

The apparently stoichiometric oxidation of tryptophan by 3 atoms of oxygen leaves room for different interpretations which cannot be evaluated without further work. In addition to the behavior of these three compounds it seems worth noting that in contrast to their behavior with periodic acid, the hydroxy amino acids are not distinguished by a special reactivity toward performic acid.

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### Density and Refractive Index of Cumene

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In a recent investigation of alkyl benzenes at this Laboratory, the variation with temperature of density and refractive index of cumene (isopropyl benzene) was determined. Previous data on these properties had been found in the literature, but the inconsistency in published values led to the new measurements reported in this article.

The plots of densities and of refractive indices against temperatures defined curves which were fitted to the general equation,  $d_4^t$  or  $n_D^t = a + bt + ct^2$ , by the method of least squares. The following expressions were obtained

$$\text{Density} - d_4^t = 0.8777 - 0.73 \times 10^{-3}t - 2.8 \times 10^{-6}t^2$$

$$\text{R. I.} - n_D^t = 1.5017 - 0.54 \times 10^{-3}t + 0.46 \times 10^{-6}t^2$$

Densities were determined by means of pycnometer weighings between 6.1° and 37.8°. The close agreement between experimental data and the calculated curve is shown in Fig. 1. The

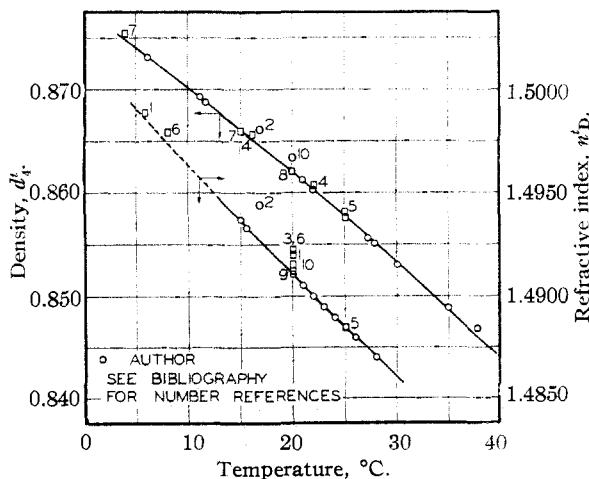


Fig. 1.

average deviation of individual points from this curve is  $\pm 0.0001$  or about 0.01%. Refractive indices were measured with an Abbé refractometer at temperatures ranging from 15–28°. Experi-

mental points, which are likewise plotted in Fig. 1, show an average deviation of only 0.002% from values indicated by the curve of the R. I. equation given above. Density and R. I. data reported by other investigators are included for comparison with the author's results.

Best grade Eastman Kodak Company cumene was used in these measurements without any further purification. This was considered acceptable since the density and refractive index of the middle cut of a redistillation (b. p. 152–153°) were not significantly different from those of the original material, which had the following properties: b. p. 151–153°, f. p.  $-95.2^\circ$ ,  $d_4^{20}$  0.8620,  $n_D^{20}$  1.4911. By comparison, best values in the literature are: b. p. 152.5°, f. p.  $-96.2^\circ$ ,  $d_4^{20}$  0.8620,  $n_D^{20}$  1.4912–1.4920.

Although the author's data may be limited somewhat in accuracy by the purity of the cumene used, it is assumed that the equations offered here are sufficiently reliable for general use in industry.

- (1) K. Auwers and H. Kolligs, *Ber.*, **55B**, 21 (1922).
- (2) K. Auwers, *Ann.*, **419**, 107 (1919).
- (3) V. N. Ipatieff, B. B. Corson and Herman Pines, *THIS JOURNAL*, **58**, 919 (1936).
- (4) H. Landolt and H. Jahn, *Z. physik. Chem.*, **10**, 303 (1892).
- (5) J. F. McKenna and F. J. Sowa, *THIS JOURNAL*, **59**, 470 (1937).
- (6) W. Perkin, *J. Chem. Soc.*, **77**, 275 (1900).
- (7) W. Perkin, *ibid.*, **69**, 1194 (1896).
- (8) T. W. Richards and J. W. Shipley, *THIS JOURNAL*, **38**, 996 (1916).
- (9) J. Smittenberg, H. Hoog and R. A. Henkes, *ibid.*, **60**, 17 (1938).
- (10) J. D. White and F. W. Rose, *J. Research Natl. Bur. Standards*, **21**, 164 (1938).

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## NEW COMPOUNDS

### 4-Nitrodiphenyl Ether-4'-Sulfonyl Chloride and -4'-Sulfonamide

*p*-Nitrodiphenyl ether was sulfonated by heating and stirring with concentrated sulfuric acid until test portions were completely soluble in water. The sodium salt was isolated, dried and converted to the sulfonyl chloride with phosphorus pentachloride. The light cream-colored sulfonyl chloride was recrystallized from isopropyl ether: m. p. 84–85° (cor.). It was analyzed by refluxing a weighed portion in 50% ethanol for three hours, evaporating to dryness repeatedly on the steam-bath to remove hydrogen chloride, and titrating the residual sulfonic acid with standard alkali.<sup>1</sup>

*Anal.* Calcd. for  $C_{12}H_9O_6NSCl$ : equiv. wt., 314.  
Found: equiv. wt., 322.

(1) Cf. Davis and Davies, *J. Chem. Soc.*, **123**, 2976 (1923).

To prove the structure of this compound, diphenyl ether was converted to diphenyl ether-4-sulfonyl chloride by the directions of Suter.<sup>2</sup> This compound was nitrated by dissolving 1 g. of it in 5 ml. of glacial acetic acid, adding 4 ml. of concentrated nitric acid, and then adding portion-wise 2 ml. of concentrated sulfuric acid while keeping the temperature at about 60–70°. After the reaction mixture had stood several hours it was poured into water and the oily nitro compound was seeded to cause crystallization. Recrystallization from ethyl ether gave a product, m. p. 85.5–86.5°, indicated by melting point and mixture melting point to be identical with that made by sulfonating *p*-nitrodiphenyl ether.

The sulfonamide was obtained from either sulfonyl chloride as very light yellow crystals from dilute ethanol, m. p. 130–131°. Before Kjeldahl digestion the sample was allowed to stand with cold sulfuric acid and zinc dust.<sup>3</sup>

*Anal.* Calcd. for  $C_{12}H_{10}O_6N_2S$ : N, 9.5. Found: N, 9.4.

Since this work indicates that 4-nitrodiphenyl ether sulfonates mainly in the 4'-position, as might be expected, the 4-nitrodiphenyl-ether-*x*-sulfonic acid of Jones and Cook<sup>4</sup> may now be concluded to have been the 4'-sulfonic acid.

#### N,N-Di-*n*-butylhydroxylamine and its Oxalate

This hydroxylamine was made by substantially Wieland's procedure.<sup>5</sup> A 5% solution of nitrogen dioxide in anhydrous ether was prepared and cautiously dropped into a well-stirred solution of *n*-butylmagnesium bromide in ether. As soon as starch-iodide paper indicated the presence of excess nitrogen dioxide, the mixture was let stand for two hours and then decomposed with a little water. The N,N-di-*n*-butylhydroxylamine was extracted with ether and precipitated therefrom by adding a solution of oxalic acid in ether. The oxalate, recrystallized from methanol, melted at 144.0–144.5°.

*Anal.* Calcd. for  $C_{10}H_{21}O_5N$ : N, 5.94; equiv. wt. (dibasic acid), 118. Found: N (Kjeldahl), 5.95; equiv. wt., 118.

(2) Suter, *THIS JOURNAL*, **53**, 1112 (1931).

(3) Weizmann, Yofe and Kirzon, *Z. physiol. Chem.*, **192**, 70 (1930).

(4) Jones and Cook, *THIS JOURNAL*, **38**, 1534 (1916).

(5) Wieland, *Ber.*, **36**, 2315 (1903).

The free N,N-di-*n*-butylhydroxylamine was obtained by warming the oxalate with concentrated alkali solution, chilling, and isolating the product by filtration. After recrystallization from aqueous ethanol it melted at 52.5–53.0°. It was very soluble in all organic solvents tested, but only slightly soluble in water, giving a neutral solution; its weakness as a base is indicated also by the fact that the acid in the oxalate may be titrated as if free. When warmed with solutions of silver, cupric or auric salts, it exhibits the expected reducing power.

*Anal.* Calcd. for  $C_8H_{19}ON$ : N, 9.66. Found: N, 9.59.

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#### 4-Toluenesulfonates of the Nitro-4-phenylphenols

**2,6-Dinitro-4-phenylphenyl 4-Toluenesulfonate.**—This compound was prepared by the treatment of 2,6-dinitro-4-phenylphenol in pyridine solution with tosyl chloride. The crude, faintly yellow product was obtained in quantitative yield and, after crystallization from propanol, from which 88% was recovered as colorless prisms, it melted at 186–187°.

*Anal.* Calcd. for  $C_{19}H_{14}O_7N_2S$ : S, 7.73. Found: S, 7.69.

**2,6-Dinitro-4-(4-nitrophenyl)-phenyl 4-Toluenesulfonate.**—For the preparation of this compound it was necessary to dissolve the 2,6-dinitro-4-(4-nitrophenyl)-phenol and the tosyl chloride in warm 1,4-dioxane and then to add the pyridine. The crude product was obtained in quantitative yield, and after crystallization from methanol the recovery was 80%. The crystals so obtained were faintly yellow prisms, but after drying at 130° and 15 mm. the color disappeared; m. p. 219–220°.

*Anal.* Calcd. for  $C_{19}H_{13}O_9N_3S$ : S, 6.97. Found: S, 6.85.

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