mmol) of ethyl formate was refluxed for 12 hr. All volatiles were removed at reduced pressure, the residual oil was dissolved in methylene chloride, washed with dilute hydrochloric acid, then water, and the organic phase was dried ($MgSO_4$). The solvent was removed and the residual oil was distilled, giving 1.39 g (58%) of formamide **2**: bp 121–122° (0.6 mm); $n^{25}D$ 1.5433; ir (neat) 1675 (amide C=O) and 3290 cm^{-1} (amide NH); nmr ($CDCl_3$) δ (TMS) 8.15 (s, 1, HCON), 7.13 (m, 3, ArH), 6.75 (m, 1, NH), 5.23 (m, 1, J = 16.5, 7.5 Hz, CH), 1.87 (m, 2, J = 7.5 Hz, $-CH_2-$), and 0.93 ppm (t, 3, J = 7.5 Hz, $-CH_3$); mass spectrum (70 eV) m/e (rel intensity) 169 (30), 140 (100), 113 (36), 97 (7), 85 (25).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.77; H, 6.55; N, 8.28. Found: C, 56.60; H, 6.43; N, 8.44.

Addition of deuterium oxide and a trace of trifluoroacetic acid to the nmr solution ($CDCl_3$) resulted in the complete loss of the peak at δ 6.75 due to the amide proton and the collapse of the methine AB quartet at δ 5.23 to a triplet, J = 7.5 Hz.

Registry No.—**1**, 13679-75-9; **2**, 39207-57-4; **3**, 39204-58-5; **3** picrate, 39204-59-6; 1-(2-thienyl)-1-aminopropane, 6315-55-5; formamide, 75-12-7; ethyl formate, 109-94-4.

Preparation and Purification of Tetrasodium *meso*-Tetra(*p*-sulfophenyl)porphine. An Easy Procedure[1]

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Tetraphenylporphine sulfonate was first reported by Winkelman, who studied localization of this compound in tumors. He found that it could be localized with a higher concentration ratio in animal tumors than in other tissues.[3,4] It was later found that Winkelman's sample is, in fact, a mixture of various isomers.[5] The sodium salt of *meso*-tetra(*o*-sulfophenyl)porphine was recently prepared in low yield by condensing pyrrole and benzaldehyde sulfonic acid (sodium salt) in *n*- or *tert*-butyl alcohol in the presence of sodium acetate.[6] *meso*-Tetra(*p*-sulfophenyl)porphine was prepared by heating *meso*-tetraphenylporphine and concentrated sulfuric acid on a steam bath for 4 hr. The diacid was precipitated by adding the requisite amount of water. The tetraammonium salt was precipitated by dissolving the diacid in methanolic ammonia and then adding acetone. Further purification of the tetraammonium salt was carried out by a cumbersome procedure involving six successive reprecipitations from a methanolic solution with acetone. The tetraammonium salt of *meso*-tetra(*p*-sulfophenyl)-porphine was further converted to the tetrasodium salt by treating the former with sodium methoxide.[4] We wish to report an easy preparation and purification procedure for the tetrasodium *meso*-tetra(*p*-sulfophenyl)porphine (60% yield).

(1) Unusual Metalloporphyrins. XVI.
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Experimental Section

Finely powdered *meso*-tetraphenylporphine (2 g)[7] was mixed with 50 ml of concentrated sulfuric acid. The mixture was heated on a steam bath for 4–5 hr. After cooling to room temperature, the solution was filtered through a sintered glass frit and the filtrate was diluted carefully to 1. The dilute solution was heated and a sludge of lime was added slowly with stirring until the solution changed to a permanent purple color. Calcium sulfate was filtered off and washed with a minimum quantity of hot water, which was then combined with the filtrate. Crushed Dry Ice was added to the filtrate and was filtered. The filtrate was concentrated to a small volume (about 100 ml) and the pH of the final warm solution was regulated at 8–10 by adding the required quantity of concentrated sodium carbonate solution. Calcium carbonate was removed by filtration and washed with water, which was then combined with the filtrate. Hot ethanol (90%) in small quantities was periodically added to the filtrate, which was further concentrated on a steam bath. The saturated solution was cooled at room temperature and crystals of tetrasodium *meso*-tetra(*p*-sulfophenyl)porphine (I) were obtained. They were filtered off and washed with a minimum quantity of cold 90% ethanol. Finally the material was dried at 100° for 1 hr. The water content in compound I was determined by heating it under vacuum at 140° for 15 hr. I has an empirical formula of $C_{44}H_{50}N_4O_{24}S_4Na_4$ with 12 water molecules. *Anal.*[8] Calcd for $C_{44}H_{26}N_4O_{12}S_4Na_4 \cdot 12H_2O$: N, 4.50; S, 10.29. Found: N, 4.54; S, 10.55. The compound is very soluble in water. The visible spectrum of I (H_2O) shows five peaks at 413 (soret), 506 (I), 543 (II), 570 (III), and 634 (IV) nm (rel intensity I > II > III > IV). The ir spectrum of I (KBr) shows four strong bands at 1226, 1194, 1134, and 1046 cm^{-1} due to sulfonic acid (salt) absorption[9] in addition to free porphyrin vibrations. The ^1H nmr (T-60 Varian Associates) of I (D_2O) shows pyrrole protons at δ 7.51 and two doublets due to protons of phenyl groups centered at δ 6.85 and 7.85 with a coupling constant of 8 Hz.[4] The ratio of peak areas of pyrrole protons and phenyl protons is 1:2. This excludes the possibility of substitution of the pyrrole protons and supports the substitution of the phenyl protons by four sulfonate groups. Furthermore, the presence of the two doublets at δ 6.85 and 7.85 in the ^1H nmr of I shows clearly that four sulfonate groups are substituted only at para positions of the phenyl groups.

Registry No.—Tetrasodium *meso*-tetra(*p*-sulfophenyl)porphine, 39050-26-5; *meso*-tetraphenylporphine, 917-23-7.

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The Rearrangement of α-Ethynyl Alcohols to Unsaturated Carbonyl Compounds (The Rupe Reaction)

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The identity of the products from, and the mechanism of, the Rupe reaction has been debated in the

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