorobenzoic acid. A 51.1-g. sample of *m*-fluorobenzoic acid was isolated; m.p. 121–122°.

**III. *o*-Fluorobenzoic acid.**—A 15-g. sample of *o*-fluorotoluene was oxidized with 86 ml. of 20% nitric acid solution as above. It was heated for 1 hr. to 190–200°. A 15.7-g. sample of *o*-fluorobenzoic acid (82%), m.p. 120–121°, was isolated.

**IV. 2,5-, 2,4-, and 3,4-difluorotoluenes** were oxidized in an autoclave with a 10% excess of 15% nitric acid solution, and heated to 195° as described above. The difluorobenzoic acids: **2,5-difluoro-**, m.p. 118–119° (*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>O<sub>2</sub>F<sub>2</sub>: F, 24.05. Found: F, 23.68); **2,4-difluoro-**, m.p. 182–184° (*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>O<sub>2</sub>F<sub>2</sub>: F, 24.05. Found: F, 23.94); and **3,4-difluoro-**, m.p. 119–120°; were obtained as crystalline compounds with yields 69, 65, and 70%, respectively.

By refluxing the 2,5-difluorobenzoic acid with ethanol partly saturated with hydrogen chloride, the ethyl ester was formed. The **ethyl-2,5-difluorobenzoate**, was obtained as a colorless liquid at 98–99°/18 mm.

**V. Nitration of *p*-Fluorobenzoic Acid.**—An 8-g. sample of finely powdered *p*-fluorobenzoic acid was added in small portions to 70 ml. of 1:2 (v./v.) mixture of nitric acid (*d* 1.46) and sulfuric acid (*d* 1.82) with good agitation at 0°. Within 1 hr. the suspension dissolved. After 16 hr. at room temperature the mixture was poured into 100 g. of ice, and the precipitated **3-nitro-4-fluorobenzoic acid**, washed with cold water and dried, melted at 119–120° (lit.,<sup>11</sup> 122°); yield 9 g. (86%). By refluxing the ester for 6 hr. in 0.5 *N* ammonium chloride solution containing 40 g. of powdered iron, the **ethyl 3-amino-, 4-fluorobenzoate** was formed. The solution was filtered hot and the amino

ester extracted with ether. Distillation yielded a yellowish liquid, 148–149°/14 mm; yield 89%.

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>NF: F, 9.88. Found: F, 9.73.

**VI. Vinyl *p*-Fluorobenzoate.**—A 20-g. sample of powdered *p*-fluorobenzoic acid was added to 150 ml. of freshly distilled vinyl acetate followed by 1 g. of mercury acetate and 0.5 g. of sulfur. The reaction was initiated by adding 0.5 ml. of 20% oleum, and carried out at 60°. After 48 hr. the reaction mixture was filtered and the filtrate received in ether. The unchanged acid (3.3 g.) was extracted with 10% sodium bicarbonate. By distillation the vinyl *p*-fluorobenzoate was obtained at 77–80°/14 mm; yield 16.3 g. (82.5% calculated on the changed acid).

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>F: C, 65.01; H, 4.22; F, 11.44. Found: C, 65.11; H, 4.22; F, 11.2.

**VII. Vinyl *o*-Fluorobenzoate.**—As for the previous example, this ester was prepared from 10 g. of *o*-fluorobenzoic acid; yield was 10.5 g. After 48 hr. of heating at 60°, no unchanged acid was recovered; b.p. 89–89.5°/14 mm.

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>F: C, 65.01; H, 4.22; F, 11.44. Found: C, 65.08; H, 4.25; F, 11.1, 10.92.

**VIII. Vinyl *m*-Fluorobenzoate.**—From 18 g. of *m*-fluorobenzoic acid 17.9 g. of the vinyl ester was prepared, b.p. 80–81°/14 mm. After heating for 48 hr. at 60°, the acid was found to be completely changed.

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>F: F, 11.44. Found: F, 11.23.

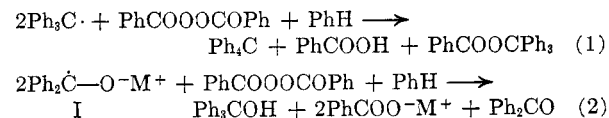
## Reaction of a Ketyl with Benzoyl Peroxide in Benzene

JOHN F. GARST, DONALD WALMSLEY,  
AND WILLIAM R. RICHARDS

Department of Chemistry, University of California, Riverside,  
California

Received March 2, 1962

Alkali benzophenone ketyls (I) are not only free radicals, but also must be good nucleophiles. In addition, they sometimes enter into reactions in which they function as alkali metal atom donors.<sup>1</sup> In fact, many of the reactions of these and other alkali metal adducts of organic compounds<sup>2</sup> can be interpreted in the latter fashion. Since benzoyl peroxide is subject to decomposition by free radicals,<sup>3</sup> it would be expected to react with I. Moreover, I bears a marked structural resemblance to triphenylmethyl, which undergoes an unusual reaction with benzoyl peroxide in benzene, resulting in the triphenylmethylation of the solvent (eq. 1).<sup>4</sup> A similar reaction involving I rather than triphenyl-



(1) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).

(2) For many examples, see W. Schlenk, *et al.*, *Ann.*, **463**, 1 (1928).

(3) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(4) H. Wieland, T. Ploetz, and H. Indest, *Ann.*, **532**, 166 (1937); G. S. Hammond, James T. Rudesill, and Frank J. Modic, *J. Am. Chem. Soc.*, **73**, 3929 (1951).

(8) D. P. Evans, J. J. Gordon and, H. B. Watson, *J. Chem. Soc.*, 1430 (1937).

(9) A. Rouche, *Bull. Acad. Roy. Med. Belg.*, 534 (1921).