Anal. Calcd for $C_2H_2N_2Se$: C, 18.06; H, 1.52; N, 21.06. Found: C, 17.88; H, 1.77; N, 21.24.

Dideuterio-1,3,4-selenadiazole.—The crude distillate above (1.0 g), containing both 1,3,4-selenadiazole and N,N-dimethylselenoformamide, was dissolved in 20 ml of 0.2 *N* sodium carbonate in D_2O (Diaprep 99.8%) and left to stand for 12 hr at room temperature. The deuterated selenadiazole was extracted from the heavy water with ethyl ether (six 50-ml portions) and the ether solution dried over magnesium sulfate. The ether was evaporated and the product purified by vpc (same conditions as above). From the mass spectrum the product contained about 75% dideuterio species and 25% monodeuterio compound. The infrared spectrum contained a strong C–D stretching band at 4.35 μ (neat).

Registry No.—IA, 289-13-4; IB, 289-06-5; IC, 288-99-3.

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1,2,4-Triazoles. XXIII. Chlorination of *s*-Triazolo[4,3-*a*]pyridine-3-thiol and the Formation of 3,5,6,7,7,8-Hexachloro-5,6,7,8-tetrahydro-*s*-triazolo[4,3-*a*]pyridine[1]

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Chlorination of *s*-triazolo[4,3-*a*]pyridine-3-thiol gave, as the major product, the above hexachloro compound together with small amounts of 3,8-dichloro- and 3,6,7,8-tetrachloro-*s*-triazolo[4,3-*a*]pyridine. Similar products were obtained from methyl-substituted derivatives of the ring system. Treatment of the thiols with aqueous sodium hypochlorite solution ("Clorox") gave the corresponding monochloro product in good yield.

Chlorination of various heterocyclic thiols under oxidizing conditions is a convenient route to sulfonyl chlorides and, in certain cases, to the corresponding chloro compounds.[2] Our interest in chloro-substituted heterocycles as precursors for the synthesis of polynuclear heterocyclic systems with bridgehead nitrogen atoms[3] led us to study the oxidative chlorination of *s*-triazolo[4,3-*a*]pyridine-3-thiol (1, R = R′ = H) as a possible route to the 3-chloro compound. This study has resulted in some interesting polychlorinated products of this bicyclic ring system.

Treatment of *s*-triazolo[4,3-*a*]pyridine-3-thiol (1, R = R′ = H) with an excess of chlorine at 0–10° in aqueous chloroform gave three products. Representation of the major product (29% yield) as 3,5,6,7,7,8-hexachloro-5,6,7,8-tetrahydro-*s*-triazolo[4,3-*a*]pyridine (2) is consistent with the following evidence. The molecular formula, $C_6H_3Cl_6N_3$, was established by, analytical and molecular weight data, the latter being determined from its mass spectrum which showed the appropriate isotopic chlorine clusters (Table I). Its nmr spectrum consisted of an AX pattern at τ 3.50 and 4.97 (rel intensity 1:1) with J = 5.6 Hz and a singlet (1 H) at τ 4.84. These data suggest the presence of vicinal hydrogens at positions 5 and 6 in a diaxial relationship and a proton at position 8 of the nucleus, the 7 position being occupied by a *gem* dichloro group. The absence of a low field signal (below τ 2.00) attributable to a 3-hydrogen atom in *s*-triazolo[4,3-*a*]-pyridine[4] places the sixth chlorine atom in the 3 position. The ultraviolet absorption spectrum (λ_{max} 275, 220 mμ; log ϵ 3.89, 3.98) indicated that the conjugated system present in 3-chloro-*s*-triazolo[4,3-*a*]pyridine (8, R′ = H) (λ_{max} 297, 265, 258, 208 mμ; log ϵ 3.79, 3.79, 3.83, 4.69) was no longer present in the hexachloro product and the infrared spectrum was devoid of any characteristic absorption in the carbon–carbon double-bond region.

TABLE I

MASS SPECTRAL DATA[a] FOR SEVERAL DERIVATIVES OF THE *s*-TRIAZOLO[4,3-*a*]PYRIDINE SYSTEM

Compound	*m/e* (rel intensity)
2	327(5.5), 294(100), 292(80), 223(49), 221(52), 187(52), 127(26), 99(20)
3, R = R′ = H	187(100), 127(95), 100(29)
4	257(100), 255(70), 194(44), 167(12.5), 133(22), 98(12.5)
3, R = H; R′ = CH_3	201(100), 166(22), 140(11), 105(10), 85(9), 79(9), 65(9)
6	273(13), 238(33), 203(66), 201(100), 166(16), 140(12), 105(13), 78(20), 75(10), 64(8), 63(10), 62(10), 61(8), 60(5)
3, R = R′ = CH_3	215(100), 214(7), 180(7), 153(7), 127(5), 119(25), 92(8), 78(7), 77(5), 67(6), 66(7), 65(5)

[a] Determined at 70 eV.

The following chemical transformations show that no skeletal rearrangement had occurred and offer support for the above assignments.[5] Reaction of the hexachloro compound 2 with dilute ammonia or barium hydroxide gave a product 4 which was also found as a minor constituent of the original chlorination reaction. The

(1) (a) Partial financial support of this work by U. S. Public Health Service Research Grant No. CA 08495, National Cancer Institute, and USAMRDC Contract No. DA-49-193-MD-3012, is gratefully acknowledged; (b) Communication No. 728 in the U. S. Army Research Program on Malaria.

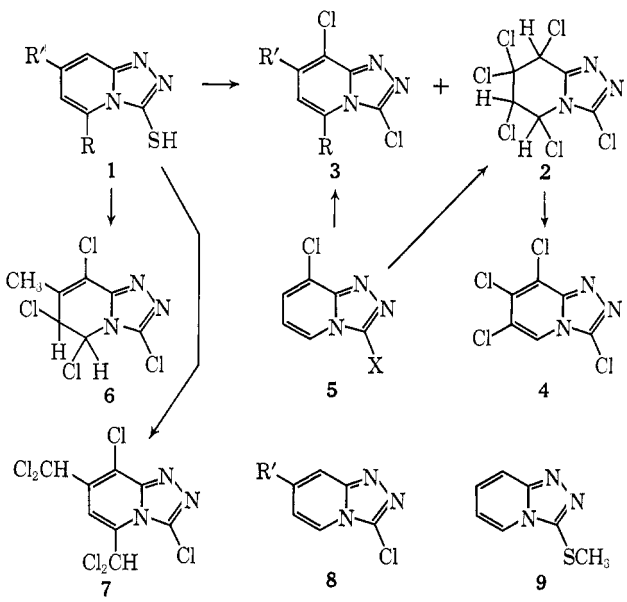
(2) For papers detailing earlier work in this area, see R. O. Roblin, Jr., and J. W. Clapp, *J. Amer. Chem. Soc.*, **72**, 4890 (1950); C. W. Noell and R. K. Robins, *ibid.*, **81**, 5997 (1959); R. K. Robins, *J. Org. Chem.*, **26**, 447 (1961); N. K. Basu and F. L. Rose, *J. Chem. Soc.*, 5660 (1963); W. Broadbent, C. W. Miller, and F. L. Rose, *ibid.*, 3369 (1965); G. S. Sidhu, S. Naqui, and D. S. Iyengar, *J. Heterocycl. Chem.*, **3**, 158 (1966); H. L. Yale and J. J. Piala, *J. Med. Chem.*, **9**, 42 (1966).

(3) For example, see K. T. Potts, U. P. Singh, and J. Bhattacharyya, *J. Org. Chem.*, **33**, 3766 (1968).

(4) K. T. Potts, H. R. Burton, T. H. Crawford, and S. W. Thomas, *ibid.*, **31**, 3522 (1966).

(5) It is recognized that our data do not rigorously exclude the possibility that this hexachloro product could be an isomeric one. However, its relationship to the tetrachloro and dichloro products, together with mechanistic considerations, lead us to put more emphasis on the proposed structure. Tlc analysis always indicated that we were dealing with only one hexachloro product.

presence of four chlorine atoms was evident from the mass spectrum of this product (Table I) which established the molecular weight as 255. The conjugated system of *s*-triazolo[4,3-*a*]pyridine was shown to be present by the ultraviolet absorption spectrum of the product (λ_{max} 315, 295, 224 mμ; log ϵ 3.59, 3.54, 4.61). The presence of one hydrogen atom in this tetrachloro product **4** ($C_6HCl_4N_3$) was confirmed by a singlet at τ 1.87 in its nmr spectrum, a chemical shift which excludes the possibility that this could be the 3 proton of the *s*-triazolo[4,3-*a*]pyridine system[4] (τ 1.14–1.28, 3H). This chemical shift is consistent with that of a proton adjacent to a nitrogen and also *ortho* to a chlorine atom.[6] In addition, the effect of the 3-chlorine atom has also to be considered (in 3-chloro-*s*-triazolo[4,3-*a*]pyridine[4] the 5-proton chemical shift is τ 2.01 compared with that of τ 1.79 in the unsubstituted product), and it is most unlikely that any proton other than the 5 proton would resonate at such a low field. Position 8 for the hydrogen atom can be excluded from consideration as 8-chloro-*s*-triazolo[4,3-*a*]pyridine-3-thiol (**5**, X = SH) gave the hexachloro product **2** on treatment with chlorine under the initial reaction conditions. Conversion of the tetrachloro product **4** into the hexachloro compound **2** could not be effected under the initial chlorination conditions and it is most likely that **4** is an artifact produced by decomposition of the major hexachloro product during the reaction work-up.



Reduction of the hexachloro product **2** with zinc dust and acetic acid gave a dichloro product (**3**, R = R′ = H) which was identical with that obtained *via* a Sandmeyer reaction from 3-amino-8-chloro-*s*-triazolo[4,3-*a*]pyridine (**5**, X = NH_2). This clearly established the structure of the dichloro product as 3,8-dichloro-*s*-triazolo[4,3-*a*]-pyridine (**3**, R = R′ = H). This same dichloro product was also isolated as a minor product from the chlorination of *s*-triazolo[4,3-*a*]pyridine-3-thiol. Spectral data were in agreement with structure **3** for the dichloro product.

Introduction of a methyl substituent[7] into the pyridine ring of the fused system does not alter appreciably the overall chlorination process. **7**-Methyl-*s*-triazolo[4,3-*a*]pyridine-3-thiol (**1**, R = H; R′ = CH_3) gave 3,8-dichloro-7-methyl-*s*-triazolo[4,3-*a*]pyridine (**3**, R = H; R′ = CH_3) and 5,6-dihydro-3,5,6,8-tetrachloro-7-methyl-*s*-triazolo[4,3-*a*]pyridine (**6**), these structures being assigned mainly on the basis of analytical and spectral data. The molecular formula $C_7H_5Cl_2N_3$ for compound **3** (R = H, R′ = CH_3) was established by analytical and mass spectral data (Table I), and the ultraviolet spectrum indicated that the fused-ring system was still intact. The absence of a low field proton in its nmr spectrum showed the presence of a 3-chloro substituent and, apart from the methyl resonance at τ 7.45, the nmr spectrum showed an AB pattern at τ 2.50 and 3.29, J = 8.0 Hz.

The second product **6** obtained from the chlorination of **1** (R = H, R′ = CH_3) was found to contain four chlorine atoms (Table I) and its molecular formula was established as $C_7H_5Cl_4N_3$. This requires disruption of the conjugation of the fused system, which was also clear from the ultraviolet absorption spectrum of the product. The nmr spectrum showed that no reaction had occurred at the methyl group (resonance at τ 7.75) and that the remaining two protons at τ 3.85 (J = 2.2 Hz) and 5.15 (J = 2.2 Hz) were in an environment analogous to that for the 5,6 protons of compound **2**. The smaller coupling constants found for the 5,6 protons can be attributed to the change in their dihedral angle[8] (*ca.* 110°) resulting from the presence of the 7,8 double bond in the six-membered ring.

Chlorination of 5,7-dimethyl-*s*-triazolo[4,3-*a*]pyridine (**1**, R = R′ = CH_3) resulted in a dichloro product as well as a hexachloro product. Structure **3** (R = R′ = CH_3), 3,8-dichloro-5,7-dimethyl-*s*-triazolo[4,3-*a*]-pyridine, was assigned to the former product using analytical and spectral data in the same manner as described above. The hexachloro product obtained from this reaction was a strong lachrymator and skin irritant, and underwent deep-seated decomposition on electron impact[9] after losing two chlorine atoms from the molecular ion at *m/e* 350. The ultraviolet spectrum indicated that no major structural change had occurred in the nucleus and the nmr spectrum consisted of three well-defined singlets at τ 1.95, 2.25, and 2.85. These data are best accommodated by the structure **7** for this hexachloro product. Though it is not possible to unambiguously assign the above chemical shifts to the three protons present in **7**, assignment of the dichloromethyl group proton at position 5 to the resonance at τ 1.95, the 6 proton to 2.25, and the dichloromethyl group proton at position 8 to 2.85, is not without merit.

In contrast to the complex chlorination reactions described above, it was possible to convert the 3-thiols into the corresponding 3-chloro compounds **8** in excellent yield by reaction with sodium hypochlorite solution.[10] This chlorination procedure should be of use in numerous other heterocyclic systems.

Chlorination of *s*-triazolo[4,3-*a*]quinoline-3-thiol[11a]

(6) Numerous examples of this effect are known, *e.g.*, W. Brugel, *Z. Elektrochem.*, **66**, 159 (1962).

(7) K. T. Potts and H. R. Burton, *J. Org. Chem.*, **31**, 251 (1966).

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(9) In other studies (K. T. Potts and R. Armbruster, unpublished observations) we have found that *gem*-dichloro compounds undergo very facile decomposition on electron impact.

(10) Commercial preparations of bleach (*e.g.*, Clorox) were found to be quite satisfactory for these reactions.

(11) Unpublished observations: (a) K. T. Potts and S. Husain; (b) K. T. Potts and C. Lovelette.

and *s*-triazolo[3,4-*a*]phthalazine-3-thiol[11b] with chlorine as described above resulted in the ready formation of the 3-chloro compounds. The marked divergence in behavior of the *s*-triazolo[4,3-*a*]pyridine system was especially interesting as it might be developed as a procedure for obtaining polychlorinated heterocycles. The 3-thiol group was found to be essential for polychlorination to occur. This was established by reaction of 3-methylthio-*s*-triazolo[4,3-*a*]pyridine (**9**) as well as *s*-triazolo[4,3-*a*]pyridine itself with chlorine under analogous reaction conditions; from these reactions 3-chloro-*s*-triazolo[4,3-*a*]pyridine only was obtained. Oxidative chlorination of a thiol and its ether to the corresponding sulfonyl chloride and sulfone are well known, and rationalization of the above polychlorination as being due to the inductive effect of the 3-sulfonyl chloride substituent resulting in more double-bond character for the pyridine double bonds is equally true for a 3-sulfone substituent. The dispositions of the chlorine substituents in the above products indicate that a multiple addition–elimination sequence was operative and that both free-radical and polar processes were involved.

Alkyl chlorides are formed from alkanesulfonyl chlorides by a free-radical process,[12] and the difference in behavior between *s*-triazolo[4,3-*a*]pyridine-3-thiol and its methylthio ether may be rationalized in these terms. Free-radical decomposition of *s*-triazolo[4,3-*a*]-pyridine-3-sulfonyl chloride would give the resonance stabilized *s*-triazolo[4,3-*a*]pyridyl free radical, sulfur dioxide, and a chlorine radical (initiation step), and further reaction of this product with chlorine should occur readily. However, free-radical decomposition of the corresponding 3-sulfone would involve generation of an energetically unfavorable methyl radical. In this case an ionic type mechanism most likely prevails, with displacement of a methyl sulfinate ion by a chloride ion.

Polychlorination of substituted pyridines has been described[13] in the literature and 5-aminobenzothiophene and its 2-carboxylic acid have also yielded[14] complex chlorination products under such exhaustive chlorination conditions.

Experimental Section[15]

The *s*-triazolo[4,3-*a*]pyridine derivatives were prepared by standard procedures described earlier.[7]

3-Amino-8-chloro-*s*-triazolo[4,3-*a*]pyridine (**5**, **X** = **NH₂**) separated from ethanol as colorless needles: mp 275–276°; ir (KBr) 3300, 3050, 2900, 1650, 1575, 1500, 1470, 1465, 1435, 1410, 1240, 1160, 1138, 1140, 948, 885, 870, 760, 730, 680, 655 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 230 (4.26), 272 (3.09), 288 (3.95), 325 (3.20).

Anal. Calcd for $C_6H_5ClN_4$: C, 42.70; H, 2.97; N, 33.21. Found: C, 42.86; H, 3.12; N, 33.03.

8-Chloro-*s*-triazolo[4,3-*a*]pyridine-3-thiol (**5**, **X** = **SH**) formed cream needles from ethanol: mp 295–296°; ir (KBr) 3095, 2930, 2780, 1630, 1525, 1500, 1455, 1450, 1395, 1310, 1295, 1228, 1160, 1120, 1090, 1035, 945, 870, 780, 738, 680, 660, 640 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 250 (4.19), 290 (3.91).

Anal. Calcd for $C_6H_4ClN_3S$: C, 38.81; H, 2.15; N, 22.63. Found: C, 39.07; H, 2.04; N, 22.65.

3-Chloro-2-hydrazinopyridine, used for the preparation of the above products, was prepared by the action of hydrazine hydrate on 2,3-dichloropyridine.[10] It formed colorless needles from ethanol: mp 160–161°; ir (KBr) 3290, 3200, 2900, 1620, 1600, 1500, 1460, 1420, 1275, 1175, 1132, 1080, 1040, 1000, 960, 935, 860, 790, 765, 752, 720 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 246 (3.94), 258 (3.96), 310 (3.73).

Anal. Calcd for $C_5H_6ClN_3$: C, 41.82; H, 4.18; N, 29.27. Found: C, 41.92; H, 4.30; N, 29.32.

General Chlorination Procedure. Chlorination of *s*-Triazolo[4,3-*a*]pyridine-3-thiol (**1**, **R** = **R′** = **H**).—A suspension of the thiol (5.0 g) in chloroform (100 ml) and water (60 ml) at 0° was treated with a slow stream of chlorine for 4–5 hr keeping the reaction temperature below 10°. The reaction mixture was allowed to come slowly to room temperature on standing overnight. The small amount of undissolved material was removed and the chloroform layer separated and then evaporated to dryness. The gummy residue was triturated with ethanol and the resultant solid collected, washed with aqueous sodium hydroxide solution (0.5 *N*) and water, and after drying, recrystallized from benzene–petroleum ether (40–60°). It formed fine, silky, colorless needles of the hexachloro product **2**: 3.5 g (29%); mp 186–187°; ir (KBr) 2975, 1325, 1280, 1215, 1130, 1080, 1050, 1028 cm^{-1}.

Anal. Calcd for $C_6H_3Cl_6N_3$: C, 21.82; H, 0.90; N, 12.43; Cl, 64.51; mol wt, 327. Found: C, 22.25; H, 0.86; N, 12.77; Cl, 65.12; mol wt, 327.

The above aqueous layer was extracted with benzene; the extract was dried ($CaCl_2$) and then concentrated to half-volume. Addition of petroleum ether caused the precipitation of a colorless, crystalline product (250 mg) which separated from benzene–petroleum ether as colorless needles of 3,8-dichloro-*s*-triazolo[4,3-*a*]pyridine (**3**, R = R′ = H): mp 162–163°; ir (KBr) 3130, 3080, 1630, 1500, 1460, 1440, 1405, 1310, 1230, 1155, 1100, 1085, 940 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 302 (3.74), 278 (3.75), 212 (4.57); nmr ($CDCl_3$) τ 7.03 (t, 1, *J* = 7.2 Hz, 6-H), 7.49 (d, 1, *J* = 7.2 Hz, 7-H), 8.07 (d, 1, *J* = 6.6 Hz, 5-H).

Anal. Calcd for $C_6H_3Cl_2N_3$: C, 38.28; H, 1.59; N, 22.34. Found: C, 38.51; H, 1.88; N, 22.46.

The above aqueous layer from the benzene extraction was basified with aqueous sodium hydroxide solution (5 *N*) and again extracted with benzene. After drying and concentration of the benzene extract, petroleum ether was added and the product that separated collected. 3,6,7,8-Tetrachloro-*s*-triazolo[4,3-*a*]-pyridine (**4**) crystallized from benzene–petroleum ether as colorless, shiny plates: 500 mg; mp 166–167°; ir (KBr) 2950, 1700, 1602, 1480, 1460, 1425, 1400, 1310, 1285, 1235, 1220, 1165, 1095, 1045, 892 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 315 (3.59), 295 (3.54), 224 (4.61); nmr ($CDCl_3$) τ 1.87 (s, 5-H).

Anal. Calcd for $C_6HCl_4N_3$: C, 28.01; H, 0.38; N, 16.30. Found: C, 28.25; H, 0.39; N, 16.32.

In a similar fashion 7-methyl-*s*-triazolo[4,3-*a*]pyridine-3-thiol (**1**, R = H; R′ = CH_3) (2.0 g) gave, as the water-insoluble product, 3,8-dichloro-7-methyl-*s*-triazolo[4,3-*a*]pyridine (**3**, R = H; R′ = CH_3) which, after several recrystallizations from benzene–petroleum ether, formed fine colorless needles: 0.2 g; mp 217–218°; ir (KBr) 3075, 1650, 1500, 1460, 1430, 1400, 1360, 1330, 1300, 1235, 1130, 1052, 1022, 900, 895, 750, 665, 605 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 207 (4.62), 258 (3.86), 275 (3.92), 290 (3.83); nmr ($CDCl_3$) τ 7.45 (s, 3, 7-CH_3), 3.22 (d, 1, *J* = 8.00 Hz, 6-H), 2.15 (d, 1, *J* = 8.00 Hz, 5-H).

Anal. Calcd for $C_7H_5Cl_2N_3$: C, 41.58; H, 2.47; N, 20.79. Found: C, 41.49; H, 2.42; N, 20.82.

A further quantity of the dichloro compound (0.6 g, mp 215–217°) was isolated from the aqueous phase by benzene extraction. From the initial chloroform layer after a reaction work-up involving evaporation to dryness, trituration with benzene, and recrystallization from methanol, 7-methyl-3,5,6,8-tetrachloro-5,6-dihydro-*s*-triazolo[4,3-*a*]pyridine (**6**) was obtained as colorless shiny plates: 0.2 g; mp 163–165°; ir (KBr) 2998, 1645, 1525, 1480, 1460, 1445, 1385, 1295, 1275, 1260, 1218, 1160, 1070, 1040, 900, 865, 795, 745, 720, 690 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ε), 217 (4.15), 275 (4.10); nmr ($CDCl_3$) τ 7.75 (s, 3, 7-CH_3), 5.15 (d, 1, *J* = 2.20 Hz, 6-H), 3.85 (d, 1, *J* = 2.20 Hz, 5-H).

Anal. Calcd for $C_7H_5Cl_4N_3$: C, 30.77; H, 1.83; N, 15.38. Found: C, 30.47; H, 1.82; N, 15.68.

(12) H. F. Herbrandson, W. S. Kelly, and J. Versnel, *J. Amer. Chem. Soc.*, **80**, 3301 (1958).

(13) E. T. McBee, H. B. Hass, and E. M. Hondett, *Ind. Eng. Chem.*, **39**, 389 (1947); C. R. Kolder and H. J. Hertog, *Rec. Trav. Chim. Pays-Bas*, **72**, 285 (1953).

(14) K. Fries, H. Heering, E. Hemmecke, and G. Siebert, *Ann. Chem.*, **527**, 83 (1937).

(15) Infrared spectra were measured on a Perkin-Elmer Model 337 spectrophotometer and ultraviolet spectra on a Cary Model 14 spectrophotometer. Nmr spectra were determined in $CDCl_3$ solution on a Varian A-60 spectrometer using TMS as internal standard, and mass spectra were obtained from an Hitachi Perkin-Elmer RMU-6E mass spectrometer using the direct insertion probe at a temperature of *ca.* 150°. All evaporations were done under reduced pressure using a rotavap apparatus.

On chlorination of 5,7-dimethyl-*s*-triazolo[4,3-*a*]pyridine-3-thiol (**1**, R = R′ = CH_3) (3.0 g) by the above general procedure, the water-insoluble product was identified as 3,8-dichloro-5,7-dimethyl-*s*-triazolo[4,3-*a*]pyridine (**3**, R = R′ = CH_3) which crystallized from benzene–petroleum ether as colorless needles: 0.2 g; mp 210–213°; ir (KBr) 3050, 1640, 1500, 1476, 1472, 1445, 1425, 1400, 1385, 1360, 1340, 1300, 1235, 1130, 1085, 1055, 1025, 900, 890, 750, 665, 640, 605 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 207 (4.46), 272 (3.79), 282 (3.89), 300 (3.80); nmr ($CDCl_3$) τ 7.55 (s, 3, 7-CH_3), 7.15 (s, 3, 5-CH_3), 3.60 (s, 1, 6-H).

Anal. Calcd for $C_8H_7Cl_2N_3$: C, 43.52; H, 3.24; N, 19.44. Found: C, 43.37; H, 3.16; N, 19.04.

A further quantity (0.8 g, mp 210–213°) of the above dichloro compound was obtained by benzene extraction of the aqueous phase.

Evaporation of the chloroform layer gave a highly resinous mass which was triturated with a small amount of methanol and cooled. The solid which separated was recrystallized from methanol forming pale yellow, shiny plates of 3,8-dichloro-5,7-di(dichloromethyl)-*s*-triazolo[4,3-*a*]pyridine (**7**): mp 173–175°; ir (KBr) 3075, 3030, 1648, 1500, 1455, 1430, 1402, 1380, 1355, 1345, 1282, 1225, 1105, 1080, 1060, 1020, 912, 880, 810, 770, 730, 690, 662, 648 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 227 (4.42), 312 (3.80); nmr ($CDCl_3$) τ 2.75 (s, 1, 6-H), 2.25 (s, 1, 7-$CHCl_2$), 1.95 (s, 1, 5-$CHCl_2$).

Anal. Calcd for $C_8H_3Cl_6N_3$: C, 27.11; H, 0.85; N, 11.87. Found: C, 26.85; H, 0.84; N, 11.78.

Chlorination of 3-methylthio-*s*-triazolo[4,3-*a*]pyridine[16] (**9**, 2.0 g) under the above conditions yielded 3-chloro-*s*-triazolo-[4,3-*a*]pyridine hydrochloride which was isolated from the aqueous phase. It crystallized from ethanol–ether as colorless needles: 3.8 g; mp 236–238°; ir (KBr) 3370, 3100, 3020, 2550, 1650, 1560, 1530, 1470, 1430, 1320, 1285, 1150, 1060, 910, 880, 780, 760, 755, 660, 650 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 290 (3.48), 272 (3.58), 262 (3.52), 210 (4.40). The hydrochloride (2.0 g) in water (20 ml) was basified with sodium hydroxide solution (5 *N*) and the solution extracted with benzene. The benzene extract was worked up in the usual way and the residue recrystallized from benzene–petroleum ether. 3-Chloro-*s*-triazolo[4,3-*a*]pyridine separated as small, colorless needles, mp 125° (lit.[16] mp 125°); this was identical[17] with an authentic sample.

Under similar conditions to those described above, *s*-triazolo-[4,3-*a*]pyridine gave 3-chloro-*s*-triazolo[4,3-*a*]pyridine hydrochloride, identical with that described above.

Reaction of *s*-Triazolo[4,3-*a*]pyridine-3-thiol (1, R = R′ = H) with Sodium Hypochlorite.—The thiol (2.0 g) was stirred in "Clorox" (50 ml) at 0–10° for 2–3 hr, then allowed to come to room temperature and left overnight. A small amount of unreacted material was removed and the aqueous solution evaporated to dryness. The resulting solid was dissolved in a minimum volume of water, and the solution was cooled and basified with sodium hydroxide solution (10%). The alkaline solution was extracted with benzene and the product isolated from the benzene extract was recrystallized from benzene–petroleum ether giving colorless needles of 3-chloro-*s*-triazolo[4,3-*a*]pyridine (**8**, R′ = H): 1.5 g (72%), mp 124–125° (lit.[16] mp 125°).

Chlorination of 7-methyl-*s*-triazolo[4,3-*a*]pyridine-3-thiol (**1**, R = H; R′ = CH_3) under similar conditions gave 3-chloro-7-methyl-*s*-triazolo[4,3-*a*]pyridine (**8**, R′ = CH_3) which crystallized from benzene–petroleum ether as fluffy colorless needles: mp 86–88°; ir (KBr) 3010, 2900, 1670, 1530, 1475, 1450, 1425, 1400, 1330, 1290, 1170, 1052, 950, 880, 800, 750, 660 cm^{-1}; $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 208 (4.66), 258 (3.86), 272 (3.87), 288 (3.70).

Anal. Calcd for $C_7H_6ClN_3$: C, 50.15; H, 3.58; N, 25.07. Found: C, 50.09; H, 3.53; N, 24.97.

3,8-Dichloro-*s*-triazolo[4,3-*a*]pyridine (3, R = R′ = H) from 3-Amino-8-chloro-*s*-triazolo[4,3-*a*]pyridine (5, X = NH_2).—The amino compound (2.5 g) in dilute HCl (12 ml of concentrated acid, 6 ml of water) at −5° was treated with sodium nitrite solution (2.3 g in 15 ml of water) over 45 min. After an additional 30 min the diazonium solution was allowed to come to room temperature and decomposed by heating on the steam bath for 1 hr. The reaction mixture was basified with NaOH solution (10%) and extracted three times with benzene (50 ml each). 3,8-Dichloro-*s*-triazolo[4,3-*a*]pyridine, obtained after evaporation of the benzene and recrystallization of the residue from benzene–petroleum ether, formed colorless, shiny plates, mp 162–163°, and was identical with the dichloro product described above.

Dehydrochlorination of 3,5,6,7,7,8-Hexachloro-5,6,7,8-tetrahydro-*s*-triazolo[4,3-*a*]pyridine (2).—The hexachloro product (1.0 g) was heated under reflux (9 hr) with barium hydroxide (1.0 g) in water (40 ml). After cooling, the product was collected, washed repeatedly with cold water, and recrystallized from benzene. 3,6,7,8-Tetrachloro-*s*-triazolo[4,3-*a*]pyridine (**4**) separated as colorless, shiny needles, mp 168–169°, and was identical with the tetrachloro product isolated from the chlorination of *s*-triazolo[4,3-*a*]pyridine-3-thiol.

The use of ammonium hydroxide in this reaction procedure gave comparable results.

Treatment of 3,5,6,7,7,8-Hexachloro-5,6,7,8-tetrahydro-*s*-triazolo[4,3-*a*]pyridine (2) with Zinc and Acetic Acid.—The hexachloro product (400 mg) in methanol (100 ml) was treated with zinc dust (1.5 g) and several drops of acetic acid and the reaction mixture warmed gently on a steam bath for 1 hr. The zinc was filtered and washed with several quantities of hot methanol; the methanol was concentrated to 1/3 vol. On cooling, a colorless crystalline product separated. 3,8-Dichloro-*s*-triazolo[4,3-*a*]-pyridine (**3**, R = R′ = H) crystallized from benzene–petroleum ether as colorless shiny plates, mp 162–163°, and was identical with the dichloro product obtained from the chlorination of *s*-triazolo[4,3-*a*]pyridine-3-thiol and from 3-amino-8-chloro-*s*-triazolo[4,3-*a*]pyridine.

Anal. Calcd for $C_6H_3Cl_2N_3$: C, 38.28; H, 1.59; N, 22.34. Found: C, 38.51; H, 1.88; N, 22.46.

Registry No.—**1**, R = R′ = H, 6952-68-7; **2**, 22841-85-6; **3**, R = R′ = H, 22841-86-7; **3**, R = H, R′ = CH_3, 22841-87-8; **3**, R = R′ = CH_3, 22841-88-9; **4**, 22841-89-0; **5**, X = NH_2, 22841-90-3; **5**, X = SH, 22841-91-4; **6**, 22841-93-6; **7**, 22841-94-7; **8**, R′ = CH_3, 22841-96-9; 3-chloro-2-hydrazinopyridine, 22841-92-5; 3-chloro-*s*-triazolo[4,3-*a*]pyridine hydrochloride, 22841-95-8.

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(16) K. T. Potts and H. R. Burton, *J. Org. Chem.*, **31**, 265 (1966).

(17) The identity of any two products was established by superimposable infrared, ultraviolet, and nmr spectra, as well as no depression in the mixture melting point.