1,6-Dihydro-1,2,4-triazines

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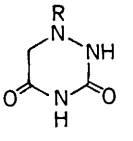
Synthetic pathways to reduced 1,2,4-triazines have been investigated. The most convenient route involved the reaction of ketones with sodium cyanide and thiosemicarbazide, under acidic conditions, to yield cyanothiosemicarbazones. These compounds were either converted into the corresponding carboxy-thiosemicarbazones which, in turn, were cyclized in diphenyl ether, or they were treated with concentrated hydrochloric acid to effect ring closure directly. The alkylation of 3-thioxo-5-oxo- and 3,5-dithioxo-derivatives was examined. Studies of replacement reaction of thioxo- and methylthio-groups in the 3- and 5-positions showed that the 5-position was more active than the 3-. I.r. and n.m.r. spectra were used to assign the preferred tautomeric form of a number of the products.

SEVERAL substituted 4,5-dihydropyrimidines [1] and 1,2-dihydro-1,3,5-triazines [2a-c] exhibit antimalarial activity. In studies dealing with bacteria, these dihydrotriazines have also been shown to be antifolic agents.[2a] The apparent biological importance of substituted 1,2-dihydro-1,3,5-triazines led us to synthesize some 1,6-dihydro-1,2,4-triazines.

Our initial approach involved reduction of 1,2,4-triazines. The hydrogenation of 1,2,4-triazines with platinum as a catalyst has been reported to give a dihydro- or a tetrahydro-derivative, depending on the solvent.[3] In the present study, reduction of 3,5-diamino-6-(3-trifluoromethylphenyl)-1,2,4-triazine under similar conditions was not achieved. When 1,2,4-triazine-3,5(2*H*,4*H*)-dione was hydrogenated over 5% rhodium–carbon, in ethanol, only the 1,6-dihydro-dione (1) was obtained. Alternative routes to dihydrotriazines were therefore investigated.

Previous workers had prepared hexahydro-1,2,4-triazine-3,5-diones such as (2) by cyclization of α-hydrazino-acid derivatives.[4] This approach suggested an analogous but more efficient synthetic path to reduced 1,2,4-triazines as illustrated in Scheme 1.

Treatment of 1-thiosemicarbazidocyclohexanecarbonitrile with concentrated hydrochloric acid yielded the



(1) R=H
(2) R=CH_2CO_2Et

acid (3) which was heated in diphenyl ether to effect ring closure. The resulting thioxotriazaspiroundecanone (4) was converted into the dithione (5) with phosphorus pentasulphide in pyridine. Compound (5) was methylated with sodium ethoxide and methyl iodide to give the corresponding 3,5-bismethylthio-derivative (6), which was not isolated but treated directly with methanolic ammonia. The greater reactivity of the 5-position was shown by the isolation of 5-amino-3-(methylthio)-1,2,4-triazaspiro[5.5]undeca-2,4-diene (7) as the only product. Methylation of (4) with an excess of methyl iodide and sodium ethoxide resulted in attack at both sulphur and

[1] G. H. Hitchings, P. B. Russell, and N. Whittaker, *J. Chem. Soc.*, 1956, 1019.

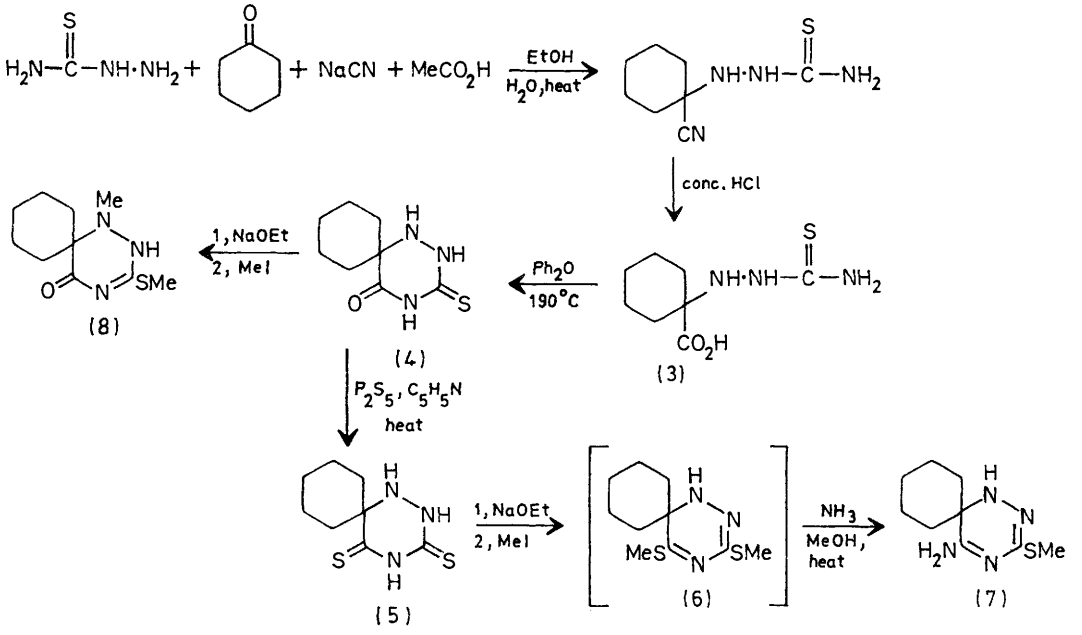
[2] (*a*) E. J. Modest, G. E. Foley, M. M. Pechet, and S. Farber, *J. Amer. Chem. Soc.*, 1952, **74**, 855; (*b*) E. J. Modest, *J. Org. Chem.*, 1956, **21**, 1; (*c*) E. J. Modest and P. Levine, *ibid.*, p. 14.

[3] M. Polonovski, M. Pesson, and P. Rajzman, *Compt. rend.*, 1954, **238**, 1134.

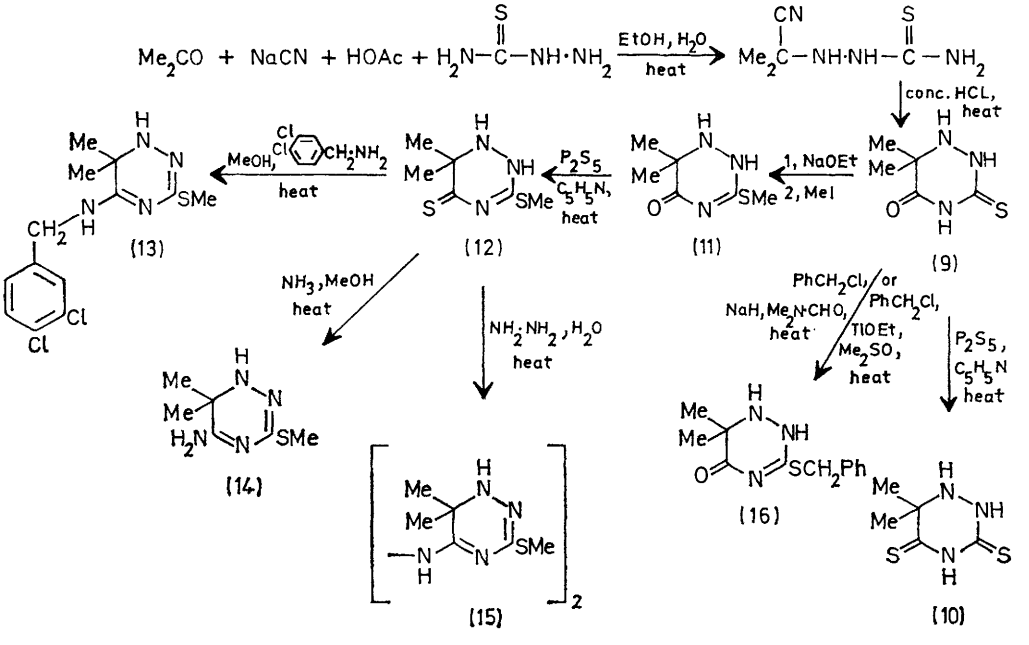
[4] J. R. Bailey and W. T. Read, *J. Amer. Chem. Soc.*, 1914, **36**, 1764.

N-1 to give (8), as observed with related 1,2,4-triazines.[5a,b]

The reaction of acetone with sodium cyanide, acetic acid, and thiosemicarbazide in aqueous ethanol according to the procedure developed by Fusco and Rossi [6] afforded with phosphorus pentasulphide in pyridine to afford the dithione (10), and was methylated with sodium ethoxide and methyl iodide to give the 3-methylthio-5-one (11). When (11) was treated with phosphorus pentasulphide in pyridine, the corresponding 5-thione (12) was obtained.



SCHEME 1



SCHEME 2

α-thiosemicarbazidoisobutyronitrile (Scheme 2). These authors report that treatment of the nitrile with concentrated hydrochloric acid produces the corresponding amide. In our study, ring closure occurred instead to give the desired triazine (9). Compound (9) was treated Treatment of (12) with 3,4-dichlorobenzylamine, ammonia, or hydrazine, resulted in replacement of the

[5] (*a*) J. Gut, M. Prystas, and J. Jonas, *Coll. Czech. Chem. Comm.*, 1961, **26**, 986; (*b*) J. Daunis, R. Jacquier, and P. Viallefont, *Bull. Soc. chim. France*, 1971, 3658.

[6] R. Fusco and S. Rossi, *Gazzetta*, 1954, **84**, 373.

5-thioxo-group to yield compounds (13)—(15), respectively. These reactions again illustrate the lesser reactivity of a 3-methylthio-group.

To further explore the alkylation of (9), benzylation was attempted with benzyl chloride and sodium hydride in dimethylformamide as well as with benzyl chloride and thallium ethoxide in dimethyl sulphoxide. The 3-benzylthio-derivative (16) was obtained in both instances.

Compounds (11), (12), and (16) could in theory exist as 1,2,5,6- or 1,4,5,6-tetrahydro-derivatives, the former tautomer being preferred on the basis of conjugation of the double bond with the carbonyl group. This conclusion was supported by the n.m.r. spectra of the products, which exhibited resonances characteristic of a proton at position 1.

The i.r. spectra of the 1,6-dihydro-1,2,4-triazines prepared showed bands in the 3 150—3 250 cm^{-1} region attributable to NH. The oxo-derivatives showed bands in the 1 690—1 710 cm^{-1} region assignable to amide carbonyl. Bands in the 1 550—1 650 cm^{-1} region were assigned to C:N bonds activated by amino- or methylthio-substituents.

The n.m.r. spectra of these reduced triazines showed three distinct types of NH resonance. The 1-proton was the most shielded (δ 5.72—6.70), followed by that at the 2-position (δ 10.44—11.63), and then the 4-proton (δ 10.96—12.36).

Compounds were tested for blood schizonticidal antimalarial activity in mice and chicks at the Leo Rane Laboratory, University of Miami.[7] Compounds (2), (4), (5), (7)—(13), and (16) were tested for activity in mice infected with *Plasmodium berghei*; compounds (9)—(11) were also tested for activity in chicks infected with *P. gallinaceum*. All the reduced triazines were inactive.

EXPERIMENTAL

M.p.s were determined with a Thomas–Hoover apparatus. Microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, or Galbraith Laboratories, Knoxville, Tennessee. The assigned structures were supported by i.r. spectra recorded on a Perkin-Elmer 137 or 521 spectrophotometer and n.m.r. spectra recorded on a Varian A-60-A or HA-100 spectrometer.

1,6-*Dihydro*-1,2,4-*triazine*-3,5(2H,4H)-*dione* (1).—1,2,4-Triazine-3,5(2*H*,4*H*)-dione (5.02 g, 0.044 mol) in ethanol (100 ml) was hydrogenated over 5% rhodium–carbon (0.75 g) for 17 h at *ca.* 55 lb in^{-2} initial pressure. The insoluble product was dissolved in a large volume of boiling ethanol and the catalyst was filtered off. Concentration of the filtrate afforded the product (3.64 g, 72% yield), m.p. 226—227° (from ethanol) (lit.,[4] 221°) (Found: C, 31.55; H, 4.2; N, 36.5. Calc. for $C_3H_5N_3O_2$: C, 31.3; H, 4.4; N, 36.5%); $\nu_{max.}$ (KBr) 3 225 (NH) and 1 690 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 10.11 (1 H, s, H-4), 8.70 (1 H, s, H-2), 5.41 (1 H, t, H-1), and 3.34 (2 H, d, H-6).

1-*Thiosemicarbazidocyclohexanecarboxylic Acid* (3).—1-Thiosemicarbazidocyclohexanecarbonitrile (20.0 g, 0.101 mol) was added with stirring to concentrated hydrochloric acid (50 ml). The precipitate that formed gradually redissolved; another solid precipitated, however, within a few minutes. After 45 min, water (25 ml) was added to the mixture and the pH was adjusted to *ca.* 7.0 with concentrated ammonium hydroxide. The solution was cooled and the resulting solid was filtered off, recrystallized from water [yield 17.93 g; m.p. 213.5—215° (decomp.)] and then added to ethanolic sodium ethoxide [from sodium (20.6 g, 0.896 g atom) and ethanol (300 ml)]. The mixture was refluxed for 30 min, the ethanol was removed under reduced pressure, and the residue was dissolved in water. Acidification of the cooled solution with concentrated hydrochloric acid afforded a precipitate which was collected and recrystallized from ethanol–water to give the *acid* (3) (12.13 g, 55%), m.p. 219—220° (decomp.) (Found: C, 44.05; H, 7.05; N, 19.25; S, 14.95. $C_8H_{15}N_3O_2S$ requires C, 44.2; H, 6.95; N, 19.35; S, 14.75%); $\nu_{max.}$ (KBr) 3 396, 3 240 (NH), 1 710, 1 698 (C=O), and 1 594 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 7.91, 7.59, and 7.31 [each 1 H, s, N*H*·N*H*·C(:N*H*)·S*H*], 5.36 (1 H, s, SH), and 1.50 (10 H, m, cyclohexyl).

3-*Thioxo*-1,2,4-*triazaspiro*[5.5]*undecan*-5-*one* (4).—Compound (3) (2.33 g, 0.107 mol) in diphenyl ether (20 ml) was heated at 190 °C for *ca.* 1 h (until gas evolution ceased) and then was set aside overnight. The solid was filtered off and recrystallized from ethanol–water to give the product (4) (1.35 g, 63%), m.p. 224—225° (lit.,[6] 224°) (Found: C, 48.45; H, 6.85; N, 21.35; S, 16.1. Calc. for $C_8H_{13}N_3OS$: C, 48.2; H, 6.6; N, 21.1; S, 16.1%); $\nu_{max.}$ (KBr) 3 178 (NH), and 1 695 cm^{-1} (C=O); δ[$(CD_3)_2SO$] 10.96 (1 H, s, H-4), 10.48 (1 H, s, H-2), 5.82 (1 H, s, H-1), and 1.49 (10 H, m, cyclohexyl).

1,2,4-*Triazaspiro*[5.5]*undecane*-3,5-*dithione* (5).—Solutions of compound (4) (5.73 g, 0.027 mol) and phosphorus pentasulphide (3.56 g, 0.016 mol) in boiling anhydrous pyridine (35 and 62 ml, respectively), were combined and the mixture was heated at reflux for 2 h. After cooling overnight, the supernatant pyridine solution was decanted and evaporated to dryness. The residue, a red oil, was dissolved in 20% sodium hydroxide. The solution was treated with activated carbon, washed three times with diethyl ether, and acidified (Congo Red). The precipitate was collected and recrystallized from ethanol–water to give the yellow *product* (5) (1.76 g, 30%), m.p. 246.5—247.5° (decomp.) (Found: C, 44.85; H, 6.2; N, 19.75; S, 29.6. $C_8H_{13}N_3S_2$ requires C, 44.6; H, 6.1; N, 19.5; S, 29.8%); $\nu_{max.}$ (KBr) 3 160 (NH) cm^{-1}; δ[$(CD_3)_2SO$] 12.36 (1 H, s, H-4), 10.88 (1 H, s, H-2), 5.72 (1 H, s, H-1), and 1.50 (10 H, m, cyclohexyl).

5-*Amino*-3-(*methylthio*)-1,2,4-*triazaspiro*[5.5]*undeca*-2,4-*diene* (7).—To a solution of compound (5) (2.87 g, 0.0134 mol) in ethanol (50 ml) was added ethanolic sodium ethoxide [from sodium (0.63 g, 0.0274 g atom) and ethanol (70 ml)]. After 30 min, methyl iodide (7 ml) was added and the mixture was set aside overnight. The ethanol was removed *in vacuo* and the residue was triturated with chloroform. The resulting solid was filtered off and discarded. The filtrate was evaporated to dryness. The residue was dissolved in methanol (100 ml) and ammonia was bubbled through for *ca.* 2 h by use of a flask fitted with a solid CO_2 condenser. The mixture was heated at reflux for 5 min and then was set aside overnight. It was concentrated *in vacuo*, and the resulting solid was collected and recrystallized from ethanol to give the *product* (7) (0.69 g, 24%), m.p. 246.5—247.5° (decomp.) (Found: C, 51.15; H, 7.65; N, 26.15; S, 15.4. $C_9H_{16}N_4S$ requires C, 50.9; H, 7.6; N, 26.4; S, 15.1%);

[7] (*a*) L. Rane and D. S. Rane, Abstracts 9th International Congress, Tropical Medicine, Malaria, 1973, 1: 281; (*b*) T. S. Osdene, P. B. Russell, and L. Rane, *J. Medicin. Chem.*, 1967, **10**, 431.

$\nu_{max.}$ (KBr) 3 307, 3 208 (NH), 1 665, 1 561, and 1 540 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 6.88br (2 H, s, NH_2), 6.61 (1 H, s, H-1), 2.18 (3 H, s, SCH_3), and 1.50 (10 H, m, cyclohexyl).

1-Methyl-3-(methylthio)-1,2,4-triazaspiro[5.5]*undec-3-en-5-one* (8).—3-Thioxo-1,2,4-triazaspiro[5.5]undecan-5-one (38 g, 0.19 mol) was dissolved in ethanolic sodium ethoxide [from sodium (4.82 g, 0.21 g atom) and ethanol (250 ml)] and then was treated with methyl iodide (54 g, 0.38 mol). The mixture was set aside overnight. The ethanol was removed *in vacuo* and the residue was treated with chloroform and water. The chloroform layer was separated, dried (Na_2SO_4), and evaporated. Treatment of the resulting oil with boiling benzene, removal of the insoluble gum by filtration, evaporation of the benzene solution to dryness, and recrystallization of the residue from ethanol–water gave the *product* (8) (8.30 g, 19%), m.p. 111—112° (Found: C, 52.9; H, 7.45; N, 18.4; S, 14.2. $C_{10}H_{17}N_3OS$ requires C, 52.85; H, 7.55; N, 18.5; S,14.1%); $\nu_{max.}$ (KBr) 3 180 (NH), 1 680 (C=O), and 1 610 cm^{-1} (C=N); δ($CDCl_3$) 8.90 (1 H, s, H-2), 2.88 (3 H, s, NCH_3), 2.40 (3 H, s, SCH_3), and 1.70 (10 H, m, cyclohexyl).

1,3,4,6-Tetrahydro-6,6-dimethyl-3-thioxo-1,2,4-triazin-5(2H)-one (9).—Compound (9), m.p. 255.5—256.5°, was prepared according to the procedure developed by Fusco and Rossi [6] (lit.,[6] m.p. 245°) (Found: C, 37.8; H, 5.8; N, 26.45; S, 20.15. Calc. for $C_5H_9N_3OS$: 37.7; H, 5.7; N, 26.4; S, 20.15%); $\nu_{max.}$ (KBr) 3 158 (NH), and 1 697 cm^{-1} (C=O); δ[$(CD_3)_2SO$] 11.02 (1 H, s, H-4), 10.54 (1 H, s, H-2), 6.00 (1 H, s, H-1), and 1.10 (6 H, s, Me_2).

1,6-Dihydro-6,6-dimethyl-1,2,4-triazine-3,5-(2H,4H)-dithione (10).—A mixture of compound (9) (5.73 g, 0.036 mol) and phosphorus pentasulphide (6.67 g, 0.03 mol) in anhydrous pyridine (90 ml; dried over CaH_2) was refluxed for 2.75 h and then set aside overnight. The solution was decanted from the resulting red oil and evaporated to dryness under reduced pressure. The residue was treated with water (65 ml) and dissolved by addition of aqueous 20% sodium hydroxide. The solution was washed four times with diethyl ether and acidified (Congo Red) with concentrated hydrochloric acid. Recrystallization of the precipitate from ethanol–water and ethanol–benzene gave the yellow *product* (10) (1.98 g, 31%), m.p. 245—245.5° (Found: C, 34.4; H, 5.2; N, 24.25; S, 36.4. $C_5H_9N_3S_2$ requires C, 34.25; H, 5.2; N, 23.95; S, 36.6%); $\nu_{max.}$ (KBr) 3 159 cm^{-1} (NH); δ[$(CD_3)_2SO$] 11.63br (2 H, s, H-4 and H-2), 5.92 (1 H, s, H-1), and 1.22 (6 H, s, Me_2).

1,6-Dihydro-6,6-dimethyl-3-(methylthio)-1,2,4-triazin-5(2H)-one (11).—A mixture of compound (9) (5.78 g, 0.0363 mol) and ethanolic sodium ethoxide [from sodium (0.835 g, 0.0363 g atom) and ethanol (125 ml)] was warmed to dissolve the triazine and to it was then added an excess of methyl iodide (5 ml). The mixture was stirred briefly and then was set aside overnight. The solvent was removed *in vacuo* and the semi-solid residue was dissolved in the minimum amount of water. Concentration of the solution under high vacuum gave a solid which was collected and dissolved in chloroform. The aqueous filtrate was extracted three times with chloroform and the combined chloroform solutions were evaporated to dryness under reduced pressure. The residue was treated with hot benzene. The insoluble solid was filtered off and the filtrate was cooled to give the *triazine* (11) (1.72 g, 27%), m.p. 163—165° (from benzene) (Found: C, 41.35; H, 6.15; N, 24.05; S, 18.8. $C_6H_{11}N_3OS$ requires C, 41.6; H, 6.4; N, 24.25; S, 18.5%); $\nu_{max.}$ (KBr) 3 280 (NH), 1 692 (C=O), and 1 613 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 10.44 (1 H, s, H-2), 6.68 (1 H, s, H-1), 2.32 (3 H, s, SCH_3), and 1.08 (6 H, s, Me_2).

1,6-Dihydro-6,6-dimethyl-3-(methylthio)-1,2,4-triazine-5(2H)-thione (12).—A mixture of compound (11) (15.73 g, 0.091 mol) and phosphorus pentasulphide (15.73 g, 0.0709 mol) in anhydrous pyridine (300 ml) was heated at reflux for 5 h and then was set aside overnight. Solvent was removed under reduced pressure. The residue was treated with water (50 ml) and dissolved by addition of aqueous 20% sodium hydroxide. The solution was washed three times with diethyl ether and acidified (Congo Red) with concentrated hydrochloric acid. The precipitate was collected and recrystallized from benzene to give the yellow *product* (12) (11.45 g, 67%), m.p. 155.5—157° (Found: C, 37.95; H, 5.65; N, 22.1; S, 34.0. $C_6H_{11}N_3S_2$ requires C, 38.05; H, 5.85; N, 22.2; S, 33.9%); $\nu_{max.}$ (KBr) 3 275 (NH) and 1 607 cm^{-1} (C=N); δ($CDCl_3$) 9.74br (1 H, s, H-2), 5.28br (1 H, s, H-1), 2.43 (3 H, s, SCH_3), and 1.39 (6 H, s, Me_2).

5-(3,4-Dichlorobenzylamino)-1,6-dihydro-6,6-dimethyl-3-(methylthio)-1,2,4-triazine (13).—A mixture of compound (12) (5.39 g, 0.0285 mol) and 3,4-dichlorobenzylamine (10.56 g, 0.06 mol) in methanol (100 ml) was heated at reflux for 3.5 h. Hydrogen sulphide was evolved. The mixture was concentrated *in vacuo* and water was added to the residue. The *product* (13) crystallized upon cooling and was collected by filtration and recrystallized from methanol–water; yield 2.0 g (22%), m.p. 156.5—157° (Found: C, 47.3; H, 4.85; Cl, 21.3; N, 16.85. $C_{13}H_{16}Cl_2N_4S$ requires C, 47.15; H, 4.85; Cl, 21.4; N, 16.9%); $\nu_{max.}$ (KBr) 3 180 (NH) and 1 550 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 7.70 (1 H, t, CH_2NH), 7.14—7.57 (3 H, m, aromatic), 6.33 (1 H, s, H-1), 4.38 (2 H, d, CH_2), and 2.18 (3 H, s, SCH_3).

5-Amino-1,6-dihydro-6,6-dimethyl-3-(methylthio)-1,2,4-triazine (14).—Ammonia was bubbled through a solution of compound (12) (5.49 g, 0.029 mol) in methanol (100 ml) for 0.5 h by using a flask fitted with a solid CO_2 condenser. The mixture was refluxed for 0.5 h with continued passage of ammonia and then set aside overnight. The solid formed was collected and recrystallized from methanol to give the *product* (14) (3.38 g, 68%), m.p. 175.5—177° (decomp.) (Found: C, 42.0; H, 7.15; N, 32.5; S, 18.9. $C_6H_{12}N_4S$ requires C, 41.85; H, 7.0; N, 32.55; S, 18.6%); $\nu_{max.}$ (KBr) 3 395, 3 293, 3 200, 3 119 (NH), 1 652, and 1 550 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 6.88br (2 H, s, NH_2), 6.17 (1 H, s, H-1), 2.21 (3 H, s, SCH_3), and 1.07 (6 H, s, Me_2).

1,2-Bis-[1,6-dihydro-6,6-dimethyl-3-(methylthio)-1,2,4-triazin-5-yl]hydrazine (15).—A mixture of compound (12) (5.104 g, 0.027 mol) and hydrazine hydrate (30ml) was heated at reflux for 4 h and then set aside overnight. The insoluble solid was filtered off and recrystallized from acetone to give the *product* (15) (1.455 g, 32%) (Found: C, 42.05; H, 6.55; N, 32.5. $C_{12}H_{22}N_8S_2$ requires C, 42.1; H, 6.45; N, 32.7%); $\nu_{max.}$ (KBr) 3 352, 3 332, 3 285, 3 245 (NH), 1 640, 1 629, and 1 610 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 8.68 (1 H, s, hydrazino NH), 6.37 (1 H, s, H-1), 2.32 (3 H, s, SCH_3), and 1.20 (6 H, s, Me_2); *m/e* 342 (M^+).

3-(Benzylthio)-1,6-dihydro-6,6-dimethyl-1,2,4-triazin-(5(2H)-one (16).—*Method A*. To a solution of compound (9) (0.8 g, 0.005 mol) in dry *NN*-dimethylformamide (50 ml) was added a suspension of 57% sodium hydride (0.2 g, 0.005 mol) in the same solvent (5 ml) over 15 min. After hydrogen evolution ceased, the mixture was heated at 60 °C for 20 min and at reflux for 40 min, and benzyl chloride (0.6 ml, 0.0055 mol) was then slowly added. The mixture was heated under reflux for 2 h and then filtered hot to

remove inorganic salts. The filtrate was cooled and treated with water. The white *precipitate* was collected (0.7 g, 57%) and recrystallized twice from benzene; m.p. 140—140.5° (Found: C, 58.0; H, 6.2; N, 16.95; S, 13.0. $C_{12}H_{15}N_3OS$ requires C, 57.8; H, 6.05; N, 16.85; S, 12.85%); $\nu_{max.}$ (KBr) 3 320 (NH), 1 710 (C=O), and 1 600 cm^{-1} (C=N); δ[$(CD_3)_2SO$] 10.68 (1 H, s, H-2), 7.32 (5 H, s, aromatic), 6.70 (1 H, s, H-1), 4.18 (2 H, s, SCH_2), and 1.03 (6 H, s, Me_2).

Method B. A mixture of compound (9) (0.8 g, 0.005 mol) and dimethyl sulphoxide (20 ml) was treated with a solution of thallium ethoxide (0.4 ml, 0.0056 mol) in dimethyl sulphoxide (10 ml). After 10 min a grey solid precipitated. The mixture was stirred for 4 h and to it was then added benzyl chloride (0.63 ml, 0.0055 mol). The mixture was stirred overnight at ambient temperature, then heated at 120—130 °C for 3 h. The precipitate dissolved, and thallium chloride was formed. Filtration, followed by distillation of the filtrate under reduced pressure gave a yellow oil. Crystallization was induced by treating the oil with benzene. The white solid thus obtained was recrystallized from benzene to give the *product* (16) (0.21 g, 20%), m.p. 139—140°, identical (spectral data) with that obtained by method A.

The antimalarial tests were performed at the Leo Rane Laboratory, University of Miami, and the results were supplied to us by the Walter Reed Army Institute of Research. This work was supported by the U.S. Army Medical Research and Development Command. We thank Dr. E. A. Steck for encouragement and Ms. J. Miller and Mr. W. Tsou for assistance with the synthetic work.

[5/1256 *Received*, 26*th June*, 1975]