tetrahydrofuran 6.2 g (95%) of **14a** as white needles, mp 162–164° (lit.[32] mp 163°).

5-Chloro-1-methyl-2-pyridone (14b).—A solution of 2.0 g (0.018 mole) of N-methyl-2-pyridone and 2.7 g (0.02 mole) of N-chlorosuccinimide in 20 ml of methylene chloride was refluxed for 24 hr and treated as above. The residue was distilled to give 0.85 g of pale yellow liquid, bp 100° (0.05 mm). Vpc analysis[31] of this material indicated it to be composed of 78% of **14b** and 22% of unreacted starting material. The product after isolation by preparative vpc had a melting point (44–46°) and infrared spectrum identical with those of an authentic sample.[33]

Registry No.—**2**, 13118-80-4; **3**, 13118-81-5; **4**, 13118-82-6; **8**, 13118-83-7; **10**, 13118-84-8; **11**, 13118-85-9; **13**, 13118-86-0.

Acknowledgment.—The authors wish to express their gratitude to Professor Jack Hine for generously reading and commenting upon this manuscript.

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[32] M. P. Cava and N. K. Bhattacharyya, *J. Org. Chem.*, **23**, 1287 (1958).

[33] A. Binz and C. Rath, *Ann. Chem.*, **486**, 71 (1931).

The Preparation and Reactions of 2-(Trichloromethyl)benzothiazoline and Some Related Compounds

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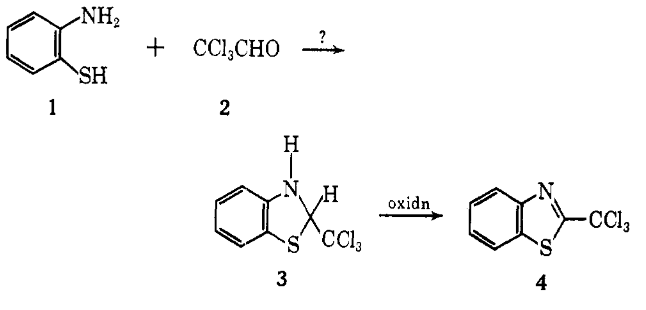
Reaction of chloral with *o*-aminobenzenethiol produced a crystalline compound, $C_8H_6Cl_3NS$, shown by chemical and spectral studies to be the novel 2-(trichloromethyl)benzothiazoline (**3**). Isolation of **3** revealed a minor, dimeric coproduct found by nuclear magnetic resonance and other studies to be 2,7-bis(trichloromethyl)-2,3,7,8-tetrahydrodibenzo[*d,i*][1,3,6,8]dithiadiazecine (**9**). Gentle pyrolysis of either **3** or of **9** effects dehydrochlorination with formation of 2-(dichloromethyl)benzothiazole (**5**). Compound **5** is also formed from **3** by treatment of the latter with ferric chloride while mild acidic permanganate oxidation of the benzothiazoline (**3**) afforded 2-(trichloromethyl)benzothiazole (**4**). Attempted ring chlorination of **5** produced only the trichloromethyl compound (**4**) in high yield, although action of a nitric–sulfuric acid mixture on **5** gave a ring-nitrated product. Cupric acetate catalyzed oxidation of **3** with gaseous oxygen proceeds exothermically with loss of hydrogen chloride and formation of a high molecular weight product of unknown structure.

Our interest in 2-(trichloromethyl)benzothiazoline (**3**) as an intermediate prompted a study of its preparation by condensation of *o*-aminobenzenethiol (**1**) with chloral (**2**), a procedure which apparently has not been described. The benzothiazoline (**3**) appeared to be an obvious intermediate for oxidative conversion to 2-(trichloromethyl)benzothiazole (**4**), reported earlier by Japanese workers[1] (in crude form) and, quite recently, by Holan, *et al.*[2] In addition, **3**, if obtainable, was considered as a possible source of a carbene resulting from thermal chloroform elimination in the manner previously described by Wanzlick.[3] Although the formation of benzothiazolines by reaction of **1** with aldehydes appears to be fairly general,[4] the reported reactions of chloral with certain aromatic amines bearing a YH (Y = O, S, or NH) substituent at the *ortho* position suggested possible acyclic Schiff-base formation as a complicating alternative.[5,6] Thus Stephens and Bower[5] have reported the synthesis of such a Schiff base from chloral and *o*-aminophenol, while Dunn, *et. al.*, have recently suggested the existence of similar Schiff bases as precursors of the corresponding benzothiazoles in a lead tetraacetate oxidation.[6] On the other hand, Sumerford and Dalton noted that reaction of chloral with aromatic amines failed to produce aldimines but led instead to both 2,2,2-trichloro-1-hydroxyethyl adducts and stable bisanilino derivatives.[7]



Results

Anhydrous chloral reacted vigorously with *o*-aminobenzenethiol (**1**) to give 71–96% yields of a crystalline compound $C_8H_6Cl_3NS$ whose infrared and nmr spectra were in accord with 2-(trichloromethyl)benzothiazoline (**3**) as the structure. On recrystallization of the crude product, it was found that a second product, constituting a dimer of **3**, was present to the extent of about 4–10% (by weight) of the crude material. Compound **3** melted with vigorous HCl evolution. Unlike the reported behavior of the Schiff bases of Stephens and Bower, **3** was insoluble in aqueous alkali at 25°.

With all evidence indicating **3** to be the structure of the condensation product, its oxidation to **4** was attempted. One of the most characteristic reactions of benzothiazolines is facile oxidation to the corresponding

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[1] Y. Mizuno, K. Adachi, and S. Kanda, *Yakugaku Zasshi*, **72**, 1268 (1952).

[2] G. Holan, E. L. Samuel, B. C. Ennis, and R. W. Hinde, *J. Chem. Soc.*, 20 (1967).

[3] H. W. Wanzlick, *Angew. Chem. Intern. Ed. Engl.*, **1** (No. 2) 75 (1962).

[4] H. P. Lankelma and P. X. Sharnoff, *J. Am. Chem. Soc.*, **53**, 2654 (1931); **54**, 379 (1932).

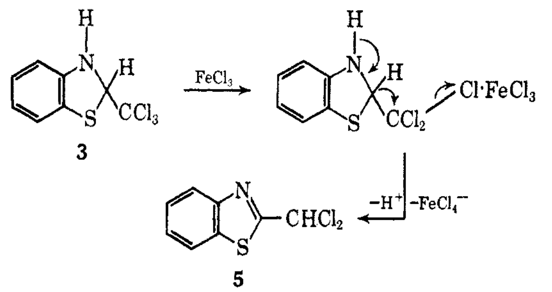
[5] F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 1722 (1950).

[6] G. L. Dunn, P. Actor, and V. J. Di Pasquo, *J. Med. Chem.*, **9**, 751 (1966).

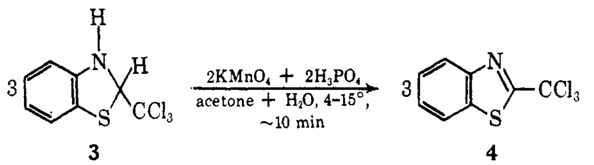
[7] W. T. Sumerford and D. N. Dalton, *J. Org. Chem.*, **9**, 81 (1944). An interesting example cited by these authors was the formation of a 2,2,2-trichloro-1-hydroxyethyl adduct from 2-amino-5-methoxycarbonylphenol which possesses an *ortho* hydroxy group available for ring closure.

benzothiazoles, often performed by ferric chloride. Action of ethanolic $FeCl_3$ on **3**, however, produced a dehydrochlorinated product, $C_8H_5Cl_2NS$, in crude yields as high as 71%. None of the expected **4** could be detected in the reaction mixture. Spectral study of the dehydrochlorination product indicated it to be the new 2-(dichloromethyl)benzothiazole (**5**) possibly formed according to Scheme I. Compound **5** showed a "second" band at 265 mμ (ε 8630) compared to 251 mμ for the similar band of 2-methylbenzothiazole (ε 7244).[8] This unexpectedly large bathochromic shift coupled with its unusual origin necessitated further verification of the structure of **5**. This was accomplished by reaction of *o*-aminobenzenethiol with dichloroacetyl chloride to give **5**, identical with the dehydrochlorination product. Mild chemical reduction of **5** afforded 2-methylbenzothiazole in 45% yield.

SCHEME I



Air is known to be effective in oxidizing benzothiazolines to benzothiazoles.[4] Action of oxygen on ethyl acetate solutions of **3**, in the presence of cupric acetate, caused exothermic oxygen uptake with concomitant loss of HCl and formation of a complex, high molecular weight product which was not identified. Mild, acidic permanganate oxidation of **3**, however, proved highly successful and afforded 2-(trichloromethyl)benzothiazole (**4**) in yields as high as 60%.



Electrophilic substitution of benzothiazoles is well known.[9] An attempted nuclear chlorination of **5** at 40° in the presence of $FeCl_3$, however, gave the pure 2-trichloromethyl compound (**4**) in 85% yield with no evidence of ring chlorination. Nitration of **5** according to the procedure of Bogert and Corbitt,[10] however, produced an apparent mixture of ring (5 and 6 positions) nitrated products.

Upon treatment of **1** with dichloroacetaldehyde, 2-(dichloromethyl)benzothiazoline (**6**) was obtained which, unlike its trichloromethyl analog **3**, melted without HCl evolution. The aromatic protons of **6** (τ 2.7–3.6) resemble those of **3** (τ 2.8–3.4) in being less deshielded than those of the benzothiazoles **4** and **5** whose benzenoid proton resonances fall at τ 1.7–2.7. Reaction of chloral with 2-amino-4-(trifluoromethyl)benzenethiol (**7**) was also attempted but without success as **7** proved essentially inert in contrast to **1**. Action of excess dichloroacetyl chloride on **7**, however, converted it to the analogous benzothiazole **8**.

The fact that **3** loses HCl at its melting point suggested 2-(dichloromethyl)benzothiazole (**5**) as the pyrolysis product. This was confirmed by heating **3** in a stream of dry nitrogen at 100° causing evolution of HCl and formation of **5** in 53.5% yield. No trace of chloroform resulting from a carbene-forming reaction was found.

The dimer (**9**) of **3** also decomposed at its melting point with vigorous evolution of HCl. When **9** was heated at 152–160° in a nitrogen stream, pure **5** was formed in 53% yield showing the dimer (**9**) to be equivalent to **3** as a source of **5** by pyrolysis.

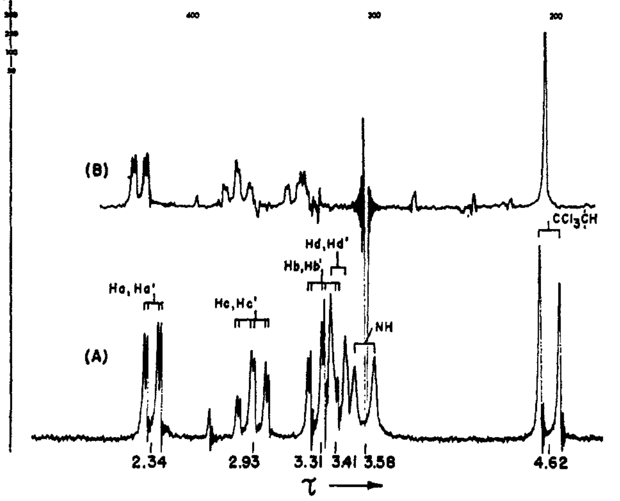
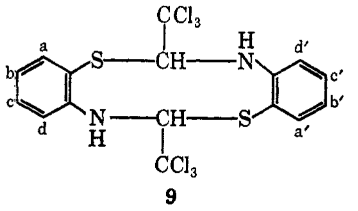


Figure 1.—(A) 100-Mc spectrum of 2,7-bis(trichloromethyl)-2,3,7,8-tetrahydrodibenzo[*d*,*i*][1,3,6,8]dithiadiazecine (**9**) in chloroform solution; (B) 100-Mc spectrum of **9** with irradiation at τ 3.58 (NH) causing spin decoupling from the adjacent methine proton (4.62) and collapse of the latter resonance to a singlet.

While freshly recrystallized **3** is stable for long periods of storage at 0–5° and remains free of dimer or other detectable decomposition products under these conditions, storage at 25° or recrystallization from ethanol, benzene, or hexane is accompanied by decomposition yielding **9**, HCl, and, probably, the benzothiazole (**5**). The infrared and mass spectral data of **9**, along with its nmr spectrum (Figure 1) have led to its formulation as 2,7-bis(trichloromethyl)-2,3,7,8-tetrahydrodibenzo[*d*,*i*]-[1,3,6,8]dithiadiazecine. The nmr spectrum reveals six different absorption multiplets, each of which represents two identical protons as a result of the symmetry of the molecule. The doublet resulting from the amino protons was assigned on the basis of the disappearance of this absorption in the nmr spectrum of the deuterated



9

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[8] A. Cernani and R. Passerini (*J. Chem. Soc.*, 2261 (1954)) attribute the second band of benzothiazoles to either a B_{1u} or to a E_{2g} state of the benzene ring.

[9] J. M. Sprague and H. A. Land in "Heterocyclic Compounds," Vol. V, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 8.

[10] M. T. Bogert and H. B. Corbitt, *J. Am. Chem. Soc.*, **48**, 783 (1926).

dimer (**10**), with the attendant coalescence of the methine (CCl$_3$CH) doublet to a singlet. Deuteration of the nitrogen was confirmed by the N–D stretching band at 4.1 μ in the infrared spectrum. Additional proof of the vicinal relationship of the NH and CCl$_3$CH was obtained by a spin-decoupling experiment (Figure 1B) in which the amino proton resonance was irradiated and the collapse of the methine doublet (τ 4.62) was observed. The remaining absorption lines are typical for the protons of an unsymmetrically *ortho*-disubstituted benzenoid substrate. The *ortho* couplings resulted in doublets and triplets having the following coupling constants: $J_{ab} = J_{a'b'} = 7.6$ cps, $J_{bc} = J_{b'c'} = 7.6$ cps, and $J_{cd} = J_{c'd'} = 8.1$ cps. Longer range *meta* coupling resulted in further splittings of the following magnitudes: $J_{ac} = J_{a'c'} = 1.6$ cps and $J_{bd} = J_{b'd'} = 1.4$ cps.

The unexpectedly large paramagnetic shift of Ha, Ha′ (τ 2.34) is attributed to the proximity of the CCl$_3$ groups with their attendant magnetic anisotropy.[11] The resonance at τ 3.41 (Hd, Hd′) exhibits electric quadrupole broadening owing to the nearby nitrogen.

An interesting contrast exists between the NH groups of **9**, whose protons exchange relatively slowly, showing coupling with the adjacent methine protons, and the NH of **3** whose rapidly exchanging amino proton appears as a singlet. While the mechanisms of formation and of pyrolysis of the dimer (**9**) are unclear, the somewhat unexpected behavior of the benzothiazoline **3** on attempted oxidation and pyrolysis is not unprecedented since Ruske and Hartmann have reported "β elimination" of HCl from some similar trichloromethyl heterocycles.[12] The latter reactions were, however, conducted under strongly basic conditions.

Experimental Section

Melting points are uncorrected unless otherwise indicated. Nuclear magnetic resonance spectra were determined on Varian A-60 and HA-100 instruments with deuteriochloroform or carbon tetrachloride as solvents and TMS as the internal reference. Mass spectrometric studies were performed with a Bendix Model 12-101 time-of-flight mass spectrometer. Ordinary molecular weight determinations were performed by a modification of the thermistor method described by Neumayer.[13]

2-(**Trichloromethyl**)**benzothiazoline** (**3**).—To a nitrogen-blanketed solution of 50.0 g (0.4 mole) of *o*-aminobenzenethiol in 150 ml of benzene was added 58.8 g (0.4 mole) of anhydrous chloral. An exothermic reaction began at once and gentle reflux of the mixture was continued with heating for a period of about 2 hr under a Dean–Stark trap, removing by-product water overhead. The organic phase was then dried (Na$_2$SO$_4$) and evaporated, and the residue recrystallized from hexane to give 80.6 g (79.5% yield) of **3**, mp 92.5–93.5° dec[14] with HCl evolution. The nmr spectrum showed an exchangeable H (broad singlet at τ 4.84), a singlet (1 H) at τ 4.2 (CCl$_3$CH), and an aromatic 4 H multiplet resulting from an ABCD spin system (τ 2.8–3.4). The infrared spectrum had bands at 2.95 μ (NH), 3.25 (aromatic CH), 3.43 (aliphatic CH), 6.33, 6.68 and 6.78 (aromatic C═C), and 12.2 and 12.57 (CCl$_3$). The ultraviolet spectrum showed λ_{max} 218 mμ (ϵ 24,300), 255 (shoulder, ϵ 4580), and 309 (ϵ 4580).

Anal. Calcd for C$_8$H$_6$Cl$_3$NS: C, 37.74; H, 2.37; N, 5.50; Cl, 41.78; mol wt, 254.6. Found: C, 37.99; H, 2.40; N, 5.58; Cl, 41.03; mol wt, 258.

In subsequent melting point determinations, it was found that prolonged heating of **3** below 90° caused melting and decomposition. Thus a sample melted (decomposed) at 74.5° after holding at 66.5–74.5° for about 15 min. Compound **3** gave no precipitate on contact with ethanolic silver nitrate for a period of 1 hr at 25°. It was found to be insoluble in aqueous 25% NaOH at room temperature, but a slow release of chloride ion occurred on standing in aqueous ethanolic NaOH. Various samples of **3** underwent slow decomposition with evolution of HCl on storage at room temperature: a sample stored at 0–5° for a period of 18 months, however, showed no evidence of decomposition or change upon visual inspection or infrared analysis.

2-(Dichloromethyl)benzothiazole (**5**). **A. By Action of FeCl$_3$ on 3.**—A solution of 25.5 g (0.10 mole) of **3** in 400 ml of ethanol was added with agitation to a solution of 39.0 g (0.24 mole) of anhydrous ferric chloride in 400 ml of ethanol. The resulting mixture was freed of ethanol under reduced pressure, neutralized with aqueous sodium bicarbonate, and subjected to continuous liquid–liquid extraction with ethyl ether for a period of 3 days. The ether solution was dried (Na$_2$SO$_4$) and evaporated to give 21.3 g of a brown solid. The crude product was recrystallized from hexane to give 13.4 g of crystals, mp 64–68°, bp 122–124° (3 mm). A second crop of product (2.1 g) brought the total yield to 71.0%. A sample of pure material, mp 72–73°,[14] showed bands at 3.25 μ (aromatic CH), 3.36 (Cl$_2$CH), 6.29 and 6.65 (aromatic C═C), and 12.77 and 13.82 (CCl). The ultraviolet spectrum showed λ_{max} 218 mμ (ϵ 18,200) and 265 (ϵ 8630). The structure was further confirmed by the nmr spectrum which displayed a singlet (1 H) at τ 2.88 (CCl$_2$H) and an aromatic 4 H multiplet at τ 1.8–2.7

Anal. Calcd for C$_8$H$_5$Cl$_2$NS: C, 44.05; H, 2.31; N, 6.42. Found: C, 44.10; H, 2.48; N, 6.37.

B. By Reaction of Dichloroacetyl Chloride with 1.—To a stirred solution of 29.6 g (0.21 mole) of dichloroacetyl chloride in 225 ml of benzene was added a solution of 25.0 g (0.20 mole) of *o*-aminobenzenethiol (**1**) and 15.9 g (0.21 mole) of pyridine in 100 ml of benzene over a 20-min period while maintaining a temperature of 6–16° by external cooling. Following the feed, the mixture was stirred at 16–20° for 10 min and then at 42–50° for about 1 hr after which it was worked up to give 38.6 g (88.6%) of **5**, mp 71–72°,[14] identical by mixture melting point and infrared spectrum with the product from the ferric chloride reaction.

Reduction of 5 to 2-Methylbenzothiazole.—To a solution of 5.45 g (0.025 mole) of **5** in 20 ml of acetic acid was added 7.3 g (0.112 g-atom) of zinc powder at 60–70°, portionwise, with agitation. A vigorous exothermic reaction ensued and, following addition of zinc, the mixture was heated on the steam bath for 20 min after which it was cooled; the resulting white solid was washed with acetic acid. The solid was worked up by trituration with water and ether extraction to give 1.65 g (45.3% yield) of 2-methylbenzothiazole, bp 90° (4 mm), identical by infrared and nmr spectral comparison with an authentic specimen.

2-(**Trichloromethyl**)**benzothiazole** (**4**).—To a cold (4°) agitated solution of 25.5 g (0.1 mole) of **3**, 7.7 g (0.067 mole) of 86% phosphoric acid, and 30 ml of water in 800 ml of acetone was added a solution of 10.6 g (0.067 mole) of potassium permanganate in *ca.* 1000 ml of H$_2$O–acetone (v/v = 1/3.2) over a 10-min period while maintaining the temperature at 4–15° by external cooling. Reaction was immediate and the by-product, manganese dioxide, was suction filtered from the reaction mixture with the aid of Hyflo. Evaporation of the filtrate and partial work-up gave a syrup (18.0 g) which was distilled through a simple system to give 9.3 g (37.1% crude yield) of 2-(trichloromethyl)benzothiazole (**4**) as a pale yellow oil, bp 117–128° (1–3 mm). The product, purified by crystallizing from pentane at −60 to −70°, weighed 6.2 g and melted at 31.5–34.0°. This material was identical with a similarly prepared specimen of **4**, mp 38°[14] (lit.[2] mp 37°), purified by vacuum sublimation. Infrared analysis revealed bands at 3.27 μ (aromatic CH), 6.44 (C═N?), 6.3, 6.35 and 6.69 (aromatic C═C), and 11.15 and 12.25 (CCl$_3$). The nmr spectrum showed only benzenoid hydrogens (4 H) in a complex multiplet at τ 1.7–2.7. The ultraviolet spectrum showed λ_{max} 216 mμ (ϵ 19,196) but with the B$_{1u}$ (or E$_{2g}$) second band[8] shifted bathochromically (λ_{max} 273 mμ, ϵ 9250) with respect to the dichloromethyl analog (**5**).

Anal. Calcd for C$_8$H$_4$Cl$_3$NS: C, 38.04; H, 1.60; N, 5.55; Cl, 42.12. Found: 38.68; H, 1.92; N, 5.59; Cl, 41.54.

It was found that the yield could be increased by omitting

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[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press Inc., Oxford, 1966, pp 136–137.

[12] W. Ruske and I. Hartmann, *J. Prakt. Chem.*, **18**, 150 (1962).

[13] J. J. Neumayer, *Anal. Chim. Acta.*, **20** (6), 519 (1959).

[14] Melting point corrected.

the distillation and simply extracting the crude syrup, obtained from evaporation of the filtered reaction mixture, with pentane. Upon drying the pentane solution and chilling it in a Dry Ice–acetone bath, **4** crystallized, in reasonable purity, in 60% yield.

Catalytic Oxidation of 2-(Trichloromethyl)benzothiazoline (3).—A solution of 25.5 g (0.1 mole) of **3** in 600 ml of ethyl acetate was charged to a large (25 in. × 2.7 in.) test tube equipped with a gas diffusor. An unsuccessful attempt was made to initiate reaction by passing in oxygen at 12° with 6 drops of a saturated solution of cupric acetate in glacial acetic acid added as catalyst. Increasing the temperature to 26° failed to initiate oxidation, but addition of 20 drops more of the catalyst solution caused an immediate exothermic reaction with uptake of oxygen and vigorous evolution of HCl and water. The exothermic process lasted 6 min during which the temperature rose from 27 to 37° and cooling was used to control the temperature. Work-up of the reaction mixture gave 6.0 g of a solid which afforded 2.9 g of buff-white crystals, mp 213–214°, after two recrystallizations from toluene.

Anal. Calcd for $C_{30}H_{20}N_4O_4S_4$: C, 57.31; H, 3.21; N, 8.91; S, 20.40; mol wt, 628. Found: C, 57.91; H, 3.33; N, 9.30; S, 19.70; mol wt, 581.

The unknown material was insoluble in water and in aqueous base. Infrared analysis showed bands at 3.0 μ (NH), 3.25 (aromatic CH), 5.90 (secondary amide C=O?), 6.35 and 6.70 (aromatic C=C), and 6.55 (NH). A satisfactory nmr spectrum could not be obtained owing to the extremely limited solubility of the substance in all available solvents.

2,7-Bis(trichloromethyl)-2,3,7,8-tetrahydrodibenzo[*d,i*]-[1,3,6,8]dithiadiazecine (9).—A 67.0-g portion of **3** was stirred with 700 ml of ethanol at *ca.* 60° until only a small amount of insoluble solid remained. Upon cooling to room temperature, the insoluble crystals were collected, washed, and dried, giving 3.26 g of crude **9**, mp 164–165° dec. Recrystallization from ethyl acetate gave 1.87 g of pure **9** as colorless, compact prisms. It had mp 167–168.5° dec, beginning at 160° with a 2°/min heating rate, which decreased to 152–155° dec when a sample was placed in the bath at 125°. The infrared spectrum showed bands at 3.0 μ (NH), 3.25 (aromatic CH), 3.4 (aliphatic CH), 6.28, 6.33 and 6.66 (aromatic C=C), 11.45–13.97 (CCl_3), and a band at 13.5 attributed to four adjacent aromatic hydrogens.

Anal. Calcd for $C_{16}H_{12}Cl_6N_2S_2$: C, 37.74; H, 2.37; N, 5.50; Cl, 41.78; mol wt, 509. Found: C, 37.66; H, 2.46; N, 5.50; Cl, 41.67; mol wt, 514.

The mass spectral studies obtained at 60° confirmed the monoisotopic mass as *m/e* 506 in showing a family of peaks, of minor intensity, at *m/e* 506, 508, 510, 512, 514, and 516 resulting from the natural isotopic abundance of Cl^{35} and Cl^{37} in two trichloromethyl groups.

Preparation of 2,7-Bis(trichloromethyl)-3,8-dideuterio-2,7-dihydrodibenzo[*d,i*][1,3,6,8]dithiadiazecine (10).—A 330-mg portion of **9** was dissolved in hot ethyl acetate containing added, excess CH_3OD and, after brief standing, a solid residue recovered by evaporation of volatiles. The process was repeated a second time after which the resulting residue was crystallized from hot ethyl acetate containing CH_3OD, giving 110 mg of **10**, mp 166–169° dec.[14] The infrared spectrum showed an N–D stretching band at 4.1 μ as well as a weak band at 3.0 μ attributable to the presence of some undeuterated starting material. The mass spectral analysis indicated that deuteration had occurred to an extent of about 90% and revealed the parent ion at *m/e* 508 (theoretical 508), a deuterated monomer ion at *m/e* 254, and the following fragmentation pattern: *m/e* 218 (loss of HCl from a monomeric species), 183 (ion resulting from loss of Cl from *m/e* 218 species), 137 (PhNDCHS ion), and 109 (PhS ion).

Pyrolysis of 2-(Trichloromethyl)benzothiazoline (3).—A 5.0-g (0.0197 mole) portion of **3** was placed in a flask with a nitrogen inlet and a side arm leading to a train of two traps cooled successively by ice water and Dry Ice–acetone mixtures. With a gentle stream of dry nitrogen flowing through the system, the pyrolysis flask was heated by a steam bath causing the charge to melt with evolution of HCl. After a 10-hr heating period, the HCl production had virtually ceased and a 0.49-g (68% of theory) weight loss in the residue (which crystallized on cooling) was noted. Recrystallization from hexane gave 2.3 g (53.3% yield) of impure 2-(dichloromethyl)benzothiazole (**5**), mp 51.5–65.5°, undepressed by admixture with pure material.

Pyrolysis of 2,7-Bis(trichloromethyl)-2,3,7,8-tetrahydrodibenzo[*d,i*][1,3,6,8]dithiadiazecine (9).—A 0.22-g (0.000433 mole) sample of **9** was heated in a gentle stream of dry nitrogen at 152–160° for a period of approximately 1 hr using the apparatus described above. At this time HCl evolution, which had been vigorous, had nearly ceased. A total of 0.10 g (53.0% yield) of **5**, mp 64.5–68.5°, was recovered as a white crystalline sublimate from the walls of the pyrolysis vessel. The mixture melting point with authentic material was undepressed.

Nitration of 5.—A 21.8-g (0.10 mole) portion of **5** was nitrated at 46–101° with 9.4 g (0.105 mole) of concentrated nitric acid and 120 g of concentrated sulfuric acid using a procedure similar to that described by Bogert and Corbitt.[10] Attempted purification of the syrupy product by crystallization from ligroin yielded four crops of a solid mixture, total weight 3.2 g, and 14.8 g of an uncrystallizable syrup with an analysis close to that of a mononitrated 2-(dichloromethyl)benzothiazole.

Anal. Calcd for $C_8H_4Cl_2N_2O_2S$: N, 10.65. Found: N, 10.33.

The infrared spectrum of the material was virtually identical with that of 6-nitrobenzothiazole through the 6–9.5-μ region.

Attempted Ring Chlorination of 5.—To a stirred solution of 43.7 g (0.2 mole) of **5** in 100 ml of tetrachloroethylene containing 0.2 g of anhydrous ferric chloride and 0.1 g of iron filings was added 17.7 g (0.25 mole, 11 ml at −75°) of liquid chlorine over a 5-min period at 17–22°. Upon completing the feed, a mild exothermic reaction occurred and the mixture was held at 29–40° for *ca.* 2 hr after which it was worked up to give 48.9 g of a dark syrup. Infrared analysis of the latter showed it to be 2-(trichloromethyl)benzothiazole (**4**). Crystallization from pentane (at −80°) gave 42.8 g (84.8% yield) of pure **4**, mp 35.5–36°, undepressed upon admixture with authentic material.

2-(Dichloromethyl)benzothiazoline (6).—A 0.3-mole portion (37.5 g) of *o*-aminobenzenethiol (**1**) was treated with 0.3 mole (33.9 g) of redistilled dichloroacetaldehyde in 75 ml of benzene under conditions very similar to those employed in the chloral reaction. Working up the reaction mixture in a similar manner afforded 26.8 g of product, mp 76.5–77.5°, after recrystallization from hexane. The nmr spectrum showed a broadened singlet (1 H) at τ 5.6 (NH), an AB pair (2 H, J = 7.9 cps) centered at 4.6 and 4.4 ($NC(S)HCHCl_2$), and a complex multiplet (4 H), at 2.7–3.6 attributable to the benzenoid protons.

Anal. Calcd for $C_8H_7Cl_2NS$: C, 43.65; H, 3.21; N, 6.36. Found: C, 43.90; H, 3.54; N, 6.50.

The yield, including a second crop (13.4 g, mp 64–70°), was 60.9%.

2-Dichloromethyl-5-(trifluoromethyl)benzothiazole (8).—To a stirred solution of 74 g (0.5 mole) of dichloroacetyl chloride in 200 ml of benzene was added, portionwise, 38.7 g (0.2 mole) of 2-amino-4-(trifluoromethyl)benzenethiol over a 1-hr period with gentle cooling to maintain a maximum temperature of 40°. The reaction mixture was then heated to reflux (78–84°) and stirred for an additional 2-hr period. The mixture was filtered and evaporated giving a syrup which was worked up, giving 29.2 g of a liquid residue which crystallized on standing. Recrystallization from hexane afforded 22.5 g (39.3%) of relatively pure **8**, mp 29–33°, with a second recrystallization giving 17.7 g of material, mp 34–34.5°. A purer sample of **8** from a similar preparation melted sharply at 39°. The infrared spectrum showed bands at 3.34 μ (CCl_2H), 3.25 (aromatic CH), 6.18 and 6.65 (aromatic C=C), 8.7–8.83 (CF_3), and 12.2 (1,2,5-trisubstituted phenyl ring).

Anal. Calcd for $C_9H_4Cl_2F_3NS$: C, 37.78; H, 1.41; N, 4.89; F, 19.92. Found: C, 37.60; H, 1.49; N, 5.02; F, 19.88.

Registry No.—**3**, 13618-97-8; **4**, 6269-43-8; **5**, 6278-69-9; **6**, 13618-99-0; **8**, 13619-00-6; **9**, 13619-01-7; **10**, 13619-02-8.

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