The Synthetic Utility of Heteroaromatic Azido Compounds. Part VII. Preparation of some 2- and 4-Substituted Thieno[3,2-*d*]pyrimidines

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Synthetically useful scission reactions of some 1*H*-1,2,3-triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidines have been studied. The net result of these reactions is an elimination of nitrogen, and a 1,1-addition of the cleaving agent, forming 2-substituted thieno[3,2-*d*]pyrimidines. The mechanism of the scission is discussed, and a concomitant nucleophilic attack and expulsion of nitrogen is proposed. An unusual reaction between the unsubstituted triazole-fused parent compound (**1**) and bromine in alkaline medium is also reported.

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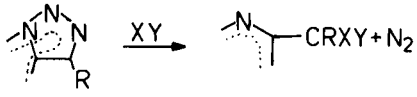
Introduction.

Fused 1,2,3-triazoles of the type depicted in Scheme 1, where one of the nitrogen atoms is also part of another aromatic ring, are very useful as precursors for the preparation of heteroaromatic systems. They often exhibit a marked "diazo" character, manifested for example by a pronounced ease of scission under a variety of conditions (1-13). The net result of non-thermal and non-photolytical scissions is generally the expulsion of nitrogen and a 1,1-addition of the cleaving agent (see Scheme 1).



Scheme 1

In the previous paper in this series (14), the preparation of some 1,2,3-triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidines from 3-azido-2-substituted thiophenes was reported. In this paper, the synthetic utility of these triazole-fused compounds for the preparation of a variety of previously unaccessible 2- and 4-substituted thieno[3,2-*d*]pyrimidines is described. The study has primarily been restricted to the parent, unsubstituted triazole-fused compound **1** (see Scheme 2), although, in order to illustrate the scope of the reactions involved, the scission of some derivatives of **1** has also been investigated.

Reactions.

Scission of the triazole ring of fused 1,2,3-triazoles is known to occur readily in acidic media (3-12). 1,2,3-Triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidine (**1**) is however quite stable in concentrated sulfuric acid, a fact which presumably reflects the low nucleophilicity of the hydrosulfate and sulfate anions. On the other hand, when **1** was treated with dilute sulfuric acid (30-50%) at room temperature, a rapid scission of the triazole ring occurred, giving 2-hydroxymethylthieno[3,2-*d*]pyrimidine (**6**) in good yield (75%). The pronounced difference in the stability of **1** in the two media must reasonably be attributed to the presence of larger amounts of nucleophilic water in the latter case. In agreement with the thus evident necessary presence of nucleophiles, scission also occurred readily in concentrated hydrochloric and hydrobromic acid, affording 2-chloromethyl- and 2-bromomethylthieno[3,2-*d*]pyrimidine (**7**,**8**), respectively, in high yields (~98%).

Scission of **1** also occurred in glacial acetic acid, although in this case heating (55-65°) was found necessary. Thus, 2-acetoxymethylthieno[3,2-*d*]pyrimidine (**9**) was obtained in 84% yield.

Compound **7** was also formed in high yield (75%) when 3-carbethoxy-1,2,3-triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidine (**5**) was heated with concentrated hydrochloric acid. This reaction probably also involves **1** as an intermediate, which under the conditions used can be formed from **5** by initial ester hydrolysis followed by decarboxylation.

In analogy with the results described above, scission also occurred when 3-phenyl-, 5-amino- and 3-phenyl-5-amino-1,2,3-triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidine (**2-4**) were treated with concentrated hydrochloric acid. Thus, the chloromethylated thienopyrimidines **10-12** were obtained in 62-91% yield. Scission of **2** and **3** was also carried out using dilute (30-50%) sulfuric acid, giving the hydroxymethylthienopyrimidines **13** and **14**.

The results described above are summarized in Scheme 2.

Comparing the relative ease of scission of the triazole-fused compounds **1-5** in concentrated hydrochloric acid, it is evident that both the phenyl- and the carbethoxy-substituted compounds, *i.e.* **2**, **4** and **5**, are less prone to react. This lower reactivity can probably be attributed to a substituent-induced inductive and/or mesomeric destabilization of the presumed reacting species (A in Scheme 3), although steric effects cannot completely be excluded.

In Scheme 3, two possible mechanistic routes for the acid-promoted scissions are outlined. Path 1, which involves scission of the triazole ring prior to attack by the nucleophile, closely resembles the reaction of diazo alkanes in acidic media (15). This route is also essentially similar to that proposed by Tennant, *et al.* (4,5). However,

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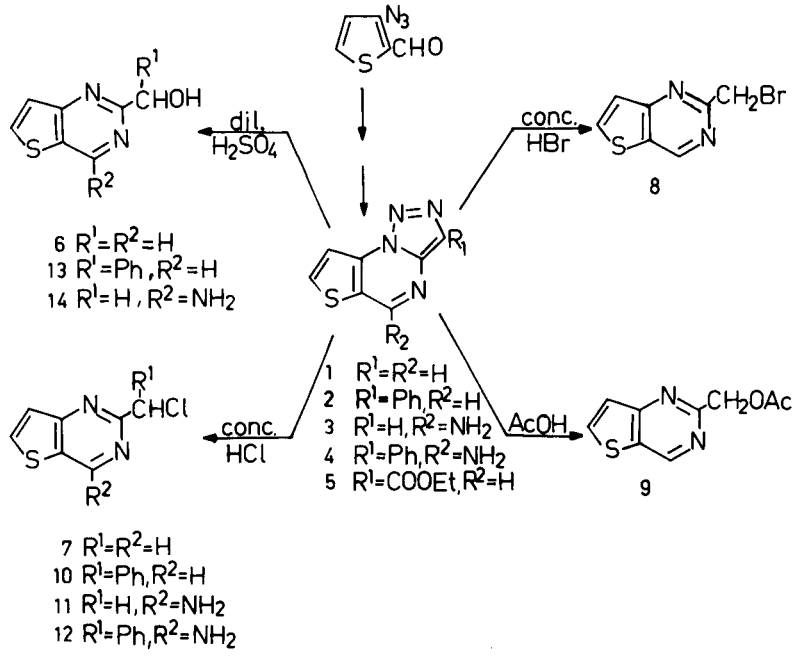
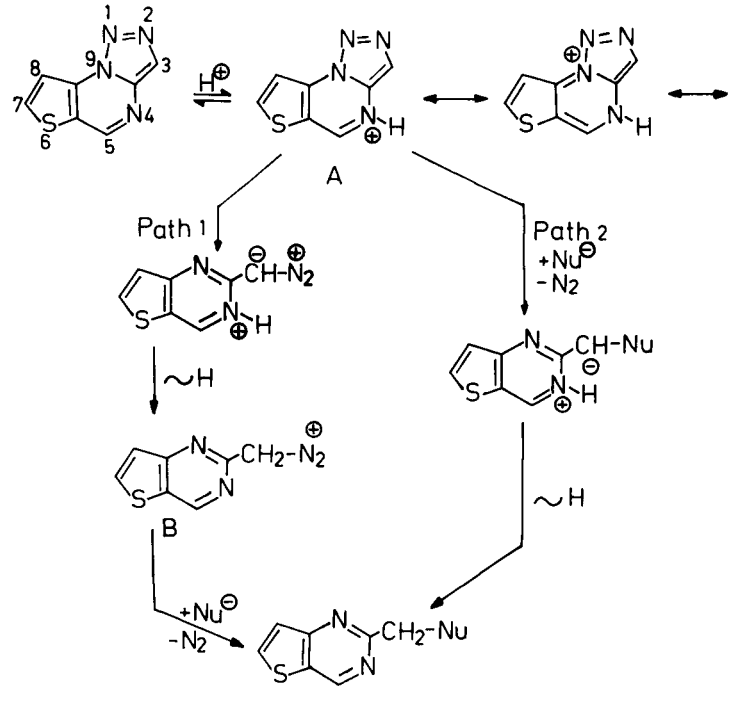


Scheme 2



Scheme 3

path 2, which entails a concomitant attack by the nucleophile and scission of the triazole ring, seems more likely. Thus, the ^{1}H nmr spectrum of **1** in concentrated sulfuric acid (14) more closely resembles what one would expect from structure A than from structure B. Based on the shifts for the benzylic protons in compounds **6-9**, and on known shifts for aliphatic diazonium ions (16,17), the shifts for the benzylic protons in structure B can be estimated to be δ ~7.5 ppm. The experimentally found shift for the only signal which could possibly be attributed to such a benzylic proton was however δ 9.82 ppm. This large difference clearly indicates that the diazonium ion B is not present to any great extent in strongly acidic solutions of **1**. The signal at δ 9.82 ppm can instead safely be assigned to H-3 in the conjugate acid of **1** (structure A). It should be noted that the downfield shift (1.4 ppm) of H-3

upon protonation is expected, and of the same magnitude as that experienced by the other protons of **1**.

The possibility that it is a small amount of B, in equilibrium with A, which is the reacting species, is ruled out by the fact that, as mentioned previously (14), no proton-deuterium exchange occurred when **1** was dissolved in concentrated, deuteriated sulfuric acid.

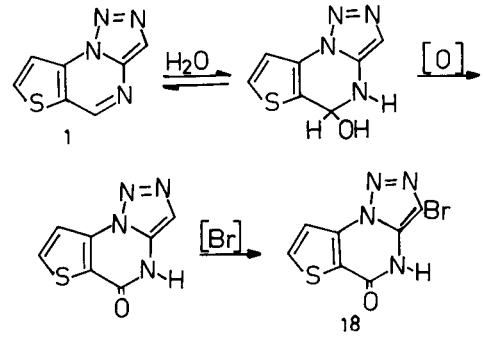
In Scheme 3 the initial protonation is assumed to take place on N-4, although of course it can also occur on the other pyridinic nitrogens, *i.e.* N-1 or N-2. The proposal of Tennant, *et al.* (5) that protonation occurs on the pyrrolic nitrogen (N-9) seems unlikely since this would result in loss of aromatic delocalization. Direct protonation on C-3, as suggested by Novinson, *et al.* (13), also seems unlikely since this presumably reversible process would lead to incorporation of deuterium in **1** upon dissolving in deuteriated sulfuric acid.

Finally, the possibility that the reacting species in aqueous media is not A but its covalent hydrate cannot be ruled out, since it is well known that quinazolines readily add water to the C4-N3 double bond under acidic conditions (*cf.* 18).

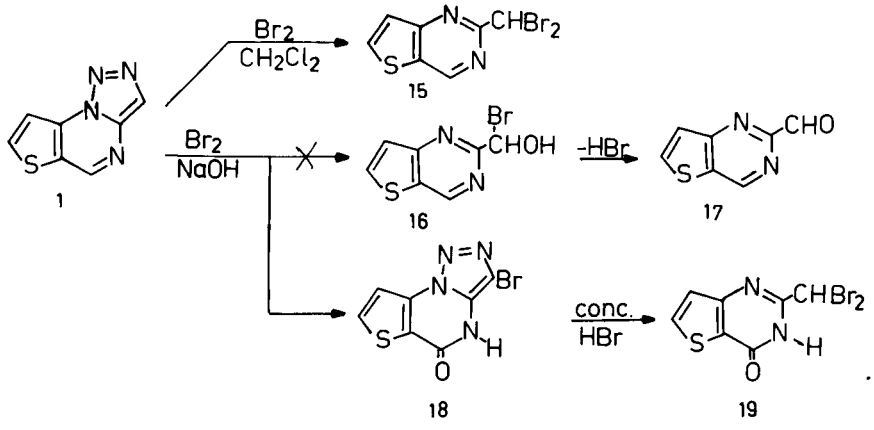
Scission of fused triazoles can also be effected under non-acidic conditions (13). Treatment of **1** at room temperature with one equivalent of bromine in methylene chloride thus resulted in the formation of 2-dibromomethylthieno[3,2-*d*]pyrimidine (**15**) in 81% yield (see Scheme 4). Also in this case the net result of the reaction was an elimination of nitrogen and a 1,1-additon of the cleaving agent. Presumably the mechanism of this reaction is similar to that suggested above for the acid-promoted scission, although an alternative mechanism involving a free diazonium ion, *i.e.* similar to path 1, cannot be excluded here.

In alkaline medium, reaction of **1** with bromine was expected, in the light of the results described above, to give the 1,1-halohydrin **16**, which would then rapidly lose hydrogen bromide, affording the 2-formyl derivative **17** (see Scheme 4). However, when **1** was treated with excess bromine in 2 *N* sodium hydroxide solution, none of the expected products was formed. The initial product was instead a sodium salt, which upon acidification was converted to a crystalline, acidic compound, **18**. This showed in ms a molecular ion peak at m/e 270/272 with an isotopic distribution corresponding to the presence of one bromine atom. The elemental composition was $C_7H_3BrN_4OS$ and the presence of a carbonyl group was indicated by ir. Based on these observations and on the ^1H nmr spectrum, the structure of **18** was assigned as 3-bromo-5-oxo-1,2,3-triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidine (see Scheme 4). This assignment was further supported by the fact that scission of **18** in concentrated hydrobromic acid afforded 2-dibromomethyl-4-oxothieno[3,2-*d*]pyrimidine (**19**).

The reaction path leading to the formation of **18** is not obvious. Possibly it involves an initial reversible addition of water across the C5-N4 double bond, followed by oxidation by hypobromite and subsequent bromination (see Scheme 5). Addition-oxidation sequences of this type have previously been observed in a number of quinazolines (18).



Scheme 5



Scheme 4

In conclusion, the addition of active methylene nitriles to 3-azido-2-substituted thiophenes and subsequent scission of the resulting triazole ring offers an attractive method for the preparation of a large variety of previously unknown 2-substituted 4-amino- and 4-oxothieno[3,2-*d*]-pyrimdines.

EXPERIMENTAL

The ^{1}H nmr spectra were obtained with a JEOL MH 100 high resolution spectrometer. The ir spectra were recorded on a Perkin-Elmer model 257 instrument and mass spectra were obtained with an LKB 9000 mass spectrometer. Elemental analyses were carried out at the Analytical Department of the Chemical Center, Lund, and by Ilse Beetz, Microanalytisches Laboratorium, Kronach, Germany.

2-Hydroxymethylthieno[3,2-*d*]pyrimidine (**6**).

To 40 ml. of stirred 40% sulfuric acid, 0.50 g. (0.0028 mole) of **1** (14) was added in small portions at room temperature. Immediately after each addition, nitrogen gas was evolved. After the addition was complete and the evolution of nitrogen has ceased, the clear solution was poured into 250 ml. of water. After neutralization with sodium hydrogen carbonate, the aqueous phase was extracted 6 times with 50 ml. of methylene chloride. The combined organic phase was then dried over magnesium sulfate. Removal of the solvent by evaporation gave 0.35 g. (75%) of **6** as a white residue. An analytical sample in the form of woolly needles was obtained by recrystallization from ligroin, m.p. 103.0-104.0°; ir (potassium bromide): ~3500 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform): δ 9.24 (d, 1H, H-4), 8.05 (d, 1H, H-6), 7.53 (2d, 1H, H-7), 4.98 (s, 2H, CH_2), 4.25 (s, 1H, OH), $J_{6,7}$ = 5.5 Hz, $J_{4,7}$ = 0.8 Hz; ms: 166 m/e (M$^+$).

Anal. Calcd. for $C_7H_6N_2S$: C, 50.6; H, 3.64; N, 16.9; S, 19.3. Found: C, 50.6; H, 3.67; N, 16.8; S, 19.3.

2-Chloromethylthieno[3,2-*d*]pyrimidine (**7**).

Method A.

To 10 ml. of stirred concentrated hydrochloric acid (36.5-38%), 0.30 g. (0.0017 mole) of **1** (14) was added in small portions at room temperature. Immediately after each addition, nitrogen gas was evolved. After the addition was complete and the evolution of nitrogen had ceased, the resulting solution was poured into 100 ml. of water. After neutralization with sodium hydrogen carbonate, the aqueous phase was extracted 4 times with 30 ml. of ether. The combined organic phase was washed once with 20 ml. of water, dried over magnesium sulfate and evaporated to dryness. This gave 0.31 g. (99%) of **7**. An analytical sample was obtained by recrystallization from ligroin, m.p. 104.5-107.0°; ^{1}H nmr (deuteriochloroform): δ 9.29 (d, 1H, H-4), 8.06 (d, 1H, H-6), 7.56 (2d, 1H, H-7), 4.89 (s, 2H, CH_2), $J_{6,7}$ = 5.6 Hz, $J_{4,7}$ = 0.8 Hz; ms: 184-186 m/e (M$^+$).

Anal. Calcd. for $C_7H_5ClN_2S$: C, 45.5; H, 2.73; S, 17.4; Cl, 19.2. Found: C, 45.6; H, 2.81; S, 17.5; Cl, 19.1.

Method B.

A suspension of 0.45 g. (0.0018 mole) of **5** (14) and 10 ml. of concentrated hydrochloric acid (36.5-38%) was heated with stirring at 40-60° until the evolution of gas had ceased. The brownish solution was then poured into 100 ml. of water. The resulting mixture was neutralized with sodium hydrogen carbonate and then extracted 4 times with 30 ml. of ether. The combined organic phase was washed once with water and dried over magnesium sulfate. Removal of the solvent by evaporation gave 0.25 g. (75%) of **7**, m.p. and spectral data were identical to those described above.

2-Bromomethylthieno[3,2-*d*]pyrimidine (**8**).

This compound was prepared as described above for **7** from 0.50 g. (0.0028 mole) of **1** (14) and 10 ml. of concentrated hydrobromic acid (46-48%). Removal of the solvent by evaporation gave 0.63 g. (98%) of **8**. An analytical sample was obtained by recrystallization from ligroin, m.p. 106.0-108.0°; ^{1}H nmr (deuteriochloroform): δ 9.28 (d, 1H, H-4), 8.06 (d, 1H, H-6), 7.54 (2d, 1H, H-7), 4.76 (s, 2H, CH_2), $J_{6,7}$ = 5.7 Hz, $J_{4,7}$ = 0.7 Hz; ms: 228/230 m/e (M$^+$).

Anal. Calcd. for $C_7H_5BrN_2S$: C, 36.7; H, 2.20; N, 12.2. S, 14.0. Found: C, 36.7; H, 2.28; N, 12.2; S, 14.1.

2-Acetoxymethylthieno[3,2-*d*]pyrimidine (**9**).

A solution of 1.30 g. (0.00738 mole) of **1** (14) in 100 ml. of glacial acetic acid was refluxed for 2 hours. After evaporation of the acetic acid, the residue was diluted with 100 ml. of water. The resulting mixture was extracted 4 times with 30 ml. of chloroform. The combined organic phase was washed repeatedly with sodium hydrogen carbonate solution and then twice with water. After drying over magnesium sulfate and evaporation of the solvent, the residue was boiled repeatedly with light petroleum (40-60°). The combined organic phase was then evaporated, giving 1.29 g. (84%) of **9**. An analytical sample was obtained by recrystallization from light petroleum (40-60°), m.p. 57.0-58.0°; ir (potassium bromide): 1730 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 9.25 (d, 1H, H-4), 8.04 (d, 1H, H-6), 7.53 (2d, 1H, H-7), 5.44 (s, 2H, CH_2), 2.23 (s, 3H, CH_3), $J_{6,7}$ = 5.4 Hz, $J_{4,7}$ = 0.7 Hz; ms: 208 m/e (M$^+$).

Anal. Calcd. for $C_9H_8N_2O_2S$: C, 51.9; H, 3.87; N, 13.5; S, 15.4. Found: C, 51.4; H, 3.89; N, 13.1; S, 15.4.

2-(α-Chlorobenzyl)thieno[3,2-*d*]pyrimidine (**10**).

A suspension of 0.50 g. (0.0020 mole) of **2** (14) in 10 ml. of concentrated hydrochloric acid (36.5-38%) was heated with stirring at 60-70° until the evolution of nitrogen gas had ceased. The dark solution was then poured into 100 ml. of water and the resulting suspension extracted 4 times with 30 ml. of ether. The combined organic phase was washed once with water and dried over magnesium sulfate. Removal of the solvent by evaporation gave 0.45 g. (86%) of **10**. An analytical sample was obtained by recrystallization from ligroin, m.p. 95.0-98.0°; ^{1}H nmr (deuteriochloroform): δ 9.24 (d, 1H, H-4), 7.97 (d, 1H, H-6), 7.53 (2d, 1H, H-7), 6.33 (s, 1H, CH), 7.22-7.77 (m, 5H, Ph), $J_{6,7}$ = 5.4 Hz, $J_{4,7}$ = 0.7 Hz; ms: 260/262 m/e (M$^+$).

Anal. Calcd. for $C_{13}H_9ClN_2S$: C, 59.9; H, 3.48; S, 12.3; Cl, 13.6. Found: C, 60.2; H, 3.55; S, 12.5; Cl, 13.5.

4-Amino-2-chloromethylthieno[3,2-*d*]pyrimidine (**11**).

This compound was prepared as described above for **7** from 0.50 g. (0.0026 mole) of **3** (14) and 10 ml. of concentrated hydrochloric acid (36.5-38%). Removal of the solvent gave 0.32 g. (62%) of **11**, which could be recrystallized from toluene, m.p. 183.0-185.0° (solidifies and does not melt again below ~350°); ir (potassium bromide): 3440, 3300, 3120 cm^{-1} (NH_2); ^{1}H nmr (DMSO-d_6): δ 8.12 (d, 1H, H-6), 7.38 (d, 1H, H-7), 4.64 (s, 2H, CH_2), 7.61 (s, 2H, NH_2), $J_{6,7}$ = 5.4 Hz; ms: 199/201 m/e (M$^+$).

Anal. Calcd. for $C_7H_6ClN_3S$: C, 42.1; H, 3.03; S, 16.1; Cl, 17.8. Found: C, 42.8; H, 3.42; S, 16.0; Cl, 17.3. Probably due to a tendency to intermolecular alkylation, **11** could not, in spite of repeated efforts, be obtained in satisfactory analytical purity.

4-Amino-2-(α-chlorobenzyl)thieno[3,2-*d*]pyrimidine (**12**).

This compound was prepared as described above for **10** from 0.60 g. (0.0020 mole) of **4** (14) and 10 ml. of concentrated hydrochloric acid (36.5-38%). Removal of the solvent gave 0.55 g. (91%) of **12**. An analytical sample was obtained by recrystallization from toluene, m.p. 156.0-157.0°; ir (potassium bromide): 3470, 3310, 3120 cm^{-1} (NH_2); ^{1}H nmr (deuteriochloroform/DMSO-d_6): δ 7.77 (d, 1H, H-6), 7.39 (d, 1H, H-7), 7.18-7.77 (m, 5H, Ph), 6.10 (s, 1H, CH), 6.74 (s, 2H, NH_2), $J_{6,7}$ = 5.5 Hz; ms: 275/277 m/e (M$^+$).

Anal. Calcd. for $C_{13}H_{10}ClN_3S$: C, 56.6; H, 3.66; Cl, 12.9; S, 11.6. Found: C, 57.0; H, 3.64; Cl, 12.8; S, 11.2.

2-(α-Hydroxybenzyl)thieno[3,2-*d*]pyrimidine (**13**).

A suspension of 0.50 g. (0.0020 mole) of **2** (14) in 50 ml. of 50% sulfuric acid was heated with stirring at ~100° until the evolution of nitrogen

gas had ceased. The resulting clear, reddish brown solution was poured into 250 ml. of water. The resulting mixture was neutralized with sodium hydrogen carbonate and then extracted 4 times with 50 ml. of ether. The combined organic phase was washed once with water and then dried over magnesium sulfate. Removal of the solvent gave 0.39 g. (80%) of **13**. An analytical sample was obtained by recrystallization from a small amount of toluene, m.p. 136.0-137.0°; ir (potassium bromide): ~3300 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 9.16 (s, 1H, H-4), 7.98 (d, 1H, H-6), 7.28 (d, 1H, H-7), 7.17-7.64 (m, 5H, Ph), 6.03 (s, 1H, CH), 4.98 (s, 1H, OH), $J_{6,7}$ = 5.5 Hz; ms: 242 m/e (M^+).

Anal. Calcd. for $C_{13}H_{10}N_2OS$: C, 64.6; H, 4.16; N, 11.6; S, 12.2. Found: C, 64.6; H, 4.27; N, 11.4; S, 12.2.

4-Amino-2-hydroxymethylthieno[3,2-*d*]pyrimidine (**14**).

This compound was prepared as described above for **6** from 0.50 g. (0.0026 mole) of **3** (14) and 20 ml. of 50% sulfuric acid. In this case, however, after neutralization, the aqueous phase was evaporated to dryness. The white residue was then continuously extracted (Soxhlet) for 4 days with toluene. After removal of the organic solvent by evaporation, the sticky residue was treated with a 1/1 mixture of light petroleum (40-60°) and ether. After cooling in a refrigerator, the white precipitate was collected by filtration, giving 0.32 g. (68%) of **14**. An analytical sample was obtained by recrystallization from toluene, m.p. 205.0-210.0°; ir (potassium bromide): 3330 cm^{-1} (OH, NH_2); ^1H nmr (DMSO-d_6): δ 8.09 (d, 1H, H-6), 7.38 (d, 1H, H-7), 4.53 (s, 2H, CH_2), 7.48 (s, 2H, NH_2), 4.91 (s, 1H, OH), $J_{6,7}$ = 5.6 Hz; ms: 181 m/e (M^+).

Anal. Calcd. for $C_7H_7N_3OS$: C, 46.4; H, 3.89; N, 23.2; S, 17.7. Found: C, 46.8; H, 4.01; N, 23.1; S, 17.6.

2-Dibromomethylthieno[3,2-*d*]pyrimidine (**15**).

To a cooled (~0°) and stirred solution of 0.50 g. (0.0028 mole) of **1** (14) in 50 ml. of methylene chloride, a solution of 0.45 g. (0.0056 mole) of bromine in 10 ml. of methylene chloride was added dropwise. After the addition was complete (~10 minutes), the solution was stirred for 0.25 hour at 0° and then for 0.5 hour at room temperature. Removal of the solvent by evaporation and recrystallization of the residue from ligroin gave 0.70 g. (81%) of **15**, m.p. 162.0-164.0°; ^1H nmr (deuteriochloroform): δ 9.34 (d, 1H, H-4), 8.13 (d, 1H, H-6), 7.61 (2d, 1H, H-7), 6.85 (s, 1H, CH), $J_{6,7}$ = 5.5 Hz, $J_{4,7}$ = 0.7 Hz; ms: 306/308/310 m/e (M^+).

Anal. Calcd. for $C_7H_4Br_2N_2S$: C, 27.3; H, 1.30; N, 9.10; S, 10.4. Found: C, 27.3; H, 1.30; N, 9.00; S, 10.5.

3-Bromo-5-oxo-1*H*-1,2,3-triazolo[1,5-*a*]thieno[3,2-*d*]pyrimidine (**18**).

To a well stirred suspension of 2.20 g. (0.0125 mole) of **1** (14) in 100 ml. of 2 *N* sodium hydroxide solution, 6.00 g. (0.0751 mole) of bromine was added. The resulting mixture was stirred at room temperature for 4 days. After cooling in a refrigerator, the precipitated white sodium salt (dec. violently when heated to ~250°) was filtered off and dissolved in 250 ml. of water. The resulting yellow solution was filtered and then acidified to *p*H 4-5 using dilute hydrochloric acid. After cooling in a refrigerator, the precipitated white solid was collected by filtration, giving 2.58 g. (76%) of **18**. An analytical sample was obtained by recrystallization from methanol, dec. violently at ~210°; ir (potassium bromide): 1670 cm^{-1} (C=O); ^1H nmr (DMSO-d_6): δ 8.43 (d, 1H, H-6), 7.87 (d, 1H, H-7), $J_{7,8}$ = 5.4 Hz; ms: 270/272 m/e (M^+).

Anal. Calcd. for $C_7H_3BrN_4OS$: C, 31.0; H, 1.12; Br, 29.5; S, 11.8. Found: C, 31.2; H, 1.25; Br, 29.2; S, 11.8.

2-Dibromomethyl-4-oxothieno[3,2-*d*]pyrimidine (**19**).

A suspension of 0.50 g. (0.0018 mole) of **18** in 15 ml. of concentrated hydrobromic acid (46-48%) was heated with stirring at 80-90° until the evolution of nitrogen gas had ceased. The clear yellow solution was poured into 150 ml. of water, and the resulting mixture neutralized with sodium hydrogen carbonate to *p*H 5-6. After extracting 4 times with 30 ml. of ether, the combined organic phase was dried over magnesium sulfate. Removal of the solvent by evaporation gave 0.47 g. (81%) of **19**. An analytical sample was obtained by recrystallization from toluene, m.p. 215.0-220.0°; ir (potassium bromide): 1655 cm^{-1} (C=O); ^1H nmr (DMSO-d_6/deuteriochloroform): δ 8.21 (d, 1H, H-6), 7.46 (d, 1H, H-7), 6.85 (s, 1H, CH), $J_{6,7}$ = 5.4 Hz; ms: 322/324/326 m/e (M^+).

Anal. Calcd. for $C_7H_4Br_2N_2OS$: C, 26.0; H, 1.24; Br, 49.3; S, 9.90. Found: C, 26.5; H, 1.28; Br, 49.1; S, 10.0.

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