polymers through polycondensation of cyclic phosphonitriles with selected diols. However, three different reaction schemes were observed depending upon reaction conditions and the diol used, resulting in the formation of (1) compounds believed to be spiro derivatives obtained by the reaction of each $PNCl_2$ group with a molecule of diol, (2) cyclic ethers by way of a dehydration reaction, and (3) polymeric substances.

Reactions of triphosphonitrilic chloride were first carried out with ethylene glycol and 2,2-bis(nitroxymethyl)-1,3-propanediol. The reaction with ethylene glycol yielded a product believed to be the five-membered ring phosphonitrilate spiro compound, tris-1,1:3,3:5,5-ethylene triphosphonitrilate. The elemental analysis and infrared spectrum were consistent with this structure. However, owing to its insolubility and noncrystalline character further identification of the product was not attempted. We previously reported the product of the reaction with 2,2-bis(nitroxymethyl)-1,3-propanediol to be the six-membered ring spiro compound, tris-1,1:3,3:5,5-[β,β-bis(nitroxymethyl)trimethylene]triphosphonitrilate.[3] Similar spiro compounds from reactions of triphosphonitrilic chloride with 1,4-tetrafluorobutanediol and 1,5-hexafluoropentanediol were reported by Rätz and co-workers;[4] Allcock reported the formation of spiro compounds with aromatic diols.[5]

With 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol, in the absence of solvent or acid acceptor, triphosphonitrilic chloride acted as a dehydrating agent to form the cyclic ethers trimethylene oxide, tetrahydrofuran, and tetrahydropyran, respectively. The evolution of large amounts of hydrogen chloride was observed at about 110° accompanied by an exothermic reaction which brought the temperature in the reaction flask to slightly above 200°.

The dehydrating action of phosphonitrilic chloride was previously noted by Bezman and Reed in their reported conversion of carboxylic acid salts to nitriles.[6] Also, we found that cyanuric chloride, whose reactions are in many ways similar to those of triphosphonitrilic chloride, reacts with 1,4-butanediol and with 1,5-pentanediol to form tetrahydrofuran and tetrahydropyran.[7] More recently Traynelis and co-workers[8] reported the formation of cyclic ethers in reactions of diols with dimethyl sulfoxide.

The reactions of triphosphonitrilic chloride with the longer chain 1,6-hexanediol, regardless of reaction conditions, gave polymeric materials which were insoluble in water or common organic solvents making it difficult to obtain a pure product for identification.

Experimental Section

Reaction of Triphosphonitrilic Chloride with Ethylene Glycol.—A solution of 0.75 g (0.012 mole) of ethylene glycol in 10 ml of pyridine was mixed with 0.7 g (0.002 mole) of triphosphonitrilic chloride. The mixture was shaken until the solid dissolved and then allowed to stand at room temperature for 24 hr. The solid was filtered and washed with water, alcohol, ether, and finally with methylene chloride. It turned brown at about 280° and melted above 300°: yield 0.67 g (33%). The infrared spectrum showed absorption peaks at 1250 cm^{-1} (trimeric P_3N_3 ring)[9] and 1040 cm^{-1} (P–O–R).[10] This compound is believed to be tris-1,1:3, 3:5,5-ethylene triphosphonitrilate.

Anal. Calcd for $C_6H_{12}N_3O_6P_3$: C, 22.85; H, 3.80; N, 13.33; P, 29.52. Found: C, 22.66; H, 4.11; Cl, negative; N, 13.08; P, 28.66.

Owing to the insolubility of this compound in common organic solvents a molecular weight was not obtained.

General Procedure for Reactions of Triphosphonitrilic Chloride in Excess of Diol.—A mixture of 1.75 g (0.005 mole) of triphosphonitrilic chloride and 10 ml of 1,4-butanediol was placed in a small flask with an attached distilling outfit and slowly heated in an oil bath. When the oil-bath temperature reached 110°, a rapid evolution of hydrogen chloride was observed and the flask temperature rose to 200–210°. The heating was continued when the evolution of gas had subsided and a liquid was collected distilling at 60–63°. The heating was stopped when no more liquid distilled. Fractional distillation resulted in a major portion of the liquid boiling at 63–65°, n^{25}_D 1.4049 (tetrahydrofuran bp 64–66°, n^{25}_D 1.4040). An unidentified solid containing no carbon remained in the distilling flask.

The reactions of triphosphonitrilic chloride with 1,3-propanediol and 1,5-pentanediol under the same conditions gave 33% yield of trimethylene oxide (bp 48°, n^{25}_D 1.3842; lit. bp 47.8°, n^{25}_D 1.3897) and 30% yield of tetrahydropyran (bp 82–84°, n^{25}_D 1.4193; lit. bp 81–82°, n^{25}_D 1.4195), respectively, based on complete hydrolysis of $(PNCl_2)_3$. In both of these reactions, an unidentified solid similar to the one noted above was obtained.

A Reaction of 1,6-Hexanediol with Triphosphonitrilic Chloride.—A solution containing 2.3 g of 1,6-hexanediol in 15 ml of pyridine was added to 3.5 g of triphosphonitrilic chloride. The reaction was exothermic. After the reaction had subsided, the mixture was allowed to stand at room temperature for 6 hr. The solid was separated by filtration and washed with alcohol, water, ether, and benzene, leaving 4.1 g of polymeric material melting at *ca.* 220°. Infrared spectra showed strong absorption at 1250 cm^{-1} indicating retention of the trimeric P_3N_3 ring structure.[9]

Anal. Found: C, 28.50, 28.76; H, 5.03, 5.01; Cl, positive; N, 12.25; P, 23.37, 23.56.

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Redetermination of the Hammett σ Value for the *m*-N,N-Dimethylamino Group[1]

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The σ value for the *m*-dimethylamino substituent was originally calculated to be −0.211 by Hammett,[2] using previously reported[3] rate constants for the reaction of substituted phenoxide ions with propylene oxide in 98% ethanol at 70.4°. The ρ value for this reaction was found to be −0.771 with a probable error of 0.046. Unfortunately it was later found that σ values calculated by similar indirect methods often

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(1) Supported in part by grant GM 11408 from the National Institutes of Health.

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vary widely; *e.g.*, depending on the side chain the figure for the p-N(CH$_3$)$_2$ group varies from -0.425 to -0.972.[4] Consequently the applicability of Hammett's value to reactions other than those of phenols seemed questionable.

We have redetermined the σ value for the m-N(CH$_3$)$_2$ group from the ionization constants of benzoic acid and m-N,N-dimethylaminobenzoic acid in 50% by volume ethanol. This solvent was chosen because the ρ value for the ionization of benzoic acids in it has been critically evaluated[5] and it can be shown that m-N,N-dimethylaminobenzoic acid in 50% ethanol is not more than 3% in the inner salt structure.

The result was -0.15 ± 0.04, a value quite close to the -0.211 calculated by Hammett and also within the range (-0.07–-0.20) assigned to the m-NH$_2$ group on the basis of pK_a' determinations in aqueous ethanol.[5]

Experimental Section[6]

Benzoic Acids.—National Bureau of Standards benzoic acid was used. The m-dimethylaminobenzoic acid was Eastman Practical Grade recrystallized from 95% ethanol to a constant melting point (calibrated electrically heated block) of 151.5–153.0° (lit.[6] 151°) and 100% purity by titration. Samples were dried to constant weight in a desiccator before use.

Acid Ionization Constants.—These were determined in duplicate by titration of the acids (2.00 mequiv dissolved in 190 ml of 50% by volume ethanol) with 0.100 *N* potassium hydroxide under nitrogen at 25 ± 0.03°. The pH was measured at each 0.2 mequiv by means of a Beckman Research Model 1010 pH meter equipped with a no. 41263 glass electrode with silver-silver chloride internal element and a Beckman No. 39071 frit-function calomel reference electrode. No significant differences were obtained with a Radiometer Model 4 pH meter equipped with a type GK 2021C combination calomel-glass electrode. The meter was calibrated before (and checked after) each titration with aqueous standard buffers. An amount of absolute ethanol equal to the volume of titrant increment was added before each measurement. The readings from 0.2 to 1.8 mequiv were converted to apparent pK_a (pK_a') values by the equation

$$\mathrm{p}K_a' = \mathrm{pH} + \log \frac{[\mathrm{HA}] - (\mathrm{H}^+)}{[\mathrm{A}^-] + (\mathrm{H}^+)}$$

These figures were converted to corresponding apparent ionization constants from which the mean values (and their standard deviations) were calculated and then reconverted to the following pK_a' values: benzoic acid, pK_a' 5.67 ± 0.03;[7] m-N,N-dimethylaminobenzoic acid, pK_{a_2}' 5.90 ± 0.03. These were substituted into the Hammett equation

$$\log K - \log K_0 = \sigma\rho \text{ with } \rho = 1.522^5$$

Basic Dissociation Constants.—The pK_1' for m-dimethylaminobenzoic acid (3.04 ± 0.08) was obtained by titration with 1.00 *N* hydrochloric acid of 4.00 mequiv of the compound in 200 ml of 50% ethanol. The pH at the beginning of the titration was 4.40 ± 0.04. The pH was measured at 1, 2, and 3 mequiv. The pK' (2.96 ± 0.08) of methyl m-N,N-dimethylaminobenzoate hydrochloride[8] (prepared from the acid chloride hydrochloride[9] and methanol) was obtained by titration of 2.00 mequiv of the salt in 190 ml of 50% ethanol. The pH was measured at 0.05, 0.10, and 0.15 mequiv. Both determinations were done in duplicate with an equivalent volume of ethanol added with each increment of titrant. The pH values were converted to apparent pK_a' values by the equation

$$\mathrm{p}K_a' = \mathrm{pH} + \log \frac{[\mathrm{ArN(CH_3)_2H^+}] - (\mathrm{H}^+)}{[\mathrm{ArN(CH_3)_2}] + (\mathrm{H}^+)]}$$

Percentage of Inner Salt.—This can be shown to be not more than 3% by calculation of per cent ionization both as acid and base of m-dimethylaminobenzoic acid solutions in 50% ethanol. The fact that the pK_1' of the amino acid is almost identical with the pK' of its methyl ester is consistent with this result.[10]

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The Reaction of Aniline with 1,2,3,4-Tetrachloro-1,2,3,4-tetrahydronaphthalene

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The two benzyl-type chlorine atoms in 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene (I) should be reactive, and therefore I should have synthetic utility. Although it is reported[2] that the α isomer (Iα) may be hydrolyzed to a dichlorodihydroxytetrahydronaphthalene, no other replacement reactions of Iα are reported, and no replacement reactions of Iγ and Iϵ are known.

The reaction of aniline with benzene hexachloride to produce an N-(dichlorophenyl)aniline[3] suggested that aniline might be an ideal reagent for exploring replacement reactions of I. When each of three isomers was heated with excess aniline, it was found that Iα yielded a product containing four anilino groups, that Iγ gave a product containing two anilino groups, and that Iϵ did not react.

The product of the reaction of Iα with aniline consisted of isomeric 1,2,3,4-tetraanilino-1,2,3,4-tetrahydronaphthalenes. The reported geometric configuration of Iα[4,5] leads us to suggest that the replacement of the nonbenzylic chlorine atoms may occur by way of an aziridine-type intermediate (II) (Scheme I). Participation by neighboring nitrogen in the solvolysis of alkyl halides is well known.[6]

The reaction of Iγ with aniline gave a 63% yield of a material that appears to be a single isomer of 1,4-dianilino-2,3-dichloro-1,2,3,4-tetrahydronaphthalene (III). The product is a useful synthetic intermediate for the preparation of 1,4-dianilinonaphthalene (IV) and the dianil (V). Since the literature preparation[7] of IV and V is not straightforward, V was hydrolyzed to yield naphthoquinone and aniline as a proof of structure (Scheme II).

The tendency of the reaction of Iγ with aniline to stop after the replacement of the two benzylic chlorine atoms may be due to the configuration of Iγ.[5] Re-

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