

oxygen equivalent data may be obtained by the dichromate method.

**Limitations.**—The one limitation to this method is the use of iodic acid as an oxidizing agent. Not all compounds are completely oxidized by this reagent at 200°. The literature, however, reveals that a great many compounds can be oxidized successfully by iodic acid under conditions here specified.

In the case of compounds with high molecular weights, the determination of the molecular formula has the same limitations in accuracy as do the traditional combustion methods.

The question of compounds containing nitrogen, sulfur and halogens has not yet been investigated in this Laboratory. However, both Strebinger, and Stanek and Nemes have oxidized successfully a number of such compounds with iodic acid. It is the opinion of the authors that the presence of nitrogen, halogen, or sulfur in an organic compound which can be completely oxi-

dized should offer no complications to the method here described.

When one considers (1) the simple apparatus, (2) adaptability of the procedure to intermittent operation, (3) the amount of information derived from a single analysis, and (4) rapidity of analysis (less than two hours), it is evident that this method offers at least a partial solution to an important organic technique.

### Summary

A simple apparatus for the determination of oxygen equivalence and percentage carbon by means of iodic acid oxidation has been described.

A modification of the Pettenkofer method for the determination of carbon dioxide has been devised.

Equations have been derived by means of which the empirical formula of an organic compound can be established readily from the data supplied by the above method.

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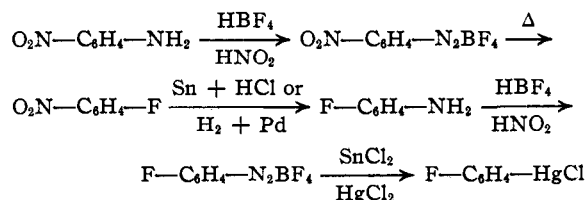
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SCHOOL OF PHARMACY, UNIVERSITY OF MARYLAND]

## Fluorinated Aromatic Mercurials

BY MELVIN F. W. DUNKER AND EDGAR B. STARKEY

The preparation and properties of some fluorinated aromatic mercurials are described. These compounds have been tested for antiseptic activity and the results are reported in detail elsewhere.<sup>1</sup>

The direct mercuriation of fluorobenzene by refluxing in glacial acetic acid with mercuric acetate yielded about 10% of *o*-fluorophenylmercuric chloride. The mercuriation of *p*-fluorophenol with mercuric acetate in water at room temperature yielded a monomercurial assumed to have the mercury ortho to the hydroxyl since *p*-chlorophenol is reported to mercurate in that position.<sup>2</sup> The fluorophenylmercuric chlorides were prepared as shown by the equations below



While the replacement of the diazonium group with mercury does not always give yields which are entirely satisfactory, yet the compounds so prepared are generally obtained more pure, or in a form more easily purified, than when other methods are employed. This has been noted before.<sup>3</sup>

### Experimental

**Fluoronitrobenzenes.**—The diazotization of *p*-nitroaniline as previously described<sup>4</sup> yielded the theoretical quantity of *p*-nitrobenzenediazonium fluoborate (ortho, 92%; meta, 92%). The decomposition of the diazonium fluoborate was carried out as described by Schiemann,<sup>5</sup> the same sand being used for repeated decompositions of the same diazonium compound. The decomposition of 1 mole of *p*-nitrobenzenediazonium fluoborate in 20-g. portions gave 82 g. of *p*-nitrofluorobenzene or 58% of the theoretical (ortho, 13%; meta, 43%).

**Fluoroanilines.**—The reduction of 100 g. (0.7 mole) of *p*-nitrofluorobenzene with tin and hydrochloric acid yielded 58 g. (75%) of *p*-fluoroaniline (ortho, 70%; meta, 89%).

(3) Nesmejanow, *et al.*, *Ber.*, **62**, 1010 (1929); *ibid.*, **67**, 130 (1934).

(4) Dunker, Starkey and Jenkins, *THIS JOURNAL*, **58**, 2308 (1936).

(5) Schiemann and Pillarsky, *Ber.*, **62**, 3035 (1929).

(1) Accepted for publication in the *Journal of Bacteriology*.

(2) German Patent 234,851.

The theoretical yield of *p*-fluoroaniline was obtained by the reduction of *p*-nitrofluorobenzene in 95% alcohol with hydrogen and palladium catalyst on charcoal.

**Fluorophenylmercuric Chlorides.**—The diazotization of the fluoroanilines gave the following yields of dry diazonium compounds: para, 86%; ortho, 70%; meta, 98%. The replacement of the diazonium group with mercury was carried out as described in an earlier paper.<sup>4</sup> *p*-Fluorophenylmercuric chloride was obtained in small glistening plates soluble in alcohol, acetone, glacial acetic acid, slightly soluble in benzene and insoluble in water. It was crystallized from hot glacial acetic acid and melted at 293–294°, decomposing slowly at the melting point (24% yield). *o*-Fluorophenylmercuric chloride was prepared similarly in 24% yield from *o*-fluorobenzenediazonium fluoborate. It was very soluble in alcohol and acetone and was recrystallized from ether, the crystals melting at 159–160°. *m*-Fluorophenylmercuric chloride was prepared in 28% yield from *m*-fluorobenzenediazonium fluoborate by the same procedure. Its solubility behavior was similar to that of the para isomer and its melting point 250–251° (all m. p. corrected).<sup>6</sup>

*Anal.*<sup>7</sup> Calcd. for C<sub>6</sub>H<sub>4</sub>ClFHg: Hg, 60.6. Found: Hg for ortho 60.5, 61.2; for meta 60.4, 60.9; for para 60.7, 60.8.

**Mercuration of Fluorobenzene.**—A mixture of 20 g. (0.21 mole) of fluorobenzene, prepared according to Balz and Schiemann,<sup>8</sup> 65 g. of mercuric acetate and 100 cc. of glacial acetic acid was refluxed for twelve hours. The cold reaction mixture was treated with dilute hydrochloric acid and then diluted with water to 700 cc. The white amorphous solid was filtered off and partially dried. The mixture was extracted with hot glacial acetic acid and the extractive, after crystallization from alcohol, gave 7 g. (about 11%) of needles melting at 156° and giving no depression of m. p. when mixed with a sample of pure *o*-fluorophenylmercuric chloride. The remainder of the white solid was amorphous, could not be separated into fractions by further crystallizations and melted over a wide range of temperature.

***p*-Fluorophenol.**—*p*-Fluorophenol was prepared from *p*-fluoroaniline in 40% yield as described by Rinke<sup>9</sup> and also from *p*-phenetidine by introducing the fluorine according to the method of Schiemann and then deethylating with aluminum chloride.<sup>10</sup>

**Mercuration of *p*-Fluorophenol.**—A solution of 13 g. (0.116 mole) of *p*-fluorophenol in 180 cc. of water was treated with a solution of 36 g. (0.113 mole) of mercuric acetate in 100 cc. of water acidulated with acetic acid. The mixture was allowed to stand for four days at room temperature and yielded 34 g. of crystals which were slightly soluble in benzene and water, soluble in acetone, alcohol and glacial acetic acid. When the compound was crystallized from glacial acetic acid, it melted at 193–194° with decomposition. A small amount (about 1 g.) of a

dimercurial was formed which was not isolated in pure condition.

*Anal.* Calcd. for C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>FHg: Hg, 54.1. Found: Hg, 52.9, 53.1.

***p*-Fluorobenzoic Acid.**—*p*-Fluorotoluene was prepared from *p*-toluidine by the Schiemann method<sup>4</sup> in 70% yield. A yield of 58% of *p*-fluorobenzoic acid melting at 183–184° was obtained on oxidation with potassium permanganate. *p*-Fluorobenzoic acid was also prepared as described by Schiemann and Winkelmüller in 50% yield.<sup>11</sup>

**Mercuration of *p*-Fluorobenzoic Acid.**—The direct mercuration of *p*-fluorobenzoic acid as described under fluorobenzene gave a poor yield of a monomercurial. The mercurichloride was a white powder which could not be crystallized from alcohol, acetone or benzene. On heating, the mercurial slowly turned yellow above 230° and melted with decomposition at 239°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>O<sub>2</sub>ClFHg: Hg, 53.5. Found: Hg, 53.4.

**3-Nitro-4-fluorobenzoic Acid.**—The nitration of *p*-fluorobenzoic acid by the method of Rouche<sup>12</sup> gave 3-nitro-4-fluorobenzoic acid, melting at 121–122° in 50% yield.

**3-Amino-4-fluorobenzoic Acid.**—The reduction of the above compound using hydrogen and palladium catalyst gave 11 g. (98%) of 3-amino-4-fluorobenzoic acid. Several crystallizations from boiling water (with charcoal) yielded tan needles. The free acid melted with decomposition at 182–183°. The hydrochloride crystallized from water in small white plates which began to darken at 215° and melted with decomposition at 240–243°. The acetylamino derivative also was prepared and obtained as white needles from water, melting with decomposition at 245–246° if heated rapidly to 240°. The acetylamino compound decomposed from 200° up if heated slowly.

*Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>FN: N, 7.11. Found: N, 7.16, 7.23, 7.03; av., 7.14.

**2-Fluoro-5-carboxybenzenediazonium Fluoborate.**—The diazotization of 8 g. of 4-fluoro-3-aminobenzoic acid yielded 10 g. (77%) of cream-colored diazonium compound, decomposition point 185°.

**4-Fluoro-3-chloromercuribenzoic Acid.**—The replacement of the diazonium group with mercury as described<sup>4</sup> gave a poor yield of highly colored mercurial. However, by repeated solution of the compound in acetone and precipitation with petroleum ether, there was obtained a small amount of cream-colored amorphous powder melting at 240–241° with decomposition. The mixed melting point of this compound with the mercurial prepared by direct mercuration was 239° with decomposition.

As additional evidence that, in the mercuration of *p*-fluorobenzoic acid, the mercury entered the ring adjacent to the fluorine, the following is offered. The compound decomposed with effervescence at its melting point and a deposit of white needles which were identified as *o*-fluorophenylmercuric chloride (mixed m. p.) sublimed on the upper portion of the tube.

## Summary

1. The three isomeric fluorophenylmercuric

(11) Schiemann and Winkelmüller, *Org. Syntheses*, **13**, 52 (1933).

(12) Rouche, *Bull. acad. roy. méd. Belg.*, 534 (1921).

(6) Kharasch, Pines and Levine, *J. Org. Chem.*, **3**, 347 (1938), reported 291° for the para compound and 243° for the meta.

(7) Mercury analyses throughout according to Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

(8) Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

(9) Rinke, *Chem. Weekblad*, **9**, 778 (1912).

(10) Swarts, *Bull. acad. roy. méd. Belg.*, 265 (1913).

chlorides have been prepared and characterized, the ortho derivative being reported for the first time.

2. The preparation and properties of the new mercurials 4-fluoro-3-chloro-mercuribenzoic acid and 4-fluoro-2-acetoxymcuriphenol are reported.

3. The preparation and melting points are given for 4-fluoro-3-aminobenzoic acid, its hydrochloride and acetyl derivative and the decomposition point for 2-fluoro-5-carboxybenzenediazonium fluoborate, all of which are new.

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## The 1,4-Diphenyl-2-mesityl 1,4-Diketones

BY ROBERT E. LUTZ AND CHARLES J. KIBLER

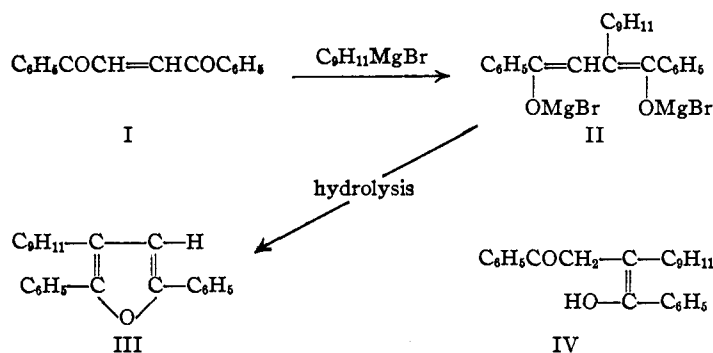
The preparation of this series of compounds was undertaken in order to study the effect of reactions of a mesityl group substituted directly at the ethylene linkage of the unsaturated 1,4-diketone system, and to determine the effect of this mesityl group on the tautomerism of the corresponding triketone enol and hydroxyfuranone.

The starting point in the synthesis was dibenzoyl ethylene, I. Mesitylmagnesium bromide adds to the unsaturated diketone readily, presumably through 1,4-addition followed by enolization at the remaining carbonyl, to give the dienolate II.<sup>1</sup> On hydrolysis 2,5-diphenyl-3-mesitylfuran, III, was formed exclusively and in good yield, with no indication of the formation of the expected and hoped for saturated diketone,  $C_6H_5COCH_2CH(C_6H_{11})COC_6H_5$ , which remains as yet unknown. This result is not particularly surprising, however, since it is known that phenylmagnesium bromide adds to dibenzoylstyrene with the formation of large amounts of the corresponding tetraphenylfuran along with the expected saturated diketone, tetraphenyl-1,4-butanedione.<sup>1b,2</sup> The mesityl group not only offers no hindrance to furanization but actually facilitates the reaction considerably. It seems very likely that the dienolic intermediate II on hydrolysis undergoes prompt ketonization at the unhindered enolic group to produce the monoenol, IV, with a normally reactive carbonyl now available for furan ring closure, and with the remaining and hindered enolic group, in the favorable configuration indicated, persisting long enough for reaction to be complete even under these mild conditions.

(1) Cf. (a) Lutz and Tyson, *THIS JOURNAL*, **56**, 1341 (1934); (b) Lutz and Reveley, *ibid.*, **61**, 1854 (1939).

(2) Hahn and Murray, *ibid.*, **36**, 1494 (1914).

The unsaturated 1,4-diketone of this series, VI, is easily obtained by the nitric-acetic acid oxidation of the furan, III, and is assigned the *cis* configuration on the basis of this mode of preparation.<sup>3</sup> It is reduced easily by zinc and acetic acid, sodium hydrosulfite, and catalytic hydro-



gen; but the furan III was the only crystalline product obtained. In the catalytic hydrogenation an attempt was made to follow the course of the reaction. Piperidine was added in the hope that ketonization would be catalyzed with the production of the saturated diketone instead of the furan. A non-crystalline product was obtained which spontaneously on standing for eight days, or immediately when treated with acetic anhydride and sulfuric acid, gave the furan, and which very evidently contained the monoenol IV. Undoubtedly, then, the reduction was 1,6.

The unsaturated diketone VI reacts with dry hydrogen chloride in acetic acid to give the chlorofuran VII which is obtained also by direct chlorination of the furan III with phosphorus pentachloride at 100° (at a higher temperature, however, some of the unsaturated chloro diketone VIII is

(3) Cf. (a) Lutz and Wilder, *ibid.*, **56**, 979 (1934); (b) Lutz, Tyson, Sanders and Fink, *ibid.*, **56**, 2679 (1934); (c) Lutz and Wilder, *ibid.*, **56**, 2145 (1934); (d) Lutz and Eisner, *ibid.*, **56**, 2698 (1934).