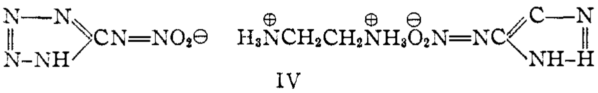
have combined in a 1:1 stoichiometric ratio. This precludes a bis-monoacid structure (IV), although one cannot distinguish the salt as being mono- or



IV

diacid. Since 5-nitroaminotetrazole does form salts with very weakly basic amines it has been assumed that the salt is diacidic.

Experimental

Nitroguanyl Azide.—This was prepared as previously described.[2] The product obtained by evaporation of the combined ether extracts, m.p. 79°, was sufficiently pure and was not recrystallized further.

Amines.—C.P. grade reagents were purified by distillation or recrystallization until they met the reported values for physical constants.

General Procedure for Reaction of Amines with Nitroguanyl Azide.—Specific illustrative examples for the preparation of the mono- and diacid salts of 5-nitroaminotetrazole have been described elsewhere.[2] In general the compounds noted in Table I were prepared by dissolving the nitroguanyl azide in ether (15 ml. for 0.01 mole) and adding the amine, in two molar proportions, also dissolved in ether (10 to 15 ml. for 0.02 mole of amine). Deviations from the use of anhydrous ether as solvent are noted in Table I. The amine salt of 5-nitroaminotetrazole, generally, immediately precipitates. However, the reaction mixture may be allowed to stand, at room temperature, for periods from 30 minutes or overnight. The crystals are removed by filtration, washed with anhydrous ethyl ether and recrystallized. The choice of solvent for recrystallization varies with the individual preparation. This has been noted in Table I.

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S-Benzylthiuronium Salts of Nitroalkyl Hydrogen Sulfates

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We have prepared as derivatives for the characterization of several low molecular weight nitroalcohols the crystalline S-benzylthiuronium salts of their sulfate esters. The latter are prepared by the addition of the nitroalcohol to a mixture of chlorosulfonic acid and dioxane.[1]

The 3,5-dinitrobenzoates of two of these nitroalcohols also have been prepared. Benzenesulfonates, *p*-toluenesulfonates[2,3] and α-naphthylurethans[4] have previously been used to characterize nitroalcohols.

Pertinent data are tabulated herewith. Melting points were determined with a Fisher–Johns apparatus which was calibrated over the 50–160° range.

TABLE I

Nitroalcohol	S-Benzylthiuronium salt M.p., °C.	Nitrogen, % Calcd.	Found
2-Nitro-1-propanol	114–115	11.96	11.81
2-Nitro-1-butanol	100–101	11.50	11.54
2-Nitro-2-methyl-1-propanol	145–146	11.50	11.46
3-Nitro-2-butanol	105–106	11.50	11.69
3-Nitro-2-pentanol	127–128	11.08	11.15
3-Nitro-3-methyl-2-butanol	119–120	11.08	11.05

Experimental

2-Nitro-2-methylpropyl 3,5-Dinitrobenzoate.—One gram of 2-nitro-2-methyl-1-propanol was dissolved in 3 ml. of anhydrous pyridine and 0.5 g. of 3,5-dinitrobenzoyl chloride was added to the stirred solution. The mixture was heated on the steam-bath for 15 minutes and then poured into 10 ml. of distilled water and stirred vigorously. The solid was collected on a filter and washed with 5 ml. of 5% sodium carbonate solution. It was recrystallized twice from 95% ethanol: m.p. 126–127°; N calcd., 13.42; N found, 13.39.

3-Nitro-3-methyl-2-butyl 3,5-Dinitrobenzoate.—Two milliliters of 3-nitro-3-methyl-2-butanol was added to 0.5 g. of 3,5-dinitrobenzoyl chloride contained in a dry test-tube. Dry pyridine was added dropwise to the mixture, allowing about five minutes for the addition of ten drops. The resulting mixture was heated over a steam-bath for 15 minutes. The reaction mixture was cooled to room temperature, and 10 ml. of distilled water was added with stirring. The product was collected and washed with 10 ml. of 2% sodium carbonate solution. Three recrystallizations from 50% aqueous ethanol gave a flaky product which melted sharply at 140°; N calcd., 12.48, N found, 12.79.

S-Benzylthiuronium 2-Nitro-1-propyl Sulfate.—Five drops of 2-nitro-1-propanol was added to a mixture of 5 drops of dry dioxane and 4 drops of chlorosulfonic acid. Hydrogen chloride was evolved immediately on shaking the test-tube. After standing 10 to 15 minutes the mixture was diluted with 1 ml. of water and added to 1 ml. of saturated aqueous S-benzylthiuronium chloride. After five minutes in an ice-bath the product precipitated, and was recrystallized three times from 10% ethanol and dried in a vacuum desiccator. The fine white needles melted at 114–115°. Analysis is given in Table I.

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Some Diels–Alder Reactions of Chloroprene[1]

BY JOHN S. MEEK AND WALTER B. TRAPP

Chloroprene has been condensed with acrolein,[2] methyl vinyl ketone,[2] methyl ethynyl ketone,[2] acrylonitrile,[3] methacrylic acid[4] and methyl methacrylate.[4]

Methyl methacrylate and methacrylic acid gave mixtures which were not separated.[4] The structure of the chloroprene–methyl ethynyl ketone adduct was shown by dehydrogenation to be *p*-chloroacetophenone.[2] The structures of the remaining adducts were not proven. However, the adducts of acrylonitrile and acrolein were converted into the same acid which was believed by Petrov and Sopov to be 4-chloro-1,2,5,6-tetrahydrobenzoic acid (I) by analogy with the chloroprene–methyl ethynyl ketone adduct.

In our work, we have shown this to be correct. This same acid, 4-chloro-1,2,5,6-tetrahydrobenzoic acid, was prepared by condensing chloroprene with acrylic acid. The adduct was brominated with N-bromosuccinimide and then dehydrohalogenated with triethylamine to give *p*-chlorobenzoic acid. Compound I was also synthesized in low yield from

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[1] This work was supported by the Office of Naval Research.

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