to precipitate the crude product. Recrystallization from ethyl acetate–petroleum ether gave 1.0 g., 82%, of the pure product, m.p. 156°.

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71. Found: C, 75.07; H, 6.61.

2-[β-(*p*-Diethylaminostyryl)]-6-methyl-4-pyrone.—This compound was prepared from the diethylamino analog by the process described in the preceding experiment; yield 68%, m.p. 128–130°. Recrystallized from methanol–water.

Anal. Calcd. for $C_{18}H_{21}O_2N$: C, 76.29; H, 7.47. Found: C, 76.32; H, 7.29.

2-(*o*-Nitrophenyl)-6-methyl-4-pyrone.—One gram of 3-(*o*-nitrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone was refluxed for 10 hours in 100 ml. of concd. hydrochloric acid. The solution was cooled and neutralized to precipitate the crude product. Recrystallization from methanol–water gave 52.5% of product, m.p. 187–189°.

Anal. Calcd. for $C_{14}H_{11}O_4N$: C, 65.36; H, 4.31. Found: C, 65.19; H, 4.30.

The 2-(*p*-Isopropylphenyl)-6-methyl-4-pyrone.—One-half gram of 3-(*p*-isopropylcinnamoyl)-4-hydroxy-6-methyl-2-pyrone was refluxed in 100 ml. of glacial acetic and 50 ml. of concd. hydrochloric acid for 6 hours. The solution was cooled and neutralized to precipitate the crude product. Recrystallization from ethanol and water gave 0.19 g. (44.5%) of product, m.p. 110–112°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.47; H, 7.13.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer using 1.00-cm. silica cells and hydrogen and tungsten discharge lamps as light sources. Methanol solutions of the compounds were used.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Preparation, Structure and Properties of 4,5,6,7-Tetrachlorobenzotriazole and its 1- and 2-Substitution Products

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4,5,6,7-Tetrachlorobenzotriazole has been prepared in 87% yield by the chlorination of benzotriazole with aqua regia. 1-Methyl- and 2-methyl-4,5,6,7-tetrachlorobenzotriazole have been obtained by alkylation and the latter by chlorination of 2-methylbenzotriazole. Ultraviolet absorption spectra establish the structural assignments and show that in 1,4-additions to unsaturated systems, a reaction giving 1-substituted derivatives from benzotriazole, the 2-substituted isomers are formed apparently for steric reasons. Tetrachlorobenzotriazole is a weak acid, pK_a 3×10^{-5}, and forms interconvertible salts in mole ratios of 2/1 and 3/1 with benzyltrimethylammonium hydroxide.

The problem of the structural isomerism of the 1- and 2-substituted-1,2,3-triazoles has been clearly resolved with only one parent triazole—benzotriazole. With benzotriazole—but not with uncondensed triazoles—ultraviolet absorption data distinguish the two isomers and chemical data establish the positions of the substituents. Because it has been necessary to extend these data to situations and structures not closely related to benzotriazole, it is highly desirable that additional data about the distinguishing characteristics of such isomers be available. One attractive source of such information lies in the possibility of separating and identifying the 1- and 2-isomers of substituted benzotriazoles. The difficulty presented by this approach is that practically nothing is known about the substitution reactions of benzotriazole and its derivatives. Fries and co-workers have reported[3] that nitration gives the 4-nitro derivative and Zincke and Arzberger that chlorination[4] converts 5-methyl- or 5-bromobenzotriazole to 4,6,7-trichloro derivatives. Some additional work has been reported on the substitution reactions of 4- and 5-hydroxy- and 4- and 5-aminobenzotriazoles.[3,5] Indeed, the few substituted benzotriazoles known—5-nitro, 5-chloro, 5-bromo, 5-methyl and 5,6-dimethyl—are the 5-substituted type which are available from *p*-substituted anilines by cyclization of the derived *o*-phenylenediamine. Since all of these substituted benzotriazoles (except the unaccessible dimethyl compound) are unsymmetrical themselves, additional structural isomeric possibilities arise. Thus, although there are only two N-methylbenzotriazoles (1-methyl and 2-methyl), there are three N-methyl-4-chlorobenzotriazoles. This complication is not present in symmetrically substituted benzotriazoles and in order to have such material readily available for study, our attention was directed to the possibility of preparing 4,5,6,7-tetrachlorobenzotriazole by the chlorination of benzotriazole. We wish to report the results of studies which make this compound, 4,5,6,7-tetrachlorobenzotriazole, readily available and studies of its reactions which considerably extend the presently available knowledge of the structural problems encountered in the 1- or 2-isomerism of triazoles.

Since Zincke had reported,[4] without complete experimental details, the chlorination by means of aqua regia of 5-bromobenzotriazole and of 5-methylbenzotriazole to the corresponding trichloro derivatives it seemed possible that 5-chlorobenzotriazole could be chlorinated in this way to 4,5,6,7-tetrachlorobenzotriazole. This chlorination now has been achieved, and, in addition, benzotriazole itself has been found to chlorinate to the same tetrachlorobenzotriazole. Yields of 87–89% of tetrachlorobenzotriazole are obtained by refluxing benzotriazole with aqua regia for 3 hours. The reaction is easy and quick so that the tetrachloro compound can be considered the most accessible symmetrically substituted benzo-

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[3] K. Fries, H. Güterbock and H. Kühn, *Ann.*, **511**, 213 (1934).

[4] Th. Zincke and H. Arzberger, *ibid.*, **249**, 370 (1888).

[5] K. Fries, *et al.*, *ibid.*, **389**, 318, 358, 367 (1912).

triazole. It seems that this is also the first symmetrically tetrasubstituted benzotriazole known. The product is weakly acidic with a dissociation constant of *ca.* 3×10^{-5}.

2-Methyl-4,5,6,7-tetrachlorobenzotriazole was synthesized by two independent routes—by methylation of the parent tetrachlorobenzotriazole with methyl sulfate in aqueous alkali and by chlorination of 2-methylbenzotriazole with aqua regia. The stability of 2-methylbenzotriazole to oxidative attack by the aqua regia treatment is further interesting evidence of the inaccuracy of any simply *o*-quinoid structure for 2-substituted benzotriazoles. The identity of the products from these two routes is complete proof for the assigned structure. From the methylation a smaller amount of 1-methyl-4,5,6,7-tetrachlorobenzotriazole was isolated from the nitric acid mother liquors. The fact that the 1-methyl derivative is more soluble in nitric acid is consistent with the behavior of the alkylated benzotriazoles of which the 1-methyl is also the more basic. From the aqua regia chlorination of 1-methylbenzotriazole a 1-methyl-x,y,z-trichlorobenzotriazole was isolated. This is most probably the 4,5,6-trichloro compound in which the 7-position, shielded by the 1-methyl group, fails to chlorinate for steric reasons consistent with other observations establishing such hindrance at the 1- and 7-positions.

The ultraviolet spectra of these two compounds are in complete accord with the structural assignments. The ultraviolet spectra of benzotriazole and its 1-alkyl derivatives are nearly identical, showing two maxima at 255 and 283 mμ.[6–8] The spectra for 2-alkylbenzotriazoles are quite different showing a single maximum at 275 mμ (*cf.* Table I). The spectra for the tetrachlorobenzotriazole and its methyl derivatives show the expected shift to longer wave lengths as compared to benzotriazole but are, in shape, practically superimposable on the spectra of the parent unchlorinated compounds. One difference does appear. The spectra of the chloro compounds have shifted so far that one new maximum has appeared, a strong maximum at 223 mμ. That this is a maximum derived from the benzenoid ring alone seems clear from the fact that the position and intensity of this maximum are the same for tetrachlorobenzotriazole which has the 1-substituted type of curve, and for the 2-substituted propionic acid derivative. These two compounds have no spectral features in common other than the benzenoid ring. This suggests that a vacuum ultraviolet study of benzotriazole and 2-methylbenzotriazole might give important evidence on the nature of the bonding in 2-alkylbenzotriazoles. The data are given in Fig. 1 and Table I.

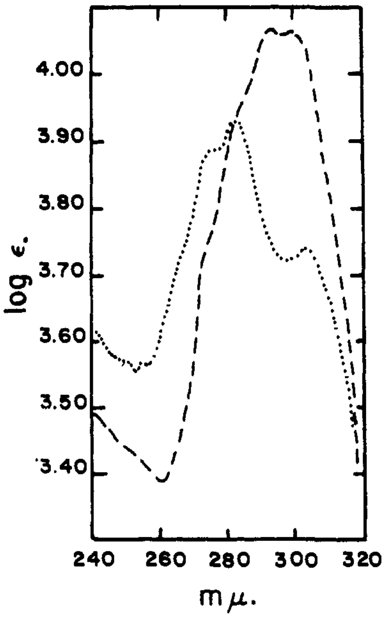

Fig. 1.—Ultraviolet absorption data: ...., 1-methyl-4,5,6,7-tetrachlorobenzotriazole; – – –, 2-methyl-4,5,6,7-tetrachlorobenzotriazole.

TABLE I

Compound	λ_{max}, mμ	log ε
Tetrachlorobenzotriazole	223	4.22
	274sh.	3.81
	280	3.84
	297	3.74
1-Methyl-	276sh.	3.89
	284	3.92
	304	3.74
2-Methyl-	294	4.06
	300	4.06
β-[2′-(4′, 5′, 6′, 7′-Tetrachlorobenzotriazolyl)]-	223	4.26
	294	4.09
Propionic acid	302	4.08
	294	4.10
Propionamide	302	4.09
	293	4.06
Propionitrile	302	4.05
	294	4.09
Butyric acid	302	4.08
β-Phenyl-β-[2′-(4′, 5′, 6′, 7′-tetrachlorobenzotriazolyl)]-propiophenone	220	4.72
	296	4.23
	ca. 302sh.	4.22
Salt I (2:1)	*ca.* 290plat.	4.23
	298	4.26
Salt II (3:1)	220	5.03
	274sh.	4.33
	282	4.38
	298	4.33
Benzotriazole[7]	254	3.74
	275	3.68
1-Methyl-[a]	255	3.81
	283	3.68
2-Methyl-[a]	275	3.90
Acetophenone	245	4.13
	282	3.15
2-Dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole	296	4.14
	301	4.14
1-Methyl-x,y,z-trichlorobenzotriazole	267	3.88
	275	3.87
	302	3.77

[a] H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942).

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(6) F. Krollpfeiffer, H. Pötz and A. Rosenberg, *Ber.*, **71B**, 596 (1938).

(7) H. Specker and H. Gawrosch, *ibid.*, **75B**, 1338 (1942).

(8) R. H. Wiley, N. R. Smith, D. M. Johnson and J. Moffat, This Journal, **76**, 4933 (1954); **77**, 2572 (1955).

As can be seen from Table I, tetrachlorobenzotriazole and its 1-methyl derivative have very similar spectra, the 274 mμ shoulder and 280 mμ maximum being a partially resolved double maximum corresponding to the 254 mμ maximum for benzotriazole, and the longer wave length maximum corresponding to the 275 mμ maximum for benzotriazole. The double maxima listed for the compounds assigned the 2-alkyl structure require comment. In each case one smooth absorption peak is noted with a slight depression in the center, never more than 0.02 different in log ϵ from the maxima flanking it. Since this behavior was observed for all these compounds we have assumed that it represents a real double maximum, barely resolved, and have so listed it. It will be seen, then, that taking the parent compounds and the two methyl derivatives of each, the average shift in position of the maxima from the benzotriazoles to the chlorinated compounds is about 23 mμ. On this basis, the 223 mμ peak for the chloro compounds should be at about 200 mμ for benzotriazole.

When tetrachlorobenzotriazole was submitted to the azole addition reaction[8] adducts were obtained readily from acrylic and crotonic acids, acrylonitrile, acrylamide and benzalacetophenone. All of these adducts were shown by ultraviolet spectra to have the "single" maximum characteristic of the 2-alkyl-4,5,6,7-tetrachlorobenzotriazoles. This is in striking contrast with the results of this reaction with benzotriazole[8] which gave only 1-alkyl derivatives. The fact that these adducts are 2-alkyl compounds, and the fact that the methylation of tetrachlorobenzotriazole gives more 2-methyl than 1-methyl derivative in contrast to the results with benzotriazole,[6,7] are clear evidence for a rather important steric hindrance by the 4,7-chlorine atoms to 1-substitution. It is to be supposed that still bulkier groups in the benzenoid ring will produce still more pronounced effects. This is under investigation in this Laboratory.

When attempts were made to extend the azole addition reaction of tetrachlorobenzotriazole to *m*-nitrobenzaldehyde, *p*-nitrobenzaldehyde and to methacrylamide, the same crystalline product (m.p. 197–199°) was isolated from all three reactions. A second product (m.p. 184–186°) was isolated from attempts to add the tetrachloro compound to *p*-methoxybenzalacetone and to benzalacetone. It was found after considerable confusion that the two compounds were interconvertible by recrystallization from suitable solvents, ethyl acetate always giving the former compound (m.p. 197–199°) and nitromethane the latter (m.p. 184–186°). Complete elemental analysis on the first compound, molecular weight determination and isolation of tetrachlorobenzotriazole and of benzyltrimethylammonium picrate by treatment with picric acid showed that this compound was an acid salt of benzyltrimethylammonium hydroxide and tetrachlorobenzotriazole in the molecular ratio of 1:2. Even more startling was the discovery that the lower melting compound was an acid salt of the same components in the ratio of 1:3. These interesting salts presumably represent partially neutralized products of a hydrogen-bonded polymeric acid. It is conceivable that similar salts could be found with simpler cations than the benzyltrimethylammonium ion.

Alkylation of tetrachlorobenzotriazole with dimethylaminoethyl chloride gave a mixture from which one isomer was isolated in the pure state and shown by ultraviolet spectrum to be 2-(2′-dimethylaminoethyl) - 4,5,6,7 - tetrachlorobenzotriazole.

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Experimental

4,5,6,7-Tetrachlorobenzotriazole. A. From 5-Chlorobenzotriazole.—A solution of 6.14 g. (0.040 mole) of 5-chlorobenzotriazole in 300 ml. of concd. hydrochloric acid and 100 ml. of concd. nitric acid was heated under reflux for 3 hours. A solid product began to precipitate after about 20–30 minutes. The product was collected on a filter, washed with hydrochloric acid and with water. There was obtained 9.1 g. (89%), of crystalline product, m.p. 253–256°. Recrystallization from methanol gave a product, m.p. 256–260°.

Anal. Calcd. for $C_6HN_3Cl_4$: C, 28.05; H, 0.39; N, 16.36; Cl, 55.20; neut. equiv., 256.9. Found: C, 28.14; H, 0.70; N, 16.54; Cl, 54.17; neut. equiv., 257.9.

This compound is soluble in cold ether and in acetone. It is insoluble in carbon tetrachloride hot or cold, and can be recrystallized from toluene, methanol, ethanol, ethyl acetate or most conveniently from nitromethane. It is very insoluble in water and in acids, except for concentrated sulfuric acid, but is easily soluble in bases. Its approximate dissociation constant from titration data is 3×10^{-5}.

B. From Benzotriazole.—A solution of 4.76 g. (0.040 mole) of benzotriazole in a mixture of 525 ml. of concd. hydrochloric acid and 175 ml. of concd. nitric acid was heated under reflux for 3 hours, cooled and diluted to precipitate 9.0 g. (87%), of product, m.p. 242–246°. Recrystallization from nitromethane gave a white crystalline solid, m.p. 256–260°, which was identical with the material from the preceding reaction.

2-Methyl-4,5,6,7-tetrachlorobenzotriazole. A. From Tetrachlorobenzotriazole.—To a solution of 6 g. (0.023 mole) of tetrachlorobenzotriazole in 100 ml. of 0.5 *N* sodium hydroxide, 3.17 g. (0.025 mole) of methyl sulfate was added dropwise over 15 minutes. The solution was heated at boiling for 0.5 hour on the steam-bath. The cooled, soapy, unfilterable solution was extracted with four 100-ml. portions of benzene. The combined benzene extracts were washed, dried and evaporated to dryness to give 4.9 g. (77%) of a crude mixture of 1- and 2-methyl derivatives melting from 120 to 160°. Two recrystallizations from concd. nitric acid gave long, white needles of pure 2-methyl-4,5,6,7-tetrachlorobenzotriazole which was identical with the material described in the following paragraph.

B. From 2-Methylbenzotriazole.—A solution of 4 g. (0.030 mole) of 2-methylbenzotriazole in 300 ml. of concd. hydrochloric acid and 100 ml. of concd. nitric acid was heated under reflux. A crystalline precipitate formed within 1 minute, melted, and redissolved as the solution warmed up. A second crystalline material gradually precipitated from the hot solution. After 6 hours heating the solution was cooled, filtered, and the crystalline product was collected, washed, and dried. There was obtained 4.0 g. (50%) of the crude 2-methyl compound, m.p. 165–170°. Several recrystallizations from methanol gave material melting 179–183° alone or mixed with a sample from the preceding reaction. A final crystallization from methanol gave an analytical sample m.p. 181–184°.

Anal. Calcd. for $C_7H_3N_3Cl_4$: C, 31.03; H, 1.12; N, 15.51; Cl, 52.35. Found: C, 31.06; H, 1.34; N, 15.50; Cl, 52.28.

1-Methyl-4,5,6,7-tetrachlorobenzotriazole.—The first nitric acid filtrate from the recrystallization of the mixture of 1- and 2-methyltetrachloro compounds was diluted with water to precipitate crude 1-methyl-4,5,6,7-tetrachlorobenzotriazole. This material was recrystallized from carbon tetrachloride three times for analysis; m.p. 193.5–196.5°.

Anal. Calcd. for $C_7H_3N_3Cl_4$: Cl, 52.35. Found: Cl, 52.56.

1-Methyl-x,y,z-trichlorobenzotriazole.—By heating 6.0 g. of 1-methylbenzotriazole for 4 hours with a mixture of 300 ml. of concd. hydrochloric acid and 100 ml. of concd. nitric acid a precipitate was obtained. This was collected, washed and dried to give 9.0 g. of crude, crystalline material, m.p. *ca.* 160°. Further treatment with hot aqua regia did not change its melting point behavior. After three recrystallizations from methanol it melted at 165–168°.

Anal. Calcd. for $C_7H_4N_3Cl_3$: Cl, 44.98. Found: Cl, 44.70.

Since there are four possible 1-methyl-x,y,z-trichlorobenzotriazoles, all unknown, it is not at present possible to assign a structure to this compound. For reasons stated previously, it is thought to be the 4,5,6-trichloro compound.

β-2′-(4′,5′,6′,7′-Tetrachlorobenzotriazolyl)-propionic Acid.—A mixture of 2.1 g. (0.082 mole) of tetrachlorobenzotriazole, 1.05 g. (0.145 mole) of acrylic acid and 1.5 ml. of pyridine was heated 17 hours on the water-bath and diluted with 100 ml. of water to precipitate 2.5 g. (92%) of crude product. Recrystallization once from benzene and three times from acetic acid–water gave white crystals, m.p. 188–192°. This substance is soluble in the cold in ether, ethanol, carbon tetrachloride, acetonitrile, acetone, ethyl acetate, acetic acid and dioxane.

Anal. Calcd. for $C_9H_5N_3Cl_4O_2$: C, 32.86; H, 1.53; N, 12.77; neut. equiv., 329. Found: C, 33.16; H, 1.74; N, 12.80; neut. equiv., 326.

β-2′-(4′,5′,6′,7′-Tetrachlorobenzotriazolyl)-propionitrile.—A mixture of 2.0 g. (0.0078 mole) of tetrachlorobenzotriazole, 5.0 g. (0.12 mole) of acrylonitrile, and 5 drops of benzyltrimethylammonium hydroxide solution was heated 18 hours at 75°. The reaction mixture was diluted with 100 ml. of ether to precipitate 1.3 g. (52%) of crude product. Recrystallization from toluene and then from methanol gave a product, m.p. 195–198°.

Anal. Calcd. for $C_9H_4N_4Cl_4$: C, 34.87; H, 1.30. Found: C, 35.01; H, 1.34.

β-2′-(4′,5′,6′,7′-Tetrachlorobenzotriazolyl)-butyric Acid.—A mixture of 2.57 g. (0.0100 mole) of tetrachlorobenzotriazole, 0.86 g. (0.0100 mole) of crotonic acid and 50 drops of pyridine was heated for 18 hours at 100°. The reaction mixture was diluted with 5 ml. of acetone and poured into 75 ml. of 0.5 *N* hydrochloric acid to precipitate 3.0 g. (87%) of the crude, crystalline product. Recrystallization several times from acetic acid-water gave the product, m.p. 201–203°.

Anal. Calcd. for $C_{10}H_7N_3Cl_4O_2$: C, 35.01; H, 2.06; neut. equiv., 343. Found: C, 35.35; H, 2.27; neut. equiv., 346.

β-2′-(4′,5′,6′,7′-Tetrachlorobenzotriazolyl)-propionamide.—Ten drops of benzyltrimethylammonium hydroxide solution was added to a melt of 2.57 g. (0.0100 mole) of tetrachlorobenzotriazole and 0.71 g. (0.0100 mole) of acrylamide. The mixture was heated 18 hours at 80°, cooled, and diluted with 125 ml. of ether to precipitate 1.9 g. (58%) of product recrystallized once from nitromethane. Two more recrystallizations from nitromethane and three from ethyl acetate were used to prepare an analytical sample, m.p. 250-253° with previous softening.

Anal. Calcd. for $C_9H_6N_4Cl_4O$: C, 32.95; H, 1.84. Found: C, 33.03; H, 1.95.

β-Phenyl-β-2′-(4′,5′,6′,7′-tetrachlorobenzotriazolyl)-propiophenone.—To a melt of 1.28 g. (0.0050 mole) of tetrachlorobenzotriazole and 0.73 g. (0.0035 mole) of benzalacetophenone was added 5 drops of benzyltrimethylammonium hydroxide solution. The mixture was heated 24 hours at 80°. Dilution of the cooled reaction mixture with 55 ml. of ether precipitated 1.68 g. (*ca.* 100%) of crude product. Three recrystallizations from nitromethane gave the product, m.p. 160–162°.

Anal. Calcd. for $C_{21}H_{13}N_3Cl_4O$: C, 54.22; H, 2.82. Found: C, 54.38; H, 2.85.

Benzyltrimethylammonium Bi-(4,5,6,7-tetrachlorobenzotriazolate). A. From Attempted Azole Addition Reaction.—When 1.285 g. of tetrachlorobenzotriazole was heated with 0.755 g. of *m*-nitrobenzaldehyde and the reaction mixture diluted with ether 0.6 g. of crystalline material, m.p. 184–187°, was isolated. This material melted 197–199° after one recrystallization from ethyl acetate, unchanged after two more recrystallizations.

Anal. Calcd. for $C_{22}H_{17}N_7Cl_8$: C, 39.85; H, 2.58; N, 14.79; Cl, 42.78; mol. wt., 633. Found: C, 39.90, 40.00; H, 2.70, 2.56; N, 14.48, 14.62; Cl, 42.71, 42.70; mol. wt., 662.

When a small sample of this compound, dissolved in methanol and mixed with excess methanolic picric acid, was poured into 100 ml. of boiling water a crystalline precipitate of tetrachlorobenzotriazole was isolated by filtration of the hot solution and recrystallized from methanol, m.p. 258.5–262°. Its mixed m.p. with a sample of tetrachlorobenzotriazole showed no depression. From the filtrate a picrate precipitated which melted at 169–172° alone or mixed with an authentic sample of benzyltrimethylammonium picrate.

B. By Direct Synthesis.—When mixtures of tetrachlorobenzotriazole and benzyltrimethylammonium hydroxide in the ratios of 2:1 and 3:1 were heated in *t*-butyl alcohol and the product precipitated by dilution with ether the 2:1 salt, m.p. 195–197°, was isolated in each case in yields of 73 and 83% based on azole.

Benzyltrimethylammonium Tri-(4,5,6,7-tetrachlorobenzotriazolate).—When a mixture of 1.76 g. of *p*-methoxybenzalacetone and 2.57 g. of tetrachlorobenzotriazole and 10 drops of benzyltrimethylammonium hydroxide solution was heated at 80° for 18 hours and then diluted with ether there was obtained 1.2 g. of crystalline material melting at 180–183°. Three recrystallizations from nitromethane gave the product, m.p. 184–186°.

Anal. Calcd. for $C_{28}H_{18}N_{10}Cl_{12}$: C, 36.55; H, 1.97; mol. wt., 290. Found: C, 36.54, 36.75; H, 2.04, 2.21; mol. wt., 291.

Interconversion of Bi- and Tri-(4,5,6,7-tetrachlorobenzotriazolates).—By a single recrystallization of the analytically pure bi-triazolate, m.p. 197–199°, from nitromethane the tri-triazolate, m.p., alone or mixed with analyzed tri-triazolate, 184–186°, was obtained. By a single recrystallization of tri-triazolate, m.p. 184–186°, from ethyl acetate there was obtained the bi-triazolate, m.p., alone or mixed with analyzed bi-triazolate, 197–199°.

2-Dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole.—A mixture of 2.57 g. (0.01 mole) of tetrachlorobenzotriazole, 1.44 g. (0.01 mole) of dimethylaminoethyl chloride hydrochloride and 1.12 g. (0.017 mole) of potassium hydroxide in 100 ml. of methanol was refluxed four hours. The reaction mixture was diluted with 100 ml. of water, made distinctly alkaline, and filtered to separate 2.5 g. (62%) of a crude product, m.p. 140–215°, which was obviously a mixture. By heating with carbon disulfide this was separated into a soluble fraction and an insoluble fraction. The insoluble fraction has not been characterized. The soluble fraction, m.p. 146–150° crude, was recrystallized from ethanol to give the product, m.p. 145°.

Anal. Calcd. for $C_{10}H_{10}N_4Cl_4$: C, 36.61; H, 3.07; N, 17.08; Cl, 43.24. Found: C, 36.62; H, 3.18; N, 17.07; Cl, 43.29.

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