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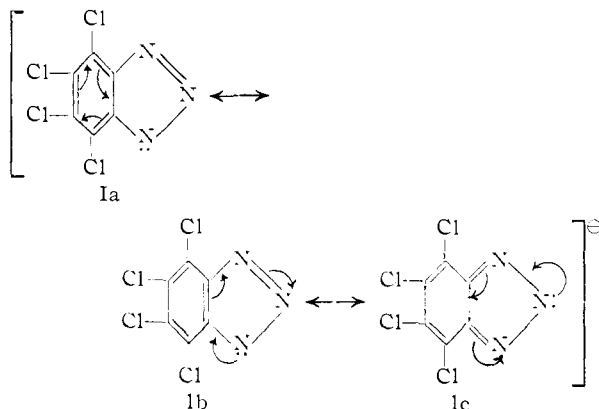
## Halogenated Benzotriazoles<sup>1</sup>

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4,7- and 5,6-dichlorobenzotriazole add to conjugated systems to give 2- and 1-substituted derivatives, respectively. This establishes with more certainty the previously postulated steric effect in which 4,7-substituents direct this type of addition to the 2-position. Tetrabromobenzotriazole and 5-methyl-4,6,7-trichlorobenzotriazole also give 2-substituted conjugate addition products. The halogenation of 2-methyl-4-nitro-, 4-nitro- and 2,5-dimethylbenzotriazoles gives the 4,5,6,7-tetrachloro derivative with replacement of the bz substituent by chlorine. Some previously undescribed compounds including several tetrachlorobenzotriazole derivatives, 4-iodobenzotriazole and 2-methyl-5-nitrobenzotriazole have been prepared and characterized. Nitration of 2-methylbenzotriazole gives the 5-nitro derivative whose structure has been established by comparison with 2-methyl-4-nitrobenzotriazole, the structure of which has been established by its chlorination to 2-methyl-4,5,6,7-tetrachlorobenzotriazole.

In previous papers in this series,<sup>2-4</sup> we have described the structural problems which result from the possibility for 1- and 2-isomerism in the products of the conjugate addition of azoles to unsaturated systems. One of the unusual observations in these studies was that 4,5,6,7-tetrachlorobenzotriazole adds to conjugated unsaturated systems to give 2-substituted derivatives whereas benzotriazole itself gives only 1-substituted derivatives. The absence of any obvious electronic factor attributable to the chlorine substituents, which can result in the exclusive participation of

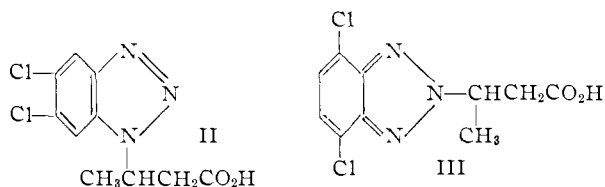


resonance structure Ic in the addition reaction, suggests that a steric factor is primarily responsible. In order to evaluate this factor in more detail the 4,7- and 5,6-dichlorobenzotriazoles, their 1- and 2-methyl derivatives have been prepared and characterized. A variety of additional types of substituted benzotriazoles, including tetrabromobenzotriazole, have been prepared and the chlorination and bromination processes have been further characterized. The results of these studies will be discussed in this paper.

5,6-Dichlorobenzotriazole was prepared from *o*-dichlorobenzene *via* 4,5-dichloro-1,2-dinitrobenzene<sup>5</sup> which was reduced to the diamine and cy-

clized to the triazole in 50% yield. 4,7-Dichlorobenzotriazole was prepared from 2,5-dichloroaniline. The acylated aniline was nitrated and converted to 2,5-dichloro-6-nitroaniline.<sup>6</sup> This was reduced to 3,6-dichloro-*o*-phenylenediamine<sup>7</sup> which was diazotized to give the triazole in 81% yield. The 1- and 2-methyl derivatives of each were separated by recrystallization from dilute sulfuric acid in which the less basic 2-methyl derivatives are less soluble. The absorption data for the 1- and 2-methyl derivatives of 5,6-dichlorobenzotriazole show maxima at 272 and 295 and at 293  $m\mu$ , respectively. The absorption data for the 1- and 2-methyl derivatives of 4,7-dichlorobenzotriazole show the same general pattern but with more structure. The principal maxima occur at 272 and 294 and at 285  $m\mu$ , respectively, with several additional slightly less intense maxima. The complete data are given in Figs. 1 and 2.

Addition reactions with crotonic acid gave  $\beta$ -1'-(5',6'-dichlorobenzotriazolyl)-butyric acid (II) and



$\beta$ -2'-(4',7'-dichlorobenzotriazolyl)-butyric acid (III).  $\beta$ -Phenyl- $\beta$ -2'-(4',7'-dichlorobenzotriazolyl)-propiophenone was obtained from benzalacetophenone and 4,7-dichlorobenzotriazole. The absorption maxima, summarized in Figs. 1 and 2, are consistent with these structural assignments. Both of the 2-substituted derivatives show single maxima at 286  $m\mu$ , and the 1-substituted derivative shows double maxima at 274 and 296  $m\mu$ . These data establish that the presence of the chlorine atoms in the 4,7-positions is sufficient to cause the addition reaction to take place in the 2-position and that the 5,6-chlorine substituents do not interfere with addition at the 1-position. In the absence of additional data relating this orientation to the inductive effect of the chlorine or to contributions from resonance structures related to the electron release characteristics of the chlorine, the orientation to the 2-position is assigned to a type

(1) The authors gratefully acknowledge a grant from Eli Lilly and Co. in partial support of this research.

(2) Richard H. Wiley, Karl F. Hussung and James Moffat, *THIS JOURNAL*, **77**, 5105 (1955).

(3) Richard H. Wiley, N. R. Smith, D. M. Johnson and James Moffat, *ibid.*, **77**, 2572 (1955).

(4) Richard H. Wiley, N. R. Smith, D. M. Johnson and James Moffat, *ibid.*, **76**, 4933 (1954).

(5) J. J. Blanksma, *Rec. trav. chim.*, **21**, 419 (1902).

(6) F. Beilstein and A. Kurbatow, *Ann.*, **196**, 215 (1879).

(7) E. Noelting and E. Kopp, *Ber.*, **38**, 3515 (1905).

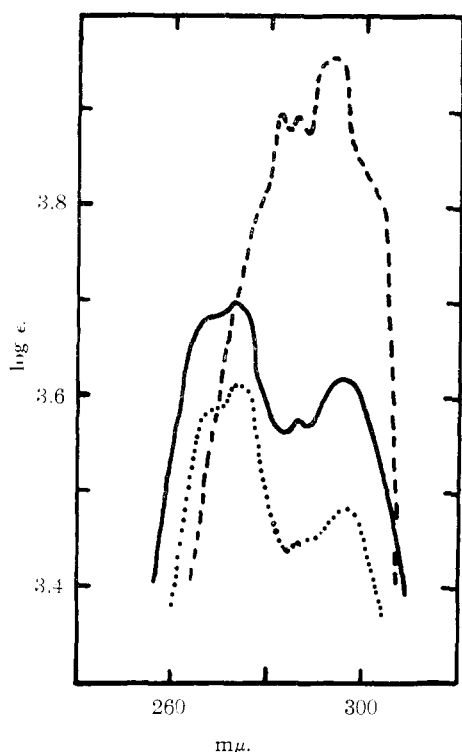


Fig. 1.—Ultraviolet absorption curves for 1-methyl-5,6-dichlorobenzotriazole (—); 2-methyl-5,6-dichlorobenzotriazole (---);  $\beta$ -1'-(5',6'-dichlorobenzotriazolyl)-butyric acid (.....).

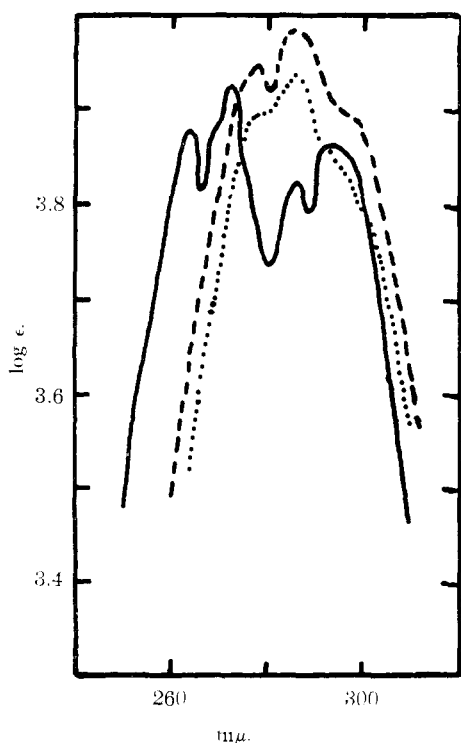


Fig. 2.—Ultraviolet absorption curves for 1-methyl-4,7-dichlorobenzotriazole (—); 2-methyl-4,7-dichlorobenzotriazole (---);  $\beta$ -2'-(4',7'-dichlorobenzotriazolyl)-butyric acid (.....).

of steric hindrance presumably characteristic of these and related systems.

The addition products obtained from tetrabromobenzotriazole are also of the 2-substituted type. Tetrabromobenzotriazole has been obtained in 54% yield from benzotriazole, bromine and concd. nitric acid. 5-Chloro-4,6,7-tribromobenzotriazole has been obtained similarly from 5-chlorobenzotriazole in 56% yields. The 1- and 2-methyl and ethyl derivatives of tetrabromobenzotriazole have been prepared by bromination of 1- and 2-alkylbenzotriazoles. The absorption data show maxima for the 1-alkyl derivatives at 278–289 and 308  $m\mu$ . The 2-alkyl derivatives show a single principal maximum at 306  $m\mu$ . The introduction of four bromo groups has produced very little, if any, bathochromic shift in these maxima as compared to the tetrachloro analog. The adduct from benzalacetophenone,  $\beta$ -phenyl- $\beta$ -2'-(4',5',6',7'-tetrabromobenzotriazolyl)-propiophenone, shows a single maximum in the 300–308  $m\mu$  range characteristic of the 2-substituted benzotriazoles. The data are given in Figure 3.

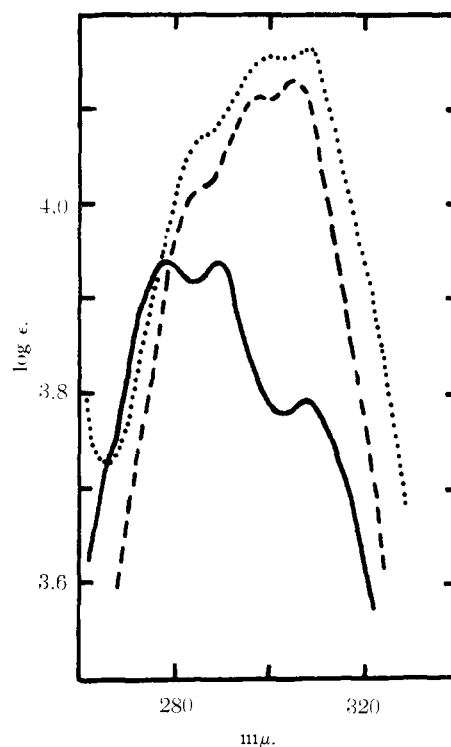


Fig. 3.—Ultraviolet absorption curves for 1-ethyl-4,5,6,7-tetrabromobenzotriazole (—); 2-ethyl-4,5,6,7-tetrabromobenzotriazole (---);  $\beta$ -phenyl- $\beta$ -2'-(4',5',6',7'-tetrabromobenzotriazolyl)-propiophenone (.....).

Addition products obtained from 5-methyl-4,6,7-trichlorobenzotriazole<sup>8</sup> are also of the 2-substituted type. Chlorination of 5-methylbenzotriazole gives the trichloro derivative. Adducts from benzalacetophenone, acrylamide and acrylonitrile show single maxima in the 295–300  $m\mu$  range characteristic of the 2-substituted derivatives.

In the course of these studies several previously

(8) T. Zincke and H. Arzberger, *Ann.*, **249**, 370 (1888).

undescribed derivatives of benzotriazole have been obtained. These include the methiodide and dimethochloride of 2-(2-dimethylaminoethyl)-tetrachlorobenzotriazole, 1-dimethylamino-4,5,6,7-tetrachlorobenzotriazole,  $\beta$ -2'-(tetrachlorobenzotriazolyl)-butyramide,  $\beta$ -1'-(benzotriazolyl)-butyramide and the 1- and 2-ethyl derivatives of tetrachlorobenzotriazole. 4-Iodobenzotriazole has been prepared from 4-nitrobenzotriazole<sup>9</sup> by reduction and replacement of the amino group. 1-Methyl-6-chlorobenzotriazole has been prepared from 4-chloro-1,2-dinitrobenzene<sup>10</sup> via 5-chloro-2-nitro-N-methylaniline,<sup>11</sup> reduction to the diamine and cyclization with nitrous acid. Bromination gave the tribromo derivative.

Some new observations about substitution reactions in the benzotriazole series are available. The nitration of 2-methylbenzotriazole has been shown to give 2-methyl-5-nitrobenzotriazole, m.p. 150–152°. This structure is established by comparison with 2-methyl-4-nitrobenzotriazole, m.p. 183–184°. The latter was obtained by methylation of the known 4-nitrobenzotriazole. The structure of the 4-nitro compound as that of a 2-methyl derivative is established by the fact that it gives 2-methyl-4,5,6,7-tetrachlorobenzotriazole on chlorination. The presence of the nitro group obscures the usual absorption differences between the 1- and 2-methyl derivatives.

Several additional observations about the character of the aqua regia chlorinations are also now available. Contrary to our previous report<sup>2</sup> the persistent chlorination of 1-methylbenzotriazole gives 1-methyltetrachlorobenzotriazole. Apparently, the incomplete chlorination results from an increased insolubility of the trichloro derivative in the reaction mixture rather than from the steric effect of the 1-methyl substituent as previously postulated. Bromination of the 1-methyl derivative to the tetrabromo derivative also has been achieved. On chlorination 2-methyl-4-nitrobenzotriazole, 4-nitrobenzotriazole and 2,5-dimethylbenzotriazole are converted to tetrachlorobenzotriazoles. In these systems the bz (but not the 2) substituents are replaced by chlorine. 2,5-Dimethylbenzotriazole was prepared by alkylation and separated by precipitation of the ether-insoluble hydrochlorides of the 1-methyl analogs.

These observations establish two new factors about the substitution reactions of benzotriazoles: (1) substitution takes place at the 5-position in the 2-substituted types and (2) replacement of nitro and methyl by chloro takes place during chlorination.

### Experimental<sup>12</sup>

**5,6-Dichlorobenzotriazole.**—To a solution of 16.3 g. (0.069 mole) of 4,5-dichloro-1,2-dinitrobenzene<sup>5</sup> in 75 ml. of concd. hydrochloric acid was added 93.5 g. (0.414 mole) of stannous chloride dissolved in 300 ml. of concd. hydrochloric acid. The resulting solution was heated with stirring until all the dinitrobenzene was reacted as indicated by the disappearance of an orange color. The solution was cooled, filtered and the resulting product washed with

concd. hydrochloric acid. The dihydrochloride of the diamine thus obtained was dissolved in water, cooled to 0° and treated with 4.75 g. (0.069 mole) of sodium nitrite in 15 ml. of water. The solid product was filtered, washed with water, recrystallized from ethanol-water and dried to give 6.5 g. (50%) of crude product. Two recrystallizations from nitromethane and one from ethyl acetate gave an analytical sample, m.p. 264–266°;  $\lambda_{\max}$ , 265 (s = shoulder) (log  $\epsilon$  3.50), 270(3.53), 286(s)(3.61), 292(3.67).

*Anal.* Calcd. for  $C_6H_5N_3Cl_2$ : N, 22.35; neut. equiv., 188.0. Found: N, 22.42; neut. equiv., 188.3.

**2-Methyl-5,6-dichlorobenzotriazole.**—To a solution of 3.7 g. (0.02 mole) of 5,6-dichlorobenzotriazole in 100 ml. of 1 N sodium hydroxide was added 2.5 g. (0.02 mole) of dimethyl sulfate dropwise over a period of 10 minutes. The resulting mixture was heated on a steam-bath for 1 hr. The solid product which separated on cooling was collected on a filter, washed with water and dried to give 2.0 g. of a crude mixture of 1- and 2-methyl derivatives. Two recrystallizations from dilute sulfuric acid gave 0.75 g. (18%) of reasonably pure 2-methyl derivative. Two additional recrystallizations from methanol gave an analytical sample, m.p. 186–188°;  $\lambda_{\max}$ , 282(3.89), 286(3.89), 293(3.95), 300(s)(3.84).

*Anal.* Calcd. for  $C_7H_5N_3Cl_2$ : N, 20.80. Found: N, 20.65.

**1-Methyl-5,6-dichlorobenzotriazole.**—The sulfuric acid filtrates from the recrystallization of the above mixture of 1- and 2-methyl-5,6-dichlorobenzotriazole were diluted with water to precipitate 1.25 g. (31%) of reasonably pure 1-methyl derivative. Three additional recrystallizations from nitromethane gave an analytical sample, m.p. 210–212°;  $\lambda_{\max}$ , 268(s)(3.68), 272(3.70), 286(s)(3.57), 295(3.62).

*Anal.* Calcd. for  $C_7H_5N_3Cl_2$ : N, 20.80. Found: N, 20.60.

**$\beta$ -1'-(5',6'-Dichlorobenzotriazolyl)-butyric Acid (II).**—A mixture of 1.5 g. (0.08 mole) of 5,6-dichlorobenzotriazole, 0.86 g. (0.01 mole) of crotonic acid and 20 drops of pyridine was heated for 15 hr. at 100°. The reaction mixture was poured into 100 ml. of 1.0 N hydrochloric acid to precipitate the crude product which was filtered, dried and washed with 100 ml. of ether to give 1.4 g. (64%) of the product. Three recrystallizations from acetic acid-water gave an analytical sample, m.p. 174–175°;  $\lambda_{\max}$ , 268(s)(3.57), 274(3.61), 290(s)(3.45), 296(3.48).

*Anal.* Calcd. for  $C_{10}H_9N_3Cl_2O_2$ : N, 15.33; neut. equiv., 274.1. Found: N, 15.60; neut. equiv., 271.2.

**4,7-Dichlorobenzotriazole.**—To a solution of 25.91 g. (0.1465 mole) of 3,6-dichloro-*o*-phenylenediamine<sup>6,7</sup> dissolved in 245 ml. of glacial acetic acid was added 45 ml. of water. The resulting solution was cooled to 5° and 11.03 g. (0.16 mole) of sodium nitrite dissolved in 20 ml. of water was added with stirring. The precipitate from the reaction mixture was filtered, dried and recrystallized from dilute ethanol to give 22.4 g. (81%) of crude product. Three recrystallizations from nitromethane gave an analytical sample, m.p. 275–277°;  $\lambda_{\max}$ , 264(3.82), 270(3.85), 285(3.81), 292(s)(3.79).

*Anal.* Calcd. for  $C_6H_5N_3Cl_2$ : N, 22.35; neut. equiv., 188.0. Found: N, 22.07; neut. equiv., 188.9.

**2-Methyl-4,7-dichlorobenzotriazole.**—To a solution of 5.64 g. (0.03 mole) of 4,7-dichlorobenzotriazole in 200 ml. of 0.5 N sodium hydroxide was added 3.8 g. (0.03 mole) of dimethyl sulfate dropwise with stirring over a period of 10 minutes. The resulting mixture was heated on a steam-bath for 1 hr. After cooling, the precipitated product was collected on a filter, washed with water and dried to give 3.3 g. of a crude mixture of 1- and 2-methyl derivatives. Two recrystallizations from dilute sulfuric acid gave 1.05 g. (17%) of reasonably pure 2-methyl derivative. Four additional recrystallizations from methanol gave an analytical sample, m.p. 174–176°;  $\lambda_{\max}$ , 278(3.95), 285(3.98), 292(3.92), 296(s)(3.89).

*Anal.* Calcd. for  $C_7H_5N_3Cl_2$ : C, 41.61; H, 2.50; N, 20.80. Found: C, 41.58; H, 2.51; N, 20.30.

**1-Methyl-4,7-dichlorobenzotriazole.**—The sulfuric acid filtrates from the recrystallization of the above mixture of 1- and 2-methyl-4,7-dichlorobenzotriazole were diluted

(9) K. Fries, H. Güterbach and H. Kuhn. *Ann.*, **511**, 213 (1934).

(10) A. Laubenheimer, *Ber.*, **9**, 760 (1876).

(11) M. H. Behrens, *Rec. trav. chim.*, **21**, 276 (1902).

(12) Melting points uncorrected. Analyses by Micro Tech Laboratories, Skokie, Ill.

with water to precipitate 2.25 g. (37%) of reasonably pure 1-methyl derivative. Four additional recrystallizations from carbon tetrachloride gave an analytical sample, m.p. 150–152°;  $\lambda_{\text{max}}$ , 264(3.88), 272(3.93), 286(3.82), 294(3.86).

*Anal.* Calcd. for  $C_7H_5N_3Cl_2$ : N, 20.80. Found: N, 20.60.

**$\beta$ -2'-(4',7'-Dichlorobenzotriazolyl)-butyric Acid (III).**—A mixture of 3.76 g. (0.02 mole) of 4,7-dichlorobenzotriazole, 1.72 g. (0.02 mole) of crotonic acid and 5 ml. of pyridine was heated for 14 hr. at 80°. The reaction mixture was poured into 300 ml. of 0.5 *N* hydrochloric acid to precipitate 2.5 g. (45%) of the crude product. Three recrystallizations from acetic acid–water gave an analytical sample, m.p. 158–160°;  $\lambda_{\text{max}}$ , 280(s)(3.90), 286(3.94), 292(s)(3.86), 295(s)(3.84).

*Anal.* Calcd. for  $C_{10}H_9N_3Cl_2O_2$ : N, 15.33; neut. equiv., 274.1. Found: N, 15.18; neut. equiv., 278.8.

**$\beta$ -Phenyl- $\beta$ -2'-(4',7'-dichlorobenzotriazolyl)-propiofenone.**—To a melt of 1.88 g. (0.01 mole) of 4,7-dichlorobenzotriazole and 2.08 g. (0.01 mole) of benzalacetophenone was added 4 drops of benzyltrimethylammonium hydroxide solution. The mixture was heated for 3 hr. at 80°, cooled and dissolved in 50 ml. of ether. Addition of petroleum ether precipitated 2.65 g. (67%) of the crude product. Three recrystallizations from ethanol gave an analytical sample, m.p. 150–151°;  $\lambda_{\text{max}}$ , 280(s)(3.97), 286(4.03), 298(s)(3.83).

*Anal.* Calcd. for  $C_{21}H_{18}N_3Cl_2O$ : N, 10.60. Found: N, 10.75.

**4,5,6,7-Tetrabromobenzotriazole.**—A solution of 11.9 g. (0.10 mole) of benzotriazole and 72.0 g. (0.45 mole) of bromine in 150 ml. of concd. nitric acid was heated for 30 hr. under reflux. The crystalline product was collected on a filter, washed and dried to give 23.5 g. (54%) of the crude product. Several recrystallizations from acetic acid gave the pure product, m.p. 262–266°;  $\lambda_{\text{max}}$ , 278(4.01), 285(4.03), 300(3.94).

*Anal.* Calcd. for  $C_6H_3N_3Br_4$ : N, 9.67; neut. equiv., 434.8. Found: N, 9.89; neut. equiv., 434.5.

**5-Chloro-4,6,7-tribromobenzotriazole.**—A solution of 4.6 g. (0.03 mole) of 5-chlorobenzotriazole and 21.0 g. (0.13 mole) of bromine in 60 ml. of concd. nitric acid was heated for 22 hr. under reflux. The crystalline product was collected on a filter, washed and dried to give 6.60 g. (56%) of the crude product. Several recrystallizations from methanol gave the pure product, m.p. 249–251°;  $\lambda_{\text{max}}$ , 277(s)(3.93), 285(3.98), 302(3.91).

*Anal.* Calcd. for  $C_6H_3N_3ClBr_3$ : N, 10.77; neut. equiv., 390.3. Found: N, 11.00; neut. equiv., 398.0.

**1-Methyl-4,5,6,7-tetrabromobenzotriazole.**—A solution of 1.33 g. (0.01 mole) of 1-methylbenzotriazole and 7.00 g. (0.044 mole) of bromine in 25 ml. of concd. nitric acid was heated for 24 hr. under reflux. The crystalline product was collected on a filter, washed and dried to give 2.20 g. (48%) of the crude 1-methyl derivative. Several recrystallizations from nitromethane gave the pure product, m.p. 225–226°;  $\lambda_{\text{max}}$ , 278(3.96), 289(3.95), 308(3.80).

*Anal.* Calcd. for  $C_7H_5N_3Br_4$ : N, 9.36. Found: N, 9.35.

**2-Methyl-4,5,6,7-tetrabromobenzotriazole.**—A solution of 1.33 g. (0.01 mole) of 2-methylbenzotriazole and 7.00 g. (0.044 mole) of bromine in 25 ml. of concd. nitric acid was heated for 8 hr. under reflux. The crystalline product was collected on a filter, washed and dried to give 3.0 g. (67%) of the crude 2-methyl derivative. Several recrystallizations from nitromethane gave the pure product, m.p. 250–253°;  $\lambda_{\text{max}}$ , 285(s)(3.99), 294(4.10), 299(4.10), 306(4.12).

*Anal.* Calcd. for  $C_7H_5N_3Br_4$ : C, 18.73; H, 0.67; Br, 71.23. Found: C, 19.12; H, 0.79; Br, 70.83.

**1-Ethyl-4,5,6,7-tetrabromobenzotriazole.**—A solution of 3.0 g. (0.02 mole) of 1-ethylbenzotriazole and 14.0 g. (0.088 mole) of bromine in 75 ml. of concd. nitric acid was heated for 24 hr. under reflux. The crystalline product was collected on a filter, washed and dried to give 6.3 g. (68%) of the crude 1-ethyl derivative. Several recrystallizations from ethyl acetate gave the pure product, m.p. 150–152°;  $\lambda_{\text{max}}$ , 278(3.94), 290(3.94), 308(3.79).

*Anal.* Calcd. for  $C_8H_7N_3Br_4$ : N, 9.08; Br, 69.07. Found: N, 9.00; Br, 69.05.

**2-Ethyl-4,5,6,7-tetrabromobenzotriazole.**—A solution of 3.0 g. (0.02 mole) of 2-ethylbenzotriazole and 14.0 g. (0.088 mole) of bromine in 75 ml. of concd. nitric acid was heated for 18 hr. under reflux. The crystalline product was collected on a filter, washed and dried to give 1.60 g. (21%) of the crude 2-ethyl derivative. Several recrystallizations from ethyl acetate gave the pure product, m.p. 167–170°;  $\lambda_{\text{max}}$ , 285(s)(4.01), 298(4.11), 305(4.13).

*Anal.* Calcd. for  $C_8H_7N_3Br_4$ : N, 9.08; Br, 69.07. Found: N, 9.26; Br, 68.85.

**1-Methyl-6-chloro-4,5,7-tribromobenzotriazole.**—A solution of 0.70 g. (0.0042 mole) of 1-methyl-6-chlorobenzotriazole and 4.00 g. (0.025 mole) of bromine in 25 ml. of concd. nitric acid was heated for 24 hr. under reflux. The crystalline product was collected on a filter, washed and dried. There was obtained 1.20 g. (71%) of the crude 1-methyl derivative. Several recrystallizations from nitromethane gave the pure product, m.p. 213–214.5°;  $\lambda_{\text{max}}$ , 277(3.88), 287(3.92), 307(3.78).

*Anal.* Calcd. for  $C_7H_5N_3ClBr_3$ : N, 10.39. Found: N, 10.35.

**$\beta$ -Phenyl- $\beta$ -2'-(4',5',6',7'-tetrabromobenzotriazolyl)-propiofenone.**—To a melt of 4.35 g. (0.01 mole) of tetrabromobenzotriazole and 2.08 g. (0.01 mole) of benzalacetophenone was added 10 drops of benzyltrimethylammonium hydroxide solution. The mixture was heated 20 hr. at 80°. Dilution of the cooled reaction mixture with ether precipitated 3.6 g. of crude product. This product was extracted with carbon tetrachloride to separate the insoluble, unreacted tetrabromobenzotriazole. Evaporation of the filtrate gave 2.9 g. (45%) of the crude addition product. Several recrystallizations from nitromethane gave the pure product, m.p. 195–198°;  $\lambda_{\text{max}}$ , 287(s)(4.11), 300(4.20), 308(4.20).

*Anal.* Calcd. for  $C_{21}H_{18}N_3Br_4O$ : C, 39.22; H, 2.04; Br, 49.71. Found: C, 39.29; H, 2.00; Br, 49.62.

**$\beta$ -Phenyl- $\beta$ -2'-(4',6',7'-trichloro-5'-methylbenzotriazolyl)-propiofenone.**—To a melt of 2.36 g. (0.01 mole) of 4,6,7-trichloro-5'-methylbenzotriazole<sup>8</sup> and 2.08 g. (0.01 mole) of benzalacetophenone was added 5 drops of benzyltrimethylammonium hydroxide. The mixture was heated 15 hr. at 80°. Dilution of the cooled reaction mixture with ether precipitated 2.3 g. (52%) of crude product. Three recrystallizations from nitromethane gave the pure product, m.p. 173–175°;  $\lambda_{\text{max}}$ , 285(s)(4.14), 290(s)(4.17), 294(4.20), 298(4.20).

*Anal.* Calcd. for  $C_{22}H_{17}N_3Cl_3O$ : N, 9.43. Found: N, 9.68.

**$\beta$ -2'-(4',6',7'-Trichloro-5'-methylbenzotriazolyl)-propionamide.**—To a melt of 2.36 g. (0.01 mole) of 4,6,7-trichloro-5'-methylbenzotriazole and 0.71 g. (0.01 mole) of acrylamide was added 5 drops of benzyltrimethylammonium hydroxide. The mixture was heated for 15 hr. at 80°. Dilution of the cooled reaction mixture with ether precipitated 2.6 g. (85%) of the crude product. Three recrystallizations from ethyl acetate gave the pure product, m.p. 259–260°;  $\lambda_{\text{max}}$ , 280(4.01), 290(4.12), 294(4.11), 298(4.13).

*Anal.* Calcd. for  $C_{10}H_9N_4Cl_3O$ : N, 18.22. Found: N, 17.97.

**$\beta$ -2'-(4',6',7'-Trichloro-5'-methylbenzotriazolyl)-propionitrile.**—A mixture of 2.36 g. (0.01 mole) of 4,6,7-trichloro-5'-methylbenzotriazole, 5 ml. of acrylonitrile and 5 drops of benzyltrimethylammonium hydroxide was heated 18 hr. at 80°. Dilution of the cooled reaction with ether precipitated 0.7 g. (24%) of crude product. Three recrystallizations from methanol gave the pure product, m.p. 189–190°;  $\lambda_{\text{max}}$ , 280(4.05), 290(4.17), 294(4.14), 298(4.16).

*Anal.* Calcd. for  $C_{10}H_7N_4Cl_3O$ : N, 19.35. Found: N, 19.54.

**2-Dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole Methiodide.**—To a solution of 2.8 g. (0.0085 mole) of 2-dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole in 175 ml. of acetone was added 4.0 g. (0.03 mole) of methyl iodide. The precipitate was collected on a filter and dried to give 3.2 g. (80%) of the crude product. Several recrystallizations from ethanol gave the pure product, m.p. 249–250° dec.;  $\lambda_{\text{max}}$ , 294(4.09), 304(4.10).

*Anal.* Calcd. for  $C_{11}H_{13}N_4Cl_4I$ : N, 11.92. Found: N, 11.92.

**2-Dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole Dimethochloride.**—To a solution of 3.28 g. (0.01 mole) of 2-dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole in 75 ml. of methanol was added 1.26 g. (0.01 mole) of dimethyl sulfate. The resulting solution was then evaporated to dryness and the crude salt redissolved in a mixture of 50 ml. of water and 10 ml. of concd. hydrochloric acid. After heating to boiling, 2.44 g. (0.01 mole) of barium chloride dihydrate was added. After boiling several minutes, the hot solution was filtered to remove the barium sulfate. The filtrate was cooled and the precipitate collected on a filter, washed, dried and extracted with 100 ml. of ethanol. The filtered ethanol solution was evaporated to precipitate 3.4 g. (79%) of the crude product. Several recrystallizations from nitromethane gave the pure product, m.p. 236–237°;  $\lambda_{\text{max}}$ , 294(4.13), 300(4.13), 306(4.12).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_4\text{Cl}_6$ : C, 33.59; H, 3.76. Found: C, 33.80; H, 3.77.

**1-Dimethylaminoethyl-4,5,6,7-tetrachlorobenzotriazole.**—To 21 g. (0.082 mole) of 4,5,6,7-tetrachlorobenzotriazole dissolved in 500 ml. of 0.5 N potassium hydroxide was added 11.7 g. (0.082 mole) of dimethylaminoethyl chloride hydrochloride. The resulting solution was heated for 30 minutes on a steam-bath. The oil which separated solidified on cooling. The product was collected on a filter, dried and taken up in ether. Evaporation to dryness gave 3.5 g. (13%) of the crude product. Several recrystallizations from ethanol gave an analytical sample, m.p. 93–95°;  $\lambda_{\text{max}}$ , 276(3.90), 283(3.92), 305(3.73).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{10}\text{N}_4\text{Cl}_4$ : N, 17.08; Found: N, 17.16.

**$\beta$ -2'-(4',5',6',7'-Tetrachlorobenzotriazolyl)-butyramide.**—To 10 ml. of thionyl chloride was added in small portions 1.7 g. (0.005 mole) of  $\beta$ -2'-(4',5',6',7'-tetrachlorobenzotriazolyl)-butyric acid. After solution was complete, the thionyl chloride was removed on a steam-bath. The remaining solution was added dropwise with stirring to 20 ml. of cold concd. ammonium hydroxide to precipitate 1.6 g. (95%) of crude product. Several recrystallizations from nitromethane gave the pure product, m.p. 228–229°;  $\lambda_{\text{max}}$ , 294(4.09), 302(4.08).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_8\text{N}_4\text{Cl}_4\text{O}$ : N, 16.38; Cl, 41.47. Found: N, 16.51; Cl, 41.50.

**1-Ethyl-4,5,6,7-tetrachlorobenzotriazole.**—A solution of 1.5 g. (0.01 mole) of 1-ethylbenzotriazole in 300 ml. of concd. hydrochloric acid and 100 ml. of concd. nitric acid was heated for 52 hr. under reflux. The solution was cooled and the crystalline product collected on a filter, washed and dried to give 2.3 g. (81%) of the crude product. Several recrystallizations from methanol gave the pure product, m.p. 114–117°;  $\lambda_{\text{max}}$ , 276(s)(3.86), 283(3.89), 304(3.71).

*Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{N}_3\text{Cl}_4$ : N, 14.75; Cl, 49.77. Found: N, 14.77; Cl, 49.82.

**2-Ethyl-4,5,6,7-tetrachlorobenzotriazole.**—A solution of 1.5 g. (0.01 mole) of 2-ethylbenzotriazole in 300 ml. of concd. hydrochloric acid and 100 ml. of concd. nitric acid was heated for 50 hr. under reflux. The solution was cooled and the crystalline product collected on a filter, washed and dried to give 1.8 g. (63%) of the crude product. Several recrystallizations from methanol gave the pure product, m.p. 160–163°;  $\lambda_{\text{max}}$ , 294(4.11), 300(4.10).

*Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{N}_3\text{Cl}_4$ : N, 14.75; Cl, 49.77. Found: N, 14.55; Cl, 49.80.

**4-Iodobenzotriazole.**—To 13.5 g. (0.06 mole) of stannous chloride in 50 ml. of concd. hydrochloric acid was added in small portions a mixture of 3.28 g. (0.02 mole) of 4-nitrobenzotriazole in 20 ml. of concd. hydrochloric acid. The resulting solution was heated to boiling and allowed to cool. The chlorostannate, which crystallized on cooling, was collected on a filter and washed with concd. hydrochloric acid. The crystalline product was dissolved in water and hydrogen sulfide bubbled through until no more precipitation of tin sulfides was evident. The tin sulfides were removed by filtration and the filtrate made strongly acidic by the addition of 50% sulfuric. The solution was cooled to 0°, and sodium nitrite was added until a slight excess existed. The clear solution was then poured into 300 ml. of ice-water, and an excess of potassium iodide in water was added slowly with stirring. The free iodine which formed was

reduced with sodium sulfite, and 10 g. of sodium acetate was added. The solution was then neutralized to a pH 3 with 6 N sodium hydroxide and extracted with three 300-ml. portions of ether. The combined ether extracts were dried over sodium sulfate and evaporated to give 0.8 g. (16.3%) of crude product. Several recrystallizations from water gave the pure product, m.p. 216–218°;  $\lambda_{\text{max}}$ , 264(3.95), 272(3.95), 286(3.90), 290(3.88).

*Anal.* Calcd. for  $\text{C}_6\text{H}_4\text{N}_3\text{I}$ : N, 17.15. Found: N, 17.20.

**1-Methyl-6-chlorobenzotriazole.**—A solution of 15.5 g. (0.083 mole) of 2-nitro-5-chloro-N-methylaniline<sup>10,11</sup> in 20 ml. of concd. hydrochloric acid was added in small portions to 56.4 g. (0.25 mole) of stannous chloride dissolved in 150 ml. of concd. hydrochloric acid. This solution was poured into 500 ml. of water and made distinctly basic by the addition of aqueous potassium hydroxide. The resulting solution was extracted with three 100-ml. portions of ether. The combined ether extracts were then extracted with three 100-ml. portions of 1 N hydrochloric acid. The aqueous extracts were combined, chilled to 10° and treated with 6.35 g. (0.092 mole) of sodium nitrite. The dark colored solution was made distinctly basic and extracted with three 100-ml. portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate, the ether removed on a steam-bath and the product fractionated. There was obtained 4.0 g. (29%) of the crude 1-methyl derivative, b.p. 165° (25 mm.). Two recrystallizations of the solidified liquid from carbon tetrachloride gave the pure product, m.p. 121–123°;  $\lambda_{\text{max}}$ , 270(3.83), 282(3.77).

*Anal.* Calcd. for  $\text{C}_7\text{H}_8\text{N}_3\text{Cl}$ : N, 25.07. Found: N, 24.82.

**2-Methyl-4-nitrobenzotriazole.**—A solution of diazomethane in ether was added to 1.64 g. (0.01 mole) of 4-nitrobenzotriazole dissolved in 75 ml. of ether until a light yellow color persisted. Evaporation of the ether gave 1.7 g. (95.5%) of crude product. One recrystallization from dilute ethanol and two recrystallizations from ethyl acetate gave an analytical sample, m.p. 183–184° (light yellow needles).

*Anal.* Calcd. for  $\text{C}_7\text{H}_8\text{N}_4\text{O}_2$ : N, 31.45. Found: N, 31.52.

**2-Methyl-5-nitrobenzotriazole.**—A solution of 4.0 g. (0.03 mole) of 2-methylbenzotriazole in 40 ml. of water and 20 ml. of concd. nitric acid was heated for 60 hr. under reflux. The solution was cooled and the pale yellow crystalline product collected on a filter, washed and dried. There was obtained 1.7 g. (32%) of the crude product. Several recrystallizations from ethanol gave the pure product, m.p. 150–152°.

*Anal.* Calcd. for  $\text{C}_7\text{H}_8\text{N}_4\text{O}_2$ : C, 47.19; H, 3.40; N, 31.45. Found: C, 47.31; H, 3.17; N, 31.21.

**2-Methyl-4,5,6,7-tetrachlorobenzotriazole from 2-Methyl-4-nitrobenzotriazole.**—A solution of 0.18 g. (0.001 mole) of 2-methyl-4-nitrobenzotriazole in 39 ml. of concd. hydrochloric acid and 13 ml. of concd. nitric acid was heated under reflux for three days. The solution was cooled and diluted with water to precipitate 0.06 g. (22%) of the crude 2-methyl derivative, m.p. 179–182°. The product was recrystallized from methanol to give white needles, m.p. 182–184°. A mixed melting point with an authentic sample of 2-methyl-4,5,6,7-tetrachlorobenzotriazole showed no depression while the melting point of a mixture of the product with a pure sample of starting material was 148–157°.

**1-Methyl-4,5,6,7-tetrachlorobenzotriazole by Chlorination of 1-Methylbenzotriazole.**—A solution of 3.0 g. (0.0225 mole) of 1-methylbenzotriazole in 300 ml. of concd. hydrochloric acid and 100 ml. of concd. nitric acid was heated under reflux. The solid which had precipitated after 1 hr. heating was redissolved by the addition of 300 ml. of concd. nitric acid. This mixture was then refluxed for 72 hr. The solution was cooled and diluted with water to precipitate 3.5 g. (57%) of the crude product. Several recrystallizations from carbon tetrachloride gave the pure product, m.p. 193–196°. On admixture this material does not depress the m.p. of an authentic sample of 1-methyl-4,5,6,7-tetrachlorobenzotriazole.

**4,5,6,7-Tetrachlorobenzotriazole from 4-Nitrobenzotriazole.**—A solution of 1.2 g. (0.0075 mole) of 4-nitrobenzo-

triazole in 300 ml. of concd. hydrochloric acid and 150 ml. of concd. nitric acid was heated for one week under reflux. The solution was cooled and the crystalline product collected on a filter, washed and dried to give 1.2 g. (62%) of crude product. Recrystallization from nitromethane gave the pure product, m.p. 256–260°. On admixture this material does not depress the m.p. of an authentic sample of 4,5,6,7-tetrachlorobenzotriazole.

**2-Methyl-4,5,6,7-tetrachlorobenzotriazole from 2,5-Dimethylbenzotriazole.**—A solution of 1.5 g. (0.01 mole) of 2,5-dimethylbenzotriazole in 80 ml. of concd. hydrochloric acid and 80 ml. of concd. nitric acid was heated under reflux for 10 hr. The solution was cooled and the crystalline product collected on a filter, washed and dried. Three recrystallizations of this solid from methanol gave the pure product, m.p. 181–183°. On admixture this product does not depress the m.p. of an authentic sample of 2-methyl-4,5,6,7-tetrachlorobenzotriazole.

**2,5-Dimethylbenzotriazole.**—A solution of diazomethane in ether was added slowly to 13.3 g. (0.1 mole) of 5-methylbenzotriazole dissolved in ether until a slight yellow color persisted. The resulting solution was refluxed until the slight excess of diazomethane was removed and dried over anhydrous sodium sulfate. Dry hydrogen chloride was then bubbled through the ethereal solution. The precipitated hydrochlorides were removed by filtration. Evapora-

tion of the ethereal solution gave 8.8 g. (60%) of crude product. Fractionation gave an analytical sample, b.p. 117° (12 mm.);  $\lambda_{\text{max}}$ , 276(s)(4.12), 284(4.14), 288(4.11).

*Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{N}_3$ : N, 28.55. Found: N, 28.72.

**$\beta$ -1'-(Benzotriazolyl)-butyramide.**—To 1.0 g. (0.005 mole) of  $\beta$ -1'-(benzotriazolyl)-butyric acid was added 4.0 ml. of thionyl chloride. After solution was complete, the mixture was added dropwise with stirring to 15 ml. of cold concd. ammonium hydroxide. The product was collected on a filter, washed with water and dried to give 0.3 g. which was 30% of the theoretical amount. Several recrystallizations from water gave an analytical sample, m.p. 104–105°;  $\lambda_{\text{max}}$ , 256(3.80), 262(3.80), 280(3.61).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}$ : N, 27.44. Found: N, 27.42.

**Ultraviolet Absorption Data.**—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer with 1.00-cm. silica cells and a hydrogen discharge lamp as the light source. The measurements were made in methanol solution. The data are recorded in the preceding Experimental sections as wave lengths at which maxima or shoulders(s) occur with the corresponding  $\log \epsilon$  in parentheses.

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[CONTRIBUTION OF THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

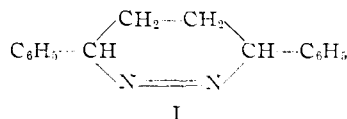
## Preparation and Decomposition of a Cyclic Azo Compound. 3,6-Diphenyl-3,4,5,6-Tetrahydropyridazine

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The azo compound I was prepared by addition of diethyl azodicarboxylate to 1,4-diphenylbutadiene-1,3, hydrogenation, hydrolysis, decarboxylation and autoxidation;  $\lambda_{\text{max}}$  387  $m\mu$ ,  $\log \epsilon$  2.89, displaced from 345  $m\mu$  of *trans*-aliphatic azo compounds. Compound I decomposes in hydrocarbon solvents, including solutions containing styrene, with essentially quantitative yield of nitrogen, and about 100 times as fast at 80° as acyclic analogs. Solid I, heated at about 125°, led in part to styrene and in part to rearrangement to the hydrazone tautomer. Attempts to obtain products of addition of the biradical 1,4-diphenyl-1,4-butadiyl to stilbene and quinone failed. The mode of decomposition of I and its possible activity as a polymerization initiator are discussed.

As part of our study of the chemistry of azo compounds<sup>2</sup> we undertook to prepare 3,6-diphenyl-3,4,5,6-tetrahydropyridazine (I) and by its decon-



position, the biradical 1,4-diphenyl-1,4-butadiyl (II),  $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_2\text{CH}_2\dot{\text{C}}\text{HC}_6\text{H}_5$ . Compound I, because of its cyclohexene type structure would be a *cis*-azo compound, while acyclic aliphatic azo compound are normally *trans*, and it seemed of interest to compare its physical properties, its ease of decomposition and its products of decomposition with those of the closely related *trans*-acyclic compounds,<sup>3</sup> 1-azo-bis-1-phenylethane or 1-azo-bis-1-

phenylpropane,  $\text{C}_6\text{H}_5 - \text{CH}(\text{R}) - \text{N} = \text{N} - \text{CH}(\text{R}) - \text{C}_6\text{H}_5$  (III),  $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ . The 1,4-biradical II, which might

be formed, would be of interest both for a study of its chemistry as such and because it is identical with the product of "tail-to-tail" reaction of two molecules of styrene which had once been proposed as the active intermediate in the initiation of the thermal polymerization of styrene,<sup>4</sup> but which is no longer supported.<sup>5</sup>

**Preparation of Compound I.**—The preparation of the azo compound I has been reported<sup>6</sup> by (1) condensation of two molecules of  $\alpha$ -chloroacetophenone semicarbazone to a compound which appears to be 2-carbamyl-3,4,5-trihydro-3,6-diphenylpyridazine (a) followed by (2) treatment with sodium ethoxide at 160°. The product was converted to 3,6-diphenylpyridazine by treatment with bromine water and was assigned structure I. We repeated this preparation and found that the compound had an absorption maximum at 292  $m\mu$ ,  $\log \epsilon$  4.19, which has been characteristic of the hydrazones tautomeric with the acyclic azo compounds in this work,<sup>2a,7</sup> and end absorption in the near ultraviolet but no maximum in the range of 300–400  $m\mu$  which would be characteristic of the azo compound.<sup>3</sup> This, coupled with the strongly

(1) F. R. Mayo, *ibid.*, **65**, 2324 (1943).

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(1) (a) This paper is derived in part from a thesis submitted by Shu-hsi Hsiao in partial fulfillment of the degree of Master of Arts in Chemistry, Brandeis University. (b) For preliminary report see C. H. Wang, S. Hsiao, E. Saklad and S. G. Cohen, *THIS JOURNAL*, **79**, 2661 (1957).

(2) (a) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955); (b) **77**, 3628 (1955).

(3) S. G. Cohen, S. J. Groszok and D. B. Sparrow, *ibid.*, **72**, 3917 (1950).