

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.⁸

The *p*-fluorobenzoic acid is readily nitrated⁹ 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.⁹ 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 C₇H₄O₂F₂: F, 24.05. Found: F, 23.68); **2,4-difluoro-**, m.p. 182–184° (*Anal.* Calcd. for C₇H₄O₂F₂: 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.,¹¹ 122°); 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 C₉H₇O₂NF: 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 C₉H₇O₂F: 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 C₉H₇O₂F: 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 C₉H₇O₂F: F, 11.44. Found: F, 11.23.

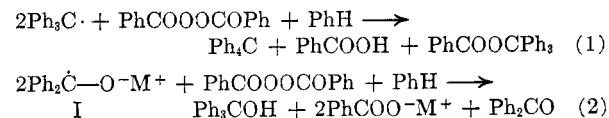
Reaction of a Ketyl with Benzoyl Peroxide in Benzene

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

Department of Chemistry, University of California, Riverside,
California

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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.¹ In fact, many of the reactions of these and other alkali metal adducts of organic compounds² can be interpreted in the latter fashion. Since benzoyl peroxide is subject to decomposition by free radicals,³ 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).⁴ 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).

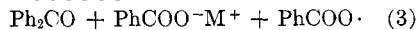
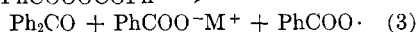
(3) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(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).

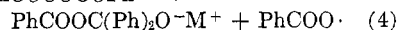
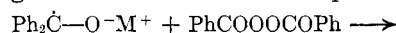
(8) D. P. Evans, J. J. Gordon and, H. B. Watson, *J. Chem. Soc.*, 1430 (1937).

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

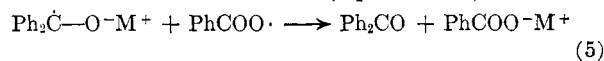
methyl would lead to triphenylcarbinol (equation 2). Homolytic induced decomposition of the peroxide by I without attack on the solvent would probably lead to high yields of alkali benzoate, whether the reaction proceeded by direct metal atom (or electron) transfer to the peroxide (equation 3) or by attack of the organic free radical to



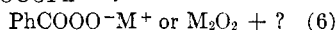
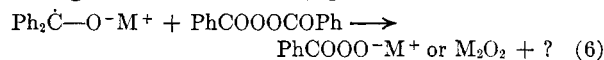
give an unstable initial product (equation 4).



Effective scavenging of the benzoyloxy radicals by ketyl would convert these to alkali benzoate with no loss of carbon dioxide (equation 5), while less



efficient scavenging would permit carbon dioxide production. A remaining possible course for the reaction would involve the decomposition of the peroxide through purely nucleophilic attack of I which might lead to products in which the peroxide linkage remained intact (equation 6). These con-



siderations led us to investigate the reaction of alkali benzophenone ketyl with benzoyl peroxide in benzene.

We find that the reaction proceeds rapidly at room temperature with the production of nearly quantitative yields of benzoic acid (on work-up) and nearly quantitative recovery of the benzophenone employed in the ketyl preparation. No peroxidic products could be detected. The stoichiometry of the reaction, then, is given by the sum of equations 3 and 5, and reactions 2 and 6 are excluded.

While the data do not permit distinction between the mechanisms of equations 3 and 4, the direct atom (or electron) transfer has the virtue of simplicity. The experimental result is novel in that it is the first reported example of the induced decomposition of benzoyl peroxide by an anion-radical and in that it is a rare example of a homolytic decomposition of benzoyl peroxide in benzene which does not lead to attack on the solvent.

Experimental

Reaction of Ketyl with Benzoyl Peroxide. Method 1.—Sodium benzophenone ketyl was prepared under solvent (benzene) vapor pressure in a vessel with two arms separated by a sintered glass disk. When the reaction of the sodium with the benzophenone had produced an intensely colored blue solution, this solution was filtered into the other arm of the vessel, which contained a solution of benzoyl peroxide. The blue color was immediately discharged, and a white gelatinous precipitate appeared. Upon dissolution of this precipitate in water, followed by acidification and cooling, benzoic acid was deposited. No other products were isolated. The methods described below were employed for determinations of yields.

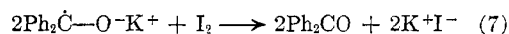
Method 2.—A solution of 0.169 mole of benzoyl peroxid in benzene was placed in a graduated dropping funnel, which was in turn attached to a 500-ml. round-bottomed flask. In the flask was placed sodium-potassium alloy (0.16 mole of each alkali metal) and benzophenone (0.318 mole), along with 100 ml. of benzene and a magnetic stirring bar. The entire apparatus was degassed and flushed with prepurified nitrogen. Stirring of the benzophenone solution generated the ketyl, which was titrated with the peroxide solution from the dropping funnel. The titration was carried out over several hours, with continual stirring, and with the exercise of caution to avoid adding excess benzoyl peroxide at any time (*i.e.*, sufficient peroxide to cause complete disappearance of the blue color was never added). This precaution was taken in order to minimize the possible reaction of the peroxide with the metal directly. The experiment consisted, then, of successive periods in which the ketyl was alternately generated and titrated with the peroxide. A 0.0878 mole sample of benzoyl peroxide was allowed to react.

When the generation of the ketyl became noticeably slow, the experiment was halted, and the benzene was removed under vacuum. Small bits of alkali metal were visible in the residue but they were not quantitatively recovered. Extraction of the residue with ethyl ether led to the recovery of 0.306 mole of crude benzophenone (m.p. 44.5–47.0°, mixed m.p. 45.0–47.0°, infrared spectrum identical with benzophenone). The residue from the ether extraction was completely water-soluble and led to 0.175 mole of benzoic acid (recovered in two fractions, m.p. 121.5–122.5° and 121.0–122.0°, infrared spectrum identical with benzoic acid) corresponding to a 100% yield based on the peroxide.

In a duplicate run, potassium metal was employed instead of the alloy. Again the yield of benzoic acid and the recovery of the benzophenone were greater than 95%. Other runs with the alloy gave similar results.

In a control experiment, potassium metal was employed and stirred with benzoyl peroxide in benzene for 14 hr. The benzoyl peroxide was recovered nearly quantitatively.

Titration of Benzoyl Peroxide and Iodine with Ketyl.—In these experiments a filtered solution of potassium benzophenone ketyl was employed to titrate a weighed quantity of iodine (and, separately, benzoyl peroxide) in an all-glass apparatus which permitted the preparation and storage of the ketyl solution in a reservoir and subsequent transference through filters to a buret. The appearance of a permanent blue color would ideally be taken as the end point, but this was never achieved in the titration of peroxide. In two sets of such experiments in which a slowly fading end point was obtained, the molar ratio of ketyl to benzoyl peroxide treated was calculated, on the assumption that the reaction with iodine is quantitatively given by eq. 7, to be 2.3 and 1.7.



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A Convenient Synthesis of Axial Amines

AJAY K. BOSE, JOHN F. KISTNER, AND LEON FARBER

*Department of Chemistry and Chemical Engineering,
Stevens Institute of Technology, Hoboken, New Jersey*

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The established procedure for the preparation of an axial amine is the hydrogenation of the appro-