

To prove the structure of this compound, diphenyl ether was converted to diphenyl ether-4-sulfonyl chloride by the directions of Suter.² 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.³

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 Cook⁴ 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.⁵ 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. (di-basic 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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RECEIVED AUGUST 17, 1942

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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RECEIVED OCTOBER 13, 1942