

3. No evidence that use of an optically active peroxide will cause an asymmetric synthe-

sis in vinyl polymerization has been obtained.  
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## NOTES

### Trimolecular Acetone Peroxide in Isopropyl Ether

BY FRED ACREE, JR., AND H. L. HALLER

During the past few years several notes have appeared in the literature citing explosions of isopropyl ether.<sup>1</sup> In all cases the ether had stood for several years and the explosion hazard was attributed to the formation of peroxides. So far as we have been able to learn, the responsible peroxide has not been isolated or described.

Recently, while an organic compound was being crystallized from isopropyl ether,<sup>2</sup> the mother liquor was evaporated on the steam-bath with the aid of a stream of air to about one-third of its original volume. On standing at room temperature, a crop of crystals, resembling common salt, separated. They melted at 94°. On recrystallization from methyl alcohol the melting point was 98°. The compound sublimed readily at room temperature, liberated iodine from potassium iodide solution, and exploded on percussion or when heated on a platinum spatula. A molecular weight determination by the Signer method as modified by Clark<sup>3</sup> gave a value of 221. The compound possessed all the properties of trimolecular acetone peroxide,<sup>4</sup> and a mixture melting point determination of the unknown peroxide with an authentic sample of trimolecular acetone peroxide showed them to be identical.

Trimolecular acetone peroxide was readily obtained in crystalline form from four out of five lots of isopropyl ether, all of which gave qualitative tests for peroxides, when the ether was evaporated to one-third of its original volume on the steam-bath with a stream of air. The fifth

(1) (a) E. F. Degering, *J. Chem. Ed.*, **13**, 494 (1936); (b) B. L. Herrington, *Ind. Eng. Chem., News Ed.*, **20**, 1458 (1942); (c) G. T. Morgan and R. H. Pickard, *Chem. and Ind.*, **55**, 421 (1936); (d) E. C. Williams, *J. Soc. Chem. Ind.*, **55**, 580 (1936).

(2) The ether was a commercial grade that had stood in the laboratory in clear glass bottles for at least five years. It was not purified before use.

(3) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

(4) R. Wolfenstein, *Ber.*, **28**, 2265 (1895).

lot gave a viscous sirup from which no crystals of the trimolecular acetone peroxide were obtained.

It is of interest to note that Radulesco<sup>5</sup> found that the photochemical oxidation of isopropyl ether was slightly autocatalytic and produced acetone, water, peroxides, acids, and gum; and that Brown<sup>6</sup> has shown the formation of acetone when the ether mixed with oxygen is passed over a silver catalyst. Whether other peroxides are also present in isopropyl ether has not been determined. Trimolecular acetone peroxide is possibly responsible for the peroxide test found by Redemann<sup>7</sup> with isopropanol.

(5) G. Radulesco, *Ann. combustible liquides*, **13**, 1071 (1938).

(6) R. L. Brown, U. S. Patent 2,246,569, June 24, 1941.

(7) C. E. Redemann, *THIS JOURNAL*, **64**, 3049 (1942).

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### Some Fluorinated Compounds of Possible Chemotherapeutical Interest

BY E. BOGRACHOV

In the course of experiments on lipophilic chemotherapeuticals<sup>1</sup> an investigation of fluorinated compounds was undertaken. As these experiments cannot be continued at present, a brief description of three of the new substances prepared may be permitted. They were obtained in well-crystallized and undoubtedly pure form. While the hydrogen and nitrogen analyses (Dumas) were satisfactory, the carbon values were throughout too low, most probably due to the formation of the volatile, stable carbon tetrafluoride.<sup>2</sup>

**N-(*o*-Fluorobenzoyl)-1-amino-4-(benzene-azo)-naphthalene.**—4-(Benzeneazo)-1-naphthylamine (12.3 g.) was dissolved in dry chloroform (100 cc.), and the solution, after addition of pyridine (4 g.), cooled to 0°. At this tempera-

(1) Bergmann, *et al.*, *THIS JOURNAL*, **63**, 2243, 2245 (1941).

(2) Satisfactory values can be obtained only by combustion with lead chromate and silver, not with the method usually applied in microcombustion analysis. Wallach and Heusler, *Ann.*, **248**, 243 (1888); Schiemann and Bolstad, *Ber.*, **61**, 1407 (1928).

ture, *o*-fluorobenzoyl chloride (8 g.) (b. p. 85° (14 mm.))<sup>2</sup> in chloroform (50 cc.) was added slowly. On standing, the condensation product (9 g.) crystallized; from the mother-liquid a second batch (2.5 g.) was obtained, when it was washed with water, dried and concentrated. It formed red leaflets, m. p. 154°, from ethyl alcohol; yield, 62%. *Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>ON<sub>2</sub>F: C, 74.8; H, 4.3; N, 11.6. Found: C, 71.9; H, 4.1; N, 11.4.

*N*-(*p*-Fluorobenzoyl)-1-amino-4-(benzene-azo)-naphthalene.—The above procedure, when carried out with *p*-fluorobenzoyl chloride (b. p. 104° (38 mm.)), gave in 65% yield brown-red needles from alcohol, m. p. 201°. *Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>ON<sub>2</sub>F: C, 74.8; H, 4.3; N, 11.6. Found: C, 73.6; H, 4.7; N, 11.4.

*N*-(*o*-Fluorobenzoyl)-sulfanilamide.—Sulfanilamide (8.6 g.) was dissolved in hot glacial acetic acid (45 cc.). The solution was quickly chilled with ice-water, and additioned with *o*-fluorobenzoyl chloride (8 g.), while stirring. The reaction product was collected after one hour and recrystallized from glacial acetic acid, m. p. 264°; yield, almost quantitative. *Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>FS: C, 53.1; H, 3.7; N, 9.5. Found: C, 51.9; H, 3.6; N, 9.4.

(3) Bergmann and Bondi, *Ber.*, **64**, 1474 (1931).

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## Identification of Organic Acids by Partition between Ethyl Ether and Water<sup>1</sup>

BY O. C. DERMER AND V. H. DERMER

Extraction of an acid from aqueous solution by an immiscible solvent is in some respects like steam distillation; in both processes the acid is distributed between phases in a characteristic ratio. The difference in volatility of various acids with steam is the basis of well-established procedures for their identification (the Duclaux method) and their estimation, but extraction with ether has been employed more for quantitative determination of organic acids<sup>2a-g</sup> than for their characterization. Werkman<sup>2c</sup> and Friedemann<sup>2g</sup> suggested using partition ratio as an aid in identifications, but both were interested primarily in mixtures of acids rather than single acids. Moreover, the usefulness of their data is somewhat limited because they measured equilibrium concentrations in the water layer only; the constants so obtained are not directly comparable to partition data in the literature because of the variation

(1) A preliminary study of this problem was made in this laboratory by Mr. Noble Smith and was reported in his M.S. thesis in 1940.

(2) (a) Behrens, *Z. anal. Chem.*, **69**, 97 (1926); (b) Werkman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 302 (1930); (c) Werkman, *Iowa State Coll. J. Sci.*, **4**, 459 (1930); **5**, 1, 121 (1930); (d) Osburn and Werkman, *Ind. Eng. Chem., Anal. Ed.*, **3**, 264 (1931); (e) Werkman and Osburn, *ibid.*, **3**, 387 (1931); (f) Osburn, Wood and Werkman, *ibid.*, **5**, 247 (1933); **8**, 270 (1936); (g) Friedemann, *J. Biol. Chem.*, **123**, 161 (1938).

in mutual solubility of ether and water in the presence of different acids.

Physical constants obtained by distribution methods, such as the Duclaux constants or ratios of partition between solvents, differ from others commonly used in qualitative organic analysis in that they may be determined with samples containing water, or even in rather dilute solution. Steam-volatile acids in aqueous solution cannot readily be obtained anhydrous for melting point or boiling point determinations, and the same may be said of lactic, hydracrylic, cyanoacetic, polyhalogenated fatty acids, etc. Even if the pure unknown acid is at hand, a partition value is a useful constant—more trouble to measure than melting point or neutralization equivalent, but no more so than to prepare a solid derivative of the acid.

Advantages of the solvent-partition method over the Duclaux procedure have been discussed by Werkman<sup>2b</sup>; those most impressive are greater simplicity, wider applicability, and higher accuracy because values for different acids are more widely separated than the Duclaux constants. Both techniques fail if any impurity is present in appreciable amount. Clearly the present method does not safely distinguish acids with very large values of  $C_w/C_e$  ( $> 50$ ), but almost everywhere else the spread of values is gratifying. The use of ethyl acetate as extracting solvent would probably give lower and thus more useful values for hydroxy acids, but has not been tried. Another obvious but hardly very promising extension is the use of more dilute solutions initially, so as to include acids less soluble in water.

To use the extraction method in identifying an unknown acid, this procedure may be followed: Adjust the acid to  $0.100 \pm 0.005 N$  by preliminary titration and appropriate dilution. Measure 50 ml. of this solution and 50 ml. of water-saturated ether, made from c. p. reagent, into a glass-stoppered bottle and shake them together for five minutes<sup>2a</sup> or more at  $25.0 \pm 0.5^\circ$ . Allow several minutes for separation of layers, then pipet two 20-ml. portions from each layer and titrate them with standard 0.1 *N* alkali, with phenolphthalein as indicator. The mean value of  $C_w/C_e$  (in terms of normalities), used in conjunction with the series of values given, provides strong evidence of the nature of the acid.

(2a) Longer equilibration did not give us measurably different values; cf. McCoy, *This Journal*, **30**, 690 (1908); Friedemann, ref. 2g.