and the aqueous layer was extracted twice with 200 ml. of ether. The combined ether solutions were dried over anhydrous sodium sulfate, filtered, and the solvents were removed under vacuum, leaving 15.0 grams of a colorless oil. The infrared spectrum of this oil, in chloroform solution, showed a peak at 3270 cm.$^{-1}$ (3.06 microns) with a shoulder at 3480 cm.$^{-1}$ (2.88 microns), indicative of a primary amine group (*21*).

A solution of 14.0 grams of the oil in 50 ml. of anhydrous ether was added with stirring to a solution of 5.0 grams (0.12 mole) of hydrogen chloride in 150 ml. of anhydrous ether. After two hours, the resulting precipitate was removed by filtration, washed with anhydrous ether, and dried under vacuum. There was obtained 10.0 grams, 61% over-all yield, of 2-phenyl-3-(*p*-thiomethoxyphenyl)propylamine hydrochloride, m.p. 152–5° C. Recrystallization from methanol-benzene gave a light yellow solid, m.p. 197–9° C.

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An Improved Preparation of 5-Dimethylamino-1-naphthalenesulfonyl Chloride

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An improved synthesis is described for 5-dimethylamino-1-naphthalenesulfonyl chloride, formed by the reaction of 5-dimethylamino-1-naphthalenesulfonic acid with phosphorus pentachloride in phosphorus oxychloride.

THE IMPORTANCE of 5-dimethylamino-1-naphthalenesulfonyl chloride (dansyl chloride) as an extrinsic fluorescent chromophore in the field of protein chemistry is well documented (*1, 4*). The need for a reasonable amount of pure dansyl chloride prompted a better synthesis, since even the poor yields (25 to 40%) reported by Weber (*5*) have not been realized in this laboratory. Furthermore, commercial preparations are of variable purity. In this improved preparation, the yield has been increased to 85%. The earlier inconvenience of tediously grinding to a melt the precursor, 5-dimethylamino-1-naphthalenesulfonic acid, with phosphorus pentachloride has been avoided by conducting the reaction in phosphorus oxychloride. Simple one-day, room-temperature stirring of this solution followed by a routine processing of the reaction mixture afforded the desired product.

EXPERIMENTAL

Melting points were taken with a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken with Perkin Elmer Models 21 and 137 spectrophotometers. Thin-layer chromatography was performed on silica gel (E. Merck, grade GF$_{254}$). Column adsorption chromatography was conducted on silica gel (Davison grade 923, 100–200 mesh, air-deactivated), and alumina (Bio-Rad acid alumina AG4, 100–200 mesh).

Preparation of 5-Dimethylamino-1-naphthalenesulfonyl Chloride. A 500-ml., 2-necked flask containing a Teflon-coated magnetic stirring bar, air-cooled condenser, and Drierite-containing drying tube was charged with 25.1 grams (0.1 mole) of 5-dimethylamino-1-naphthalenesulfonic acid (*2, 3*) and 75 ml. (125.6 grams, 0.82 mole) of phosphorus oxychloride. To this magnetically stirred mixture at ambient temperature was added portionwise, over approximately 15 minutes, with caution (exotherm!) 41.6 grams (0.2 mole) of phosphorus pentachloride. Homogeneity occurred when approximately two-thirds of the phosphorus pentachloride was added. The resulting dark amber solution was stirred for one day at room temperature—one-hour reflux led only to decomposition products. It was poured onto an excess (ca. 2 kg.) of ice, stirred efficiently to decompose phosphorus oxychloride and phosphorus pentachloride, and extracted with benzene until the benzene extracts were nearly colorless. The benzene extract was washed successively with cold dilute sodium hydroxide and water, dried (anhydrous calcium chloride), and filtered. Concentration of the filtrate left an orange oil which crystallized on standing. This solid was dissolved in a small amount of hot hexane and filtered from a small amount of hexane-insoluble material. Chilling of the filtrate deposited 23 grams (85%) of yellow-orange crystals, m.p. 66.5–68° C., [lit. (*5*), m.p. 69° C.].

A small amount (ca. 4 to 6 grams) of starting material (identified by superimposable infrared spectra) precipitated, on acidification of the combined sodium hydroxide wash, with the original aqueous extract.

Chromatography of 5-Dimethylamino-1-naphthalenesulfonyl Chloride. Ultraviolet light visualization of thin-layer chromatographed dansyl chloride (hexane recrystallized) showed a blue fluorescent spot near the origin of the chromatogram, due to small amounts of unreacted 5-dimethylamino-1-naphthalenesulfonic acid. Chromatographically pure dansyl chloride [one spot, R_f 0.62, R_f (methyl yellow) 0.52; dichloromethane] was obtained by column adsorption chromatography on silica gel, or preferably on alumina.

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Dielectric Constants, Dipole Moments, and Molecular Structure of Some Bicyclic Nitriles and Aliphatic Dinitriles

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Dielectric constants of a series of bicyclic nitriles and aliphatic dinitriles were measured as a function of temperature. Within each series, a number of compounds had a molecular configuration allowing them to exhibit rotational freedom well below their freezing point. Dipole moments for the bicyclic nitriles and aliphatic dinitriles were determined according to the method of Halverstadt and Kumler and compared with dipole moments calculated using the Onsager equation. Differences between the observed and calculated moments are explained in terms of dipolar-dipolar interaction, suggesting the possibility of several modes of association in organic nitriles.

POLAR organic materials that have a high dielectric constant in the liquid state usually have a low dielectric constant when solid, because as the material solidifies, the dipoles become frozen in, and the molecules can no longer orient with the electric field. However, a number of organic materials do not follow this general pattern of dielectric behavior. These materials, called solid rotators, retain their freedom of rotation in the solid state because their molecules approach a spherical shape and there is sufficient free volume so that there is little interference to dipolar orientation and they therefore have a high dielectric constant well below their melting points.

The literature dealing with solid rotators has been reviewed by Smyth (*17, 19*). Nearly all of the rotators discussed by Smyth have small rotational radii. However, camphor and a few other related bicyclic compounds with molecules of rather complicated but nearly spherical structure were also found to be solid rotators. We felt that systematic study of some structurally related rotators would give useful information to help explain the dielectric behavior of these materials.

Several bicyclic nitriles, having the same basic bicyclo[2,2,1]heptane skeleton as camphor, which were prepared in our laboratory (*16*), were found to have a physical property of "plastic crystallinity" usually associated with rotators (*19*). This observation sparked our interest to investigate the dielectric behavior of a group of related bicyclic nitriles, because the presence of a cyano group is known to result in very strong dipole-dipole interactions (*6*), manifested by a high degree of intermolecular association, which *a priori* would seem incompatible with the

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