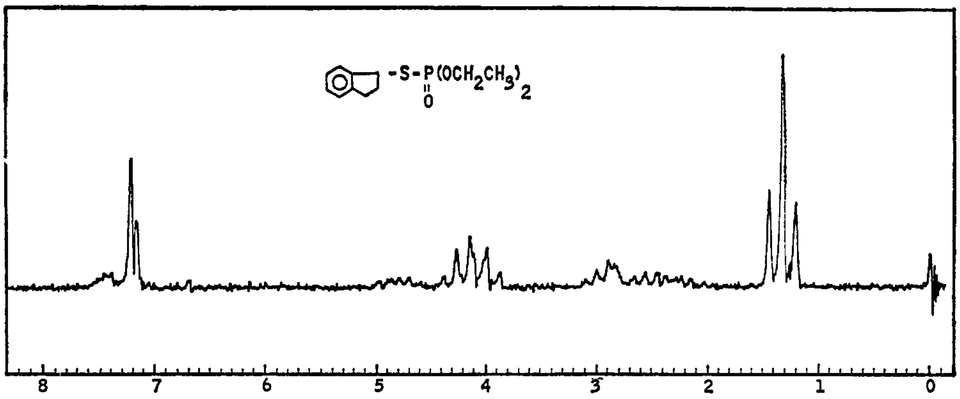

Figure 3.

last column shows clearly the difference between the effect of polar and nonpolar solvents.

These results are in qualitative agreement with the finding of Roberts and co-workers.[8] They reported that in the case of 1-phenylethyl benzyl ether the degree of magnetic nonequivalence bears an approximate inverse relation to the dielectric constant of the solvent.

In view of the preceding, it was surprising to find that O,O′-diethyl S-(1-indanyl)thiophosphate did not show a similar nonequivalence for the ethoxy groups (Figure 3). It should be noted in this connection that Roberts[8] also found, that, in contrast to the methylene group in 1-phenylethyl benzyl ether, the corresponding protons in indanyl benzyl ether were equivalent in all solvents investigated.

We have also studied a number of similar thiophosphates not containing an aromatic ring moiety and they all exhibit a single triplet at 1.33 ppm for all the methyl protons of the ethoxy groups. The indanylthiophosphate (Figure 3) also shows a triplet at this position demonstrating that the π system of the benzene ring does not effect the methyl's chemical shift. In contrast, the two triplets from compound I are both shifted upfield. Thus, the two ethoxy groups apparently experience diamagnetic shielding, although to a different extent.

More data will be necessary in order to draw valid conclusions as to the possible factors causing this nonequivalence. We feel, however, that the data supplied here are of interest to workers in this field and may stimulate such further research.

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[8] G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1058 (1965).

2-Amino-4,6-diazido-1,3,5-triazine

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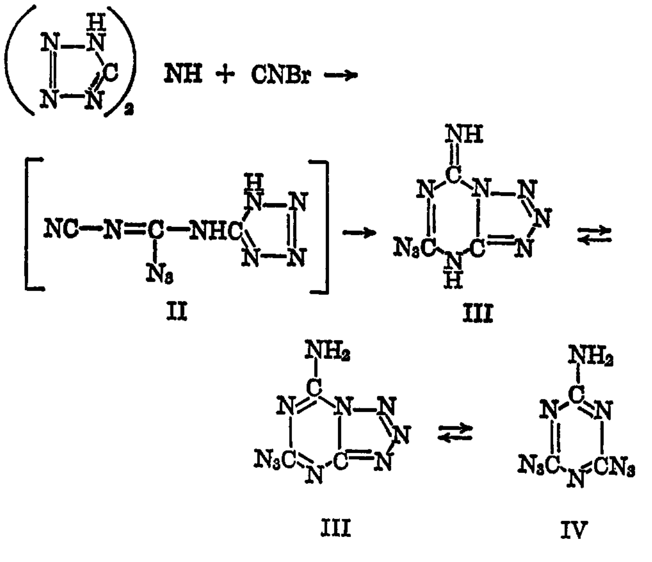
The opening of the ring in 5-(substituted-amino)-tetrazoles by cyanogen bromide to give substituted cyanoguanyl azides was recently examined in some detail.[1] When an attempt was made to extend this to the preparation of 2,4-diazido-1,5-dicyano-1,3,5-triaza-1,4-pentadiene (I), $NC—N{=}C(N_3)NHC(N_3){=}NCN$, from the disodium salt of bis(5-tetrazolyl)amine and 2 molar equiv of cyanogen bromide, there was obtained a base-insoluble product whose infrared spectrum revealed azido function at 2140 cm^{-1} (Nujol mull or N,N-dimethylformamide solution), but unexpectedly no nitrile function (cyanoguanyl azides show both functions). In addition the compound remained unchanged when treated with base under conditions which convert cyanoguanyl azide derivatives to tetrazolines.[1] A better yield of the same compound was realized when only 1 mole of cyanogen bromide was employed per mole of bis(tetrazolyl)amine.

The analytical data indicated that only one cyano group, rather than two, had been introduced per mole of starting bis(tetrazolyl)amine. Reduction of the compound with hydrogen sulfide in ammoniacal aqueous ethanol gave sulfur and melamine. A structure consistent with all of these facts is 2-amino-4,6-diazido-1,3,5-triazine (IV), whose formation can be depicted by Scheme I. One of the tetrazole rings is opened by the cyanogen bromide in the expected fashion to yield II which then undergoes an intramolecular cyclization

SCHEME I



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[1] W. P. Norris and R. A. Henry, *J. Org. Chem.*, **29**, 650 (1946).

between the nitrile group and the other tetrazole ring to give the substituted tetrazolotriazine, III. Because the triazine ring in the latter is electronegative, the second tetrazole ring is destabilized and is opened to yield the isomeric azidotriazine IV.

Previous investigations[2] have conclusively demonstrated with heterocyclic systems the existence of an azidoazomethine–tetrazole equilibrium, the position of which is dependent on solvent, temperature, and the electronegativity of the heterocyclic ring. With the present compound the evidence suggests that in solution at least the equilibrium strongly favors IV over III.[3] For example, 2 moles of nitrogen/mole of IV were rapidly evolved when the latter was treated with either potassium iodide in trichloroacetic acid solution or potassium arsenite in potassium hydroxide solution. With either reducing agent, a plot of the volume of nitrogen evolved as a function of reaction time revealed no break which might indicate a rapid evolution of 1 mole of gas followed by the slower evolution of the second. Furthermore, with a fixed-thickness cell and with solutions of the same molar concentration the intensity of the azido absorption in the infrared was the same in either N,N-dimethylformamide or trifluoroacetic acid (probably because of protonation there was a shift of *ca.* 70 cm^{-1} to a higher frequency in the latter solvent). This behavior should be contrasted with that of 2-azido-4,6-dimethylpyrimidine which reveals azido absorption in trifluoroacetic acid at 2180 cm^{-1}, but none in N,N-dimethylformamide since the equilibrium now favors the isomer, 5,7-dimethyltetrazolo[1,5-*a*]pyrimidine.[2]

Hart[4] previously prepared 2-amino-4,6-diazido-1,3,5-triazine by ammonolyzing 2,4,6-triazido-1,3,5-triazine in diethyl ether; he also reduced this compound to melamine with hydrogen sulfide.

A base-soluble material of undetermined structure was also formed in the reaction of cyanogen bromide and disodium bis(tetrazolyl)amine, and was recovered by acidifying the mother liquors after the aminodiazidotriazine was removed. This compound, which contains an azido but apparently also no cyano group and which rapidly turns purple in the light, was difficult to purify because of its gelatinous nature in aqueous solutions and its insolubility or very low solubility in all common solvents. The analyses suggest a 2:1 reaction product but its properties argue strongly against its being I.

An attempt to extend this ring-opening, recyclization reaction to the preparation of 2-azido-4,6-diamino-1,3,5-triazine, by reacting equimolar amounts of cyanogen bromide and the sodium salt of 5-guanylaminotetrazole, was unsuccessful.

Experimental Section

2-Amino-4,6-diazido-1,3,5-triazine.—A solution consisting of 8.55 g (0.05 mole) of bis(5-tetrazolyl)amine, 2.0 g (0.05 mole) of sodium hydroxide, and 75 ml of water was cooled to 5°. With stirring, 5.3 g (0.05 mole) of cyanogen bromide was added in three portions during 5 min. Then 10 ml of acetone was added; the temperature rose to 8° and held for several minutes. When the temperature had dropped to 5°, 20 ml more of acetone was added and the solution allowed to stand for 2.5 hr at 0–5°. The pH was then adjusted to the phenolphthalein end point and the product removed by filtration, washed well with cold water, and dried; yield, 5.75 g (64.7%). The gray product turned pink in sunlight. It was sparingly soluble in diethyl ether and in ethanol; a small portion (2.3 g) was recrystallized for analyses from 600 ml of 95% ethanol; the flat white needles did not melt up to 250° although they turned brown at 210–220°. When dropped on a hot surface at 300°, they exploded.

Anal. Calcd for $C_3H_2N_{10}$: C, 20.23; H, 1.13; N, 78.64; mol wt, 178; azide nitrogen, 47.2. Found: C, 19.90; H, 1.09; N, 78.8, 78.2; mol wt, 174; azide nitrogen,[5] 46.7; azide nitrogen,[6] 45.8.

When this reaction was performed using 0.1 mole of bis(tetrazolyl)amine, 0.2 mole of sodium hydroxide, and 0.2 mole of cyanogen bromide, the yield of aminodiazidotriazine was 2.3 g (12.9%).

The aminodiazidotriazine (1.03 g) was dissolved in 150 ml of 95% ethanol, 50 ml of water, and 0.5 ml of concentrated aqueous ammonium hydroxide by warming on the steam bath; hydrogen sulfide was bubbled into the hot solution until no more sulfur precipitated. (No reduction occurred in the absence of the ammonium hydroxide.) The solution was filtered hot and the sulfur washed with hot water. The yield of dried sulfur was quantitative (0.37 g). The combined filtrate and washings were evaporated to dryness and the residue extracted with carbon disulfide to remove any traces of sulfur. The yield of crude product melting above 310° and considered to be melamine was quantitative (0.73 g); the infrared spectrum was essentially the same as that for authentic melamine. The X-ray powder pattern also confirmed melamine.

The cold, aqueous mother liquors from the original reaction were acidified with an excess of concentrated hydrochloric acid. A voluminous, gelatinous, yellow solid separated; warming did not improve its physical properties. Some of the material was removed by filtration and washed well with water. The dried product decomposed explosively on a hot plate at 300°. The infrared spectrum revealed broad, hydrogen-bonded NH at 3230–3030 cm^{-1}, C=N at 1620, and azide at 2140; the latter was confirmed by the liberation of iodine when a solution of the compound in trifluoroacetic acid was treated with potassium iodide in acetonitrile. This material was purified by solution in aqueous sodium bicarbonate (rapid reaction), filtering from a small amount of insoluble, and reprecipitation in an excess of dilute, aqueous hydrochloric acid. The gelatinous solid was filtered and washed repeatedly with water until free of salt and inorganic acid. The gray-purple, amorphous compound was dried under vacuum at 85° (25 mm) for 72 hr; the infrared spectrum was identical with that for the crude product. This compound was insoluble in pyridine, acetone, ethanol, and tetrahydrofuran; it was slightly soluble in dimethylformamide and tetramethylurea; it dissolved in dimethyl sulfoxide with gas evolution and the formation of a dark-colored solution; it was sparingly soluble in hexafluoroacetone hydrate, but again the solution was very dark suggesting some decomposition. The nmr spectrum of a solution of the compound in deuterium oxide–sodium carbonate revealed only exchangeable protons; a saturated solution in tetramethylurea showed only a broad absorption centered at τ 3.6 (proton on nitrogen).

Anal. Calcd for $(C_2H_3N_6)_n$: C, 21.62; H, 2.72; N, 75.66. Found: C, 21.42, 21.50; H, 2.60, 2.79; N, 75.74, 75.50.

When some of this second compound in aqueous sodium bicarbonate was treated with hydrogen sulfide, sulfur was precipitated. The material recovered by acidifying the resulting solution showed neither azido nor cyano absorption in the infrared spectrum; the potassium iodide–trifluoroacetic acid test was also negative.

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[2] C. Temple, Jr., and J. A. Montgomery, *J. Org. Chem.*, **30**, 826 (1965), and references therein.

[3] Elucidation of the structure in the solid state is currently being attempted by Dr. G. J. Palenik from X-ray crystallographic data.

[4] C. V. Hart, *J. Am. Chem. Soc.*, **50**, 1922 (1928).

[5] Determined gasometrically by Dr. W. R. Carpenter of this laboratory; W. R. Carpenter, *Anal. Chem.*, **36**, 2352 (1964).

[6] I. Ugi, H. Perlinger, and L. Behringer, *Ber.*, **91**, 2330 (1958).