CHAPTER III

EXPERIMENTAL
The NMR spectra were recorded on 60 MHz Varian HA spectrometer and Perkin Elmer R-32 90 MHz spectrometer, respectively and the IR spectra were recorded on Beckman IR 20 and Unicam SP-1200 spectrophotometers, respectively. The chemical shifts have been given in δ ppm downfield from TMS signal.

The spots on TLC plate were developed by iodine vapour or by spraying sulphuric acid followed by heating. TLC plates were prepared from silica gel.

Petroleum ether refers to fraction boiling between 60-80° except otherwise stated. Silica gel was used for column chromatography except where otherwise stated.

Melting and boiling points are uncorrected.

Thionyl chloride was purified by distillation from quinoline followed by a second distillation from Linseed oil.\(^{191}\)
Quinoline-$N^1$-oxide (XXXIa):

To the well stirred solution of quinoline (12.9 g; 0.1 mole) in excess of glacial acetic acid (80 ml.) at room temperature was added 30% hydrogen peroxide (30 ml.) and the reaction mixture was heated on water bath for 8 hr., cooled and the contents were poured into ice-cold water (100 ml.). The mixture was basified with ammonia solution and the organic material was taken up in chloroform, washed with water and dried (MgSO$_4$). Usual workup and chromatography provided 9.2 g. (63.4%) of the quinoline-$N^1$-oxide, m.p. 60°. Lit. m.p. 62°.

Found: C, 74.3; H, 4.5; N, 9.5;

$C_9H_7NO$ requires C, 74.48; H, 4.82;
N, 9.65%.

IR (KBr) max. 1210 cm$^{-1}$ (N → O).

3-Nitroquinoline-$N^1$-oxide (XXXIb):

Benzoyl chloride (7.0 g; 0.1 mole) in dry dichloromethane (30 ml.) was gradually added to the vigorously stirred solution of silver nitrate (17.1 g; 0.1 mole) in dry dichloromethane (30 ml.). The reaction mixture was
quickly filtered and transferred to a separatory funnel and gradually added to a stirred ice-cold solution of \((XXXIa)\) quinoline-\(N^1\)-oxide (7.2 g; 0.05 mole) in dry dichloromethane at such a rate so as to maintain the temperature below 0° and stirring was continued for 30 min. The reaction mixture was refluxed on a water bath for 2 hr. After being cooled dry ammonia was passed until alkaline and filtered. The solvent was distilled off and residue, thus obtained, was finally passed through a column of silica gel and eluted with benzene : acetone (90:10) mixture. Stripped off the solvent to procure 3.0 g. (33.3%) of yellow coloured solid which melted at 181-183°.

Found: C, 56.5; H, 3.2; N, 14.5;

\(C_9H_5N_2O_3\) requires C, 56.84; H, 3.15; N, 14.73%.

\[\text{IR (KBr)}\] max. 1240 (\(\nu\rightarrow 0\)); 1370, 1510 cm\(^{-1}\) (\(-\text{NO}_2\)).

2-Chloro-3-nitroquinoline (XXXIc):

3-Nitroquinoline-\(N^1\)-oxide (1.9 g; 0.01 mole) was taken up in excess of (10 ml.) phosphorus oxychloride. The reaction mixture was refluxed for 4 hr., cooled and then poured in cold water (50 ml.), basified with ammonia and the organic material was taken up in chloroform and the usual work up and chromatography provided 1.4 g. (70.0%) of the light yellow coloured compound, m.p. 120-21°.
2-Chloro-3-nitroquinoline (1.0 g; 0.005 mole) was refluxed with excess of ammonia solution on a water bath for 8 hr. The cold reaction mixture was extracted with chloroform and the extract was dried (MgSO₄). Stripping off the solvent followed by column chromatography provided 0.71 g. (75.5%) of the yellow coloured nitroamine which melted at 116°C (Decomposed).

Found: C, 56.7; H, 3.3; N, 21.8;
C₉H₇N₃O₂ requires C, 57.14; H, 3.70; N, 22.22%.

IR (KBr) max. 3460, 3180 (NH₂); 1530, 1330 cm⁻¹ (NO₂).

2,3-Diaminoquinoline (XXXIII):

Raney Nickel (0.5 g. out of the total of 2.0 g.) followed by 98% hydrazine hydrate (1.5 ml. out of the total of 6.0 ml.) was added to a warm solution of 2-amino-3-nitroquinoline (0.47 g; 0.0025 mole) in ethanol (50 ml.). When the vigorous reaction subsided another installment of Raney-Nickel (0.5 g.) and hydrazine hydrate (1.5 ml.) was added. This procedure was repeated until the additions were complete. Refluxing was continued until yellow colour of the reaction mixture became disappears. The reaction mixture was filtered
hot and removal of the solvent from the filtrate provided the dark brown coloured residue of the diamine which was used as such for the next step.

1,2,5-Thiadiazolo[3,4-b]quinoline (XXXIV):

The above diamine was taken up in dry benzene (10 ml.), purified thionyl chloride (3 ml.) was added and the reaction mixture was refluxed for 8 hr. The excess of thionyl chloride along with benzene were distilled off, water (50 ml.) was added to the residue and the suspended material along with water was extracted with chloroform. The aqueous layer was washed twice with small portions of chloroform and the combined chloroform extracts were washed with water and dried (Na₂SO₄). The solvent was distilled off and usual chromatography afforded 0.21 g. (23.9%) of white coloured compound, m.p. 144.5°C.

Found: C, 57.6; H, 2.5; N, 22.2; S, 16.8;

C₉H₅N₃S requires C, 57.74; H, 2.67;
N, 22.46; S, 17.11%.

NMR (CDCl₃-TFA) 8.70 (1H, s, H-9); 2.28 (1H, dd, H-5);
8.00 (1H, dd, H-8); 7.656 (2H, q, H-6, H-7); J₅,₆ = 9.0; J₈,₈ = 9.0; J₈,₇ = 8.5 Hz.
3-Nitroquinoline (XXXVa):

Fuming nitric acid (12.6 g; 0.2 mole) was added dropwise to a well stirred and cooled solution of quinoline (12.9 g; 0.1 mole) in acetic anhydride (80 ml.) at such a rate (ca. 0.6 hr.) so as to maintain the temperature between 0-10°. After stirring for another half hr. the reaction mixture was poured into ice-cold water (150 ml.). The mixture was basified with ammonia solution (1:1) and the organic material was taken up in chloroform. Usual work up including chromatography provided 4.5 g. (25.8%) of light yellow coloured compound which melted at 127-28°. Lit. m.p. 129-30° 208.

Found: C, 61.8; H, 3.31; N, 16.2; C9H6N2O2 requires C, 62.06; H, 3.44; N, 16.09%.

IR (KBr) max 1360, 1570 cm⁻¹ (-NO2).

4-Amino-3-nitroquinoline (XXXVb):

3-Nitroquinoline (5.1 g; 0.03 mole) and hydroxylamine hydrochloride (6 g.) were dissolved in hot 96% ethanol (90 ml.) and allowed to cool whilst being shaken so that the sparingly soluble nitroquinoline separated in very small crystals. Then 20% methyl alcoholic potassium
Hydroxide (30 ml.) was added in one portion at room temperature. Potassium chloride separated out after brief shaking and the 3-nitroquinoline dissolved imparting yellow coloration to the solution whilst temperature rose within a few minutes by 20-30°. The aminonitroquinoline soon began to separate into a crystalline mass. Luke-warm water (300 ml.) was added and the bright coloured product was filtered under suction and dried to obtain 4.6 g. (85.1%) of desired nitroamine, m.p. 260-61°. Lit. m.p. 260°

Found: C, 56.8; H, 3.6; N, 22.7;

\[ C_9H_7N_3O_2 \] requires C, 57.14; H, 3.70; N, 22.22%.

\[ \text{IR } \nu \text{ max } \]

\[ 3420, 3340 \text{ cm}^{-1} (NH \text{ strech.}); 1620 \text{ cm}^{-1} (NH \text{ bending}); 1320, 1530 \text{ cm}^{-1} (NO_2). \]

3,4-Diaminoquinoline (XXXVI):

To a boiling hot solution of 4-amino-3-nitroquinoline (9.4 g; 0.05 mole) in (100 ml.) ethanol was added Raney-Nickel (1.0 g.) out of a total of 2.5 g. followed by 98% hydrazine hydrate (3 ml. out of a total of 7.5 ml.), when the vigorous reaction ensued. After the vigour of the reaction subsided another instalment of Raney-Nickel (0.5 g.) and hydrazine hydrate (1.5 ml.) was added.
This procedure was repeated until the additions were complete and the refluxing was continued until the yellow colour disappeared. The reaction mixture was filtered hot and the solvent removed to get a dark brown residue of the diamine (8.0 g.) which was used up as such for the next step.

1,2,5-Thiadiazolo[3,4-c]quinoline (XXXVII):

Purified thionyl chloride (5 ml.) was added to an ice-cold solution of 3,4-diaminoquinoline (3.9 g; 0.025 mole) in dry benzene (30 ml.). The reaction mixture was refluxed on a water bath for 10 hr. Benzene and excess thionyl chloride were removed, water (100 ml.) was added to the residue and the solution, thus obtained, was basified with ammonia solution (1:1) and extracted with (3 x 50 ml., portions) of chloroform and the combined chloroform extracts were washed with water and dried (Na₂SO₄). The solvent was distilled off and the residue, thus obtained, was purified by passing through a column of silica gel and eluted with pet-ether (60-80°) and benzene (50:50). Removal of the solvent gave 1.2 g. (26%) of white coloured compound, m.p. 118-19°.

Found: C, 57.3; H, 2.7; N, 22.3; S, 16.9;
\[ \text{C}_9\text{H}_5\text{N}_3\text{S} \] requires C, 57.57; H, 2.67;
N, 22.46; S, 17.11%.

KBr \( v \) max

\[ 1650 \ (C=\text{N}); \ 1610, \ 1520 \ \text{cm}^{-1} \ (\text{ring breathing}) \]
NMR (CDCl₃): 9.42 (1H, s, H-4); 8.62 (1H, dd, H-9); 8.18 (1H, dd, H-6); 7.72 & 7.80 δ (2H, each H-7 and H-8); Jₓᵧ=7.0; Jᵧz=2.5; Jᵧₓ=7.0; Jₓz=7.0

1,2,5-Thiadiazolo[3,4-c]quinoline-N-oxide (XXXVIII):

1,2,5-Thiadiazolo[3,4-c]quinoline (1.87 g, 0.01 mole) was taken up in dry methylene chloride and cooled to 0-5° and m-chloroperbenzoic acid (3.4 g, 0.02 mole) in dry methylene chloride in (15 ml.) was added dropwise with vigorous stirring keeping the temperature of the reaction mixture below 0° (ca. 1 hr.) After the complete addition the reaction mixture was further stirred for 30 min. and refluxed on a water bath for another 30 min. Dry amm. was saturated with ammonia and filtered. The solvent was stripped off and the usual work up followed by chromatography over column of silica gel afforded 1.2 g. (640%) of TLC pure light yellow coloured crystals, which on further recrystallisation from ethanol, melted at 121-22°.

Found: C, 53.1; H, 2.2; N, 21.2; S, 15.6; C₉H₅N₃SO requires C, 53.20; H, 2.46; N, 20.69; S, 15.76%.

IR (KBr) max

1240 (N O); 1610 (C=N); 1490 cm⁻¹ (ring breathing).

NMR (DMSO-d₆): 9.32 (1H, s, H-4); 8.65 (1H, dd, H-6); 8.05 (1H, dd, H-9); 7.85 & 7.53 δ (1H, each q, H-7 and H-8); Jₓᵧ=7.5; Jᵧz=8.5; Jₓz=2.5.
The 1,2,5-thiadiazolo[3,4-c]quinoline (XXXVII, 0.45 g; 0.0025 mole) was dissolved in minimum quantity of concentrated sulphuric acid (ca. 10 ml.) at 0°. To this well stirred and cooled solution was added fuming nitric acid (4 ml.) in small portions so as to maintain the temperature below 0°. The stirring was continued for another 1 hr. at room temperature and finally the reaction mixture was heated on water bath for another 1 hr. cooled the reaction mixture and the contents were poured into ice-cold water (100 ml.). The reaction mixture was basified with ammonia solution and the organic material was taken up in chloroform and dried over Na₂SO₄. Usual work up including column chromatography provided 0.34 g. (58.6%) of the desired compound, m.p. 155-56°.

Found: C, 46.2; H, 1.4; N, 25.1; S, 13.4; C₉H₄N₄O₂S requires C, 46.55; H, 1.72; N, 24.3; S, 13.79%.

**IR**

\[ KBr \]

\[ \text{max.} \]

1350, 1540 cm\(^{-1}\) (NO\(_2\)); 1620 (C=N), 1490 cm\(^{-1}\) (ring breathing).

**Methiodide of 1,2,5-thiadiazolo[3,4-c]quinoline (XL):**

Excess of distilled methyl iodide (5 ml.) was added to a solution of 1,2,5-thiadiazolo[3,4-c]quinoline
(XXXVII; 0.93 g; 0.005 mole) in dry benzene (25 ml.) and the reaction mixture was refluxed on a water bath for 4 hr. under exclusion of moisture and allowed it to stand as such for 48 hr. The precipitated red colour methiodide was filtered, washed with dry benzene and dried in vacuum to obtain 1.1 g. (84.6%) of the desired product which melted at 226-250°.

Found: C, 45.2; H, 2.8; N, 15.7; S, 12.9;

\[ \text{C}_{10} \text{H}_{8} \text{N}_3 \text{SI} \text{ requires } C, 45.19; S, 12.05; H, 3.01; \text{ N, 15.81%}. \]

IR \[ \frac{\text{KBr}}{\text{max}} \] 1620 cm\(^{-1}\) (C=N).

4-Phenyl-4,5-dihydro-5-methyl-1,2,5-thiadiazolo[3,4-c]-quinoline (XL):

To freshly prepared phenylmagnesium bromide was added methiodide (XL; 0.66 g; 0.0025 mole) and a vigorous reaction ensued. After the vigour of the reaction subsided, the reaction mixture was refluxed on a water-bath for 1 hr. Distilled off the solvent, then the residue was added to water (60 ml.) and the organic material was taken up in chloroform. The aqueous layer was washed with chloroform (2 x 50 ml.) and the combined extracts were washed with water and dried (Na\(_2\)SO\(_4\)). The solvent was
stripped off and usual work up followed by column chromatography afforded 0.4 g. (57.9%) of TLC pure white coloured compound, with characteristic smell, m.p. 56-57°.

Found: C, 68.4; H, 4.2; N, 15.3; S, 11.3;

\[ C_{16}H_{15}N_{3}S \] requires C, 68.81; H, 4.65;
N, 15.05; S, 11.47%.

IR \( \chi_{\text{KBr max.}} \) 1620 cm\(^{-1}\) (C=N).

NMR (CDCl\(_3\)): 7.55 (1H, dd, H-9); 7.48 (1H, dd, H-6);
7.40 to 7.05 (7H, phenyl, m, H-7, H-8 and phenyl protons); 1.30 (3H, s, N-Me); 2.20 (1H, s, H-4).

4-Hydroxy-4,5-dihydro-5-methyl-1,2,5-thiadiazolo[3,4-c]-quinoline (XLII):

Methiodide (XL; 0.66 g; 0.0025 mole) was treated with 10% alcoholic potassium hydroxide (15 ml.) and the contents were refluxed on a water bath for 6 hr. After cooling the reaction mixture was poured in ice-cold water (100 ml.) and the aqueous layer extracted with chloroform, dried (Na\(_2\)SO\(_4\)). Usual work up followed by column chromatography afforded 0.41 g. (44.6%) of TLC pure red coloured compound, m.p. 92-93°.
5-methyl-4-oxo-1,2,5-thiadiazolof 3,4-c quinoline (XLIII):

Potassium ferricyanide (2.5 g.) in water (40 ml.) was added to the above methiodide (XL; 0.7 g; 0.0025 mole) in water (100 ml.) and ether (100 ml.). The mixture was stirred for 1.5 hr. and 10% potassium hydroxide solution was added dropwise until the solution was alkaline. After 15 min. the ether layer was separated and aqueous layer, with its suspended material, was taken up with chloroform. The combined ether and chloroform layers were washed with water and dried (Na₂SO₄) and usual work up and column chromatography provided 0.41 g. (75.5%) of the compound which melted at 177-78°C.

Found: C, 54.1; H, 3.9; N, 19.2; S, 17.2;

C₁₀H₉N₃SO requires C, 54.79; H, 4.11; N, 19.17; S, 16.93%.

IR ν₁nujol max 3200 cm⁻¹ (broad band -OH).

NMR (DMSOD₆):
7.95 (1H, dd, H-9); 7.45 (1H, dd, H-6);
7.10 to 6.50 (2H, m, H-7, H-8); 3.00 (3H, s, N-Me); 3.80 (1H, s, H-4); 4.70 (1H, s, OH);
J₆,₇ = 9.0; J₇,₈ = 3.5; J₆,₇ = 8.5; J₇,₈ = 8.

4,5-dihydro-
5-methyl-4-oxo-1,2,5-thiadiazolo[3,4-c]quinoline (XLIII):

Potassium ferricyanide (2.5 g.) in water (40 ml.) was added to the above methiodide (XL; 0.7 g; 0.0025 mole) in water (100 ml.) and ether (100 ml.). The mixture was stirred for 1.5 hr. and 10% potassium hydroxide solution was added dropwise until the solution was alkaline. After 15 min. the ether layer was separated and aqueous layer, with its suspended material, was taken up with chloroform. The combined ether and chloroform layers were washed with water and dried (Na₂SO₄) and usual work up and column chromatography provided 0.41 g. (75.5%) of the compound which melted at 177-78°C.

Found: C, 54.9; H, 3.4; N, 19.2; S, 14.6;

C₁₀H₇N₃SO requires C, 55.30; H, 3.22; N, 19.35; S, 14.64%.
IR \(\nu\)\text{max} \(1670\,\text{cm}^{-1}\) (C=O); \(1610\,\text{cm}^{-1}\) (C=N).

NMR (CDCl\textsubscript{3}): 8.27 (1H, dd, H-9); 7.70 to 7.20 (3H, m, H-6, H-7, H-8); 3.74 (3H, s, N-Me);
\(J_{8,9} = 8.0\); \(J_{7,9} = 2.0\).

4-Chloro-1,2,5-thiadiazolo[3,4-c]quinoline (XLIV): 4,5-dihydro.

To 5-methyl-4-oxo-1,2,5-thiadiazolo[3,4-c]quinoline (XLIII; 0.43 g; 0.002 mole), p-dichlorobenzene (0.8 g.) and phosphorus pentachloride were added, the reaction mixture was heated in a sealed tube at 230-40\textdegree for 6 hr. The tube was cooled and the solid product was finely ground, triturated with ethereal hydrochloric acid, and filtered the solid hydrochloride. It was suspended in water and the suspension was made alkaline with 5\% sodium hydroxide solution. The aqueous layer was extracted with two portions (100 x 2) of chloroform and the combined organic layers were washed with water and dried (Na\textsubscript{2}SO\textsubscript{4}). Evaporation of the solvent and column chromatography (C\textsubscript{44}H\textsubscript{6}) afforded 0.25 g. (56.8\%) of white coloured compound which melted at 123-24\textdegree.

Found:  
C, 48.6; H, 1.3; N, 18.7; S, 14.4;  
\(C_9H_9NSCl\) requires C, 48.75; H, 1.80; N, 18.96; S, 14.44\%. 
IR ν\textsubscript{max} nujol 820 cm\textsuperscript{-1} (C-Cl).

NMR (CDCl\textsubscript{3}): 8.53 (1H, dd, H-9); 8.20-7.60 (3H, m, H-6, H-7, H-8 protons); J\textsubscript{H-9} = 8.0; J\textsubscript{H-8} = 2.0

6-Nitroquinoline (XLV):

Dry glycerol (184 g.) thoroughly mixed with an intimate mixture of finely powdered p-nitroaniline (69.0 g; 0.5 mole), arsenic pentaoxide (86 g.), boric acid and ferrous sulphate (5 g.) and concentrated sulphuric acid (120 ml.) was added with thorough stirring and the mixture was heated at 180° (oil bath). When a vigorous exothermic reaction ensued the flask was removed from the oil bath and cooled in tap water to moderate the reaction. When the vigorous reaction had subsided, the reaction mixture was maintained at 170° for 8 hr., cooled to room temperature and poured into cold water. The reaction mixture was basified with dilute ammonium hydroxide solution (1:1) and then the organic product was extracted with chloroform (4 x 100 ml.), the combined chloroform extracts were washed with water and dried (Na\textsubscript{2}SO\textsubscript{4}) and the solvent was stripped off. The blackish residue thus obtained, on crystallization from petroleum ether (60-80°) gave 41.0 g. (47.1%) of white flakes which melted at 147-48°. Lit. m.p. 149-50° 210
Found: C, 61.8; H, 3.4; N, 15.7;
C9H6N2O2 requires C, 62.06; H, 3.44;
N, 16.09%.

IR \( \nu_{\text{KBr max}} \) 1540, 1350 cm\(^{-1}\) (NO\(_2\)).

5-Amino-6-nitroquinoline (XLVI):

6-Nitroquinoline (XLV; 5.1 g; 0.003 mole) and hydroxylamine hydrochloride (6 g) dissolved in hot 96% ethanol (90 ml.) and allowed to cool whilst being shaken so that the sparingly soluble nitroquinoline separated in very small crystals. Then 20% methyl alcoholic potassium hydroxide (30 ml.) was added in one portion at room temperature, potassium chloride separated out and after brief shaking the 6-nitroquinoline dissolved imparting yellow coloration to the solution whilst the temperature rose by 20° within a few minutes. The nitroamine soon began to separate to a crystalline mass. Luke-warm water (250 ml.) was added and the solid, thus obtained, was filtered, dried to obtain 5.2 g. (94%) of silky needles which melted at 272°. (Lit. m.p. 272° 211.

Found: C, 57.2; H, 2.9; N, 21.7;
C9H7N3O2 requires C, 57.14; H, 3.70;
N, 22.22%.

IR \( \nu_{\text{KBr max}} \) 3290, 3400 cm\(^{-1}\) (-NH\(_2\)); 1320, 1560 cm\(^{-1}\) (NO\(_2\)).
5,6-Diaminoquinoline

To a boiling hot solution of 6-nitro-5-aminoquinoline (9.4 g; 0.05 mole) in ethanol (100 ml.) was added, Raney-Nickel (1.0 g. out of the total of 2.5 g.) followed by 98% hydrazine hydrate (3.00 ml. out of a total of 7.5 ml.) was added when a vigorous reaction ensued. After the vigour of the reaction subsided, another instalment of Raney-Nickel (0.5 g.) and hydrazine hydrate (1.5 ml.) was added. The procedure was repeated until the additions were complete and refluxing was continued until the yellow colour disappeared. The reaction mixture was filtered hot (the funnel was not allowed to dry so as to avoid catching fire by unreacted Raney-Nickel) and the solvent was removed to give a dark brown coloured residue of the diamine (8.0 g.) which was used as such in the next step.

1,2,5-Thiadiazolo[3,4-f]quinoline (XLVII):

To an ice-cold solution of 5,6-diaminoquinoline (7.9 g; 0.05 mole) in dry distilled benzene (35 ml.) was added purified thionyl chloride (10 ml.) and the reaction mixture was refluxed for 8 hr. Excess thionyl chloride and benzene were stripped off, water (100 ml.) was added to the residue and the organic material, thus obtained, was basified with ammonia hydroxide solution (1:1) and the organic material was extracted three times with chloroform.
(3 x 100 ml.) and the combined chloroform extracts were washed with water and dried ($\text{Na}_2\text{SO}_4$). The solvent was distilled off and the residue dissolved in benzene and adsorbed on a silica-gel column which was eluted with pet-ether (60-80°) and 10% benzene. The eluent was stripped off the solvent giving 2.5 g. (26.8%) of white crystals, m.p. 110-11°. Lit. m.p. 113-14°.

Found: C, 58.1; H, 2.4; N, 22.2; S, 16.8;  
requires C, 57.75; H, 2.67; N, 22.46; S, 17.11%.

IR $\nu_{\text{KBr}}$ max. 1610 cm$^{-1}$ (C=N).

NMR (CDCl$_3$): 8.95 (1H, dd, H-7); 8.85 (1H, dd, H-9); 8.25 and 7.90 (2H, s, H-5 and H-4); 7.52 (1H, q, H-8).

1,2,5-Thiadiazolo[3,4-f]quinoline-N-oxide (XLVIII):

1,2,5-Thiadiazolo[3,4-f]quinoline (XLVII; 1.87 g. 0.01 mole) was taken up in dry methylene chloride and cooled to 0-5° and m-chloroperbenzoic acid (3.4 g; 0.02 mole) in dry methylene chloride (12 ml.) was added drop-wise (ca. 1.5 hr.) with vigorous stirring maintaining the the temperature of the reaction mixture below 0°. After completion of addition the reaction mixture was further stirred for 30 min. and refluxed on water bath for another 30 min. Dry ammonia was passed in the stirred
mixture until the saturation and filtered. The solvent was stripped off and column chromatography afforded 1.4 g. (70%), TLC pure of a light yellow coloured crystals m.p. 225-26°.

Found: C, 53.1; H, 1.9; N, 20.3; S, 15.7;
C₉H₅N₃SO requires C, 53.20; H, 2.46; N, 20.69; S, 15.76%.

IR \( \text{KBr} \) max. 1275 cm⁻¹ (N→O).

NMR (CDCl₃): 8.85 (1H, dd, H-5); 8.65 (1H, broad d, H-7); 8.55 (1H, d, H-9); 8.10 (1H, dd, H-4); 7.56 (1H, q, H-8).

Methosulphate of 1,2,5-Thiadiazolo[3,4-f]quinoline (XLIX):

Distilled and dried dimethyl sulphate (2.5 g; 0.02 mole) was added to a solution of 1,2,5-thiadiazolo-[3,4-f]quinoline (XLVII; 0.93 g; 0.005 mole) in dry benzene (25 ml.) and the reaction mixture was refluxed for 2 hr. under exclusion of moisture. The precipitated methosulphate was filtered, washed with dry benzene and dried in vacuum. It was recrystallised from ethanol to obtain 1.2 g. (80%) of the desired product, which melted at 173-74°.

Found: C, 42.2; H, 2.9; N, 13.1; S, 20.2;
Potassium ferricyanide (2.5 g.) in water (50 ml.) was added to a solution of the above methosulphate (XLIX; 0.78 g; 0.0025 mole) in water (100 ml.) and ether (100 ml.) was added. The reaction mixture was stirred for 1 hr. and 10% potassium hydroxide solution was added dropwise until the solution was alkaline. After 30 min. the ether layer was separated and the aqueous layer with its suspended solid material was taken up with chloroform and the combined ether and chloroform layers were washed with water and dried (Na$_2$SO$_4$). Usual workup and column chromatography provided 0.52 g. (86.2%) of raddish compound which melted at 214°.

Found: C, 55.4; H, 3.1; N, 19.4; S, 18.8;

C$_{10}$H$_7$N$_3$S$_0$ requires C, 55.30; H, 3.22;
N, 19.35; S, 19.74%.

IR (KBr) $\nu_{\text{max.}}$ cm$^{-1}$ (C=O): 1650 (3H, s, N$_6$-Me).

NMR (CDCl$_3$): 3.88 (3H, s, N$_6$-Me); 8.55 (1H, d, H-9); 8.10 (1H, d, H-4); 7.87 (1H, d, H-5); 6.90 (1H, d, H-8).
7-Chloro-1,2,5-thiadiazolo[3,4-f]quinoline (LI):

To (0.4 g; 0.002 mole) of 6-methyl-7-oxo-1,2,5-thiadiazolo[3,4-f]quinoline, p-dichlorobenzene (0.8 g.) and phosphorus pentachloride (0.8 g.) were added, heated in a sealed tube at 230-40°C for 6 hr. The tube was cooled and the solid product was finely ground, triturated with etherial hydrochloric acid and filtered the solid hydrochloride which was suspended in water and the suspension was made alkaline with 5% sodium hydroxide solution. Extracted the aqueous layer twice with (2x100 ml.) of chloroform. The combined organic layer was washed with water and dried (Na₂SO₄). Evaporation of the solvent and column chromatography afforded 0.2 g. (50%) of white coloured compound, m.p. 165°C.

Found: C, 48.4; H, 1.9; N, 18.7; S, 14.1;
C₉H₄N₃SCl requires C, 48.75; H, 1.80;
N, 18.96; S, 14.44%.

NMR (CDCl₃): 8.97 (1H, d, H-9); 8.15 (1H, d, H-5);
8.02 (1H, d, H-4); 7.63 (1H, d, H-8).

5-Nitro-1,2,5-thiadiazolo[3,4-f]quinoline (LII):

1,2,5-Thiadiazolo[3,4-f]quinoline (XLVII; 0.93 g; 0.005 mole) was dissolved in a minimum quantity of concentrated sulphuric acid (ca. 12 ml.) at 0°C. To this well stirred and cooled solution was added fuming nitric acid (5 ml.) in small portions so as to maintain the temperature
around 0°. The stirring was continued for another 2 hr. at room temperature and finally the reaction mixture was heated on a water bath for another hr. Cooled the reaction mixture and the contents were poured into ice-cold water (100 ml.). The mixture was basified with ammonia solution and the organic material was taken up in chloroform and the usual workup including column chromatography provided 0.4 g. (36.3%) of the light yellow coloured compound, m.p. 178-79°.

Found: C, 46.3; H, 1.5; N, 24.3; S, 17.5;

\( \text{C}_9\text{H}_4\text{N}_4\text{O}_2\text{S} \) requires, C, 46.55, H, 1.72; N, 24.13; S, 17.79%.

\( \text{IR} \) \\
\( \text{KBr} \) \\
\( \text{max} \) \\
1540, 1350 cm\(^{-1}\) (\( \text{NO}_2 \)).

\( \text{NMR (CDCl}_3\text{)}: \) \\
8.43 (1H, s, H-4); 9.07 (1H, dd, H-9);
9.17 (1H, dd, H-7); 7.85 (1H, q, H-8).

**Methiodide of 1,2,5-thiadiazolo[3,4-f]quinoline (LI\( \text{III} \)):**

Excess of distilled methyl iodide (6 ml.) was added to a solution of 1,2,5-thiadiazolo[3,4-f]quinoline(XLVII; 1.8 g; 0.1 mole) in dry benzene (30 ml.) and the reaction mixture was refluxed on a water bath for 4 hr. under exclusion of moisture and allowed to stand as such for 48 hr. The precipitated methiodide was filtered, washed with dry benzene and dried in vacuum to obtain 2.0 g.
(62.5%) of the desired product which melted at 235-36°.

Found: C, 36.2; H, 2.6; N, 12.2; S, 9.6;
C\textsubscript{10}\textsubscript{H\textsubscript{8}}\textsubscript{N\textsubscript{3}}\textsubscript{S}I requires C, 36.47; H, 2.43; N, 12.76; S, 9.72%.

9-Cyano-6,9-dihydro-1,2,5-thiadiazolo[3,4-f]quinoline (LIV):

Potassium cyanide (0.65 g; 0.01 mole) in water (10 ml.) was added gradually with stirring to methiodide (LII; 1.6 g; 0.005 mole) in water (10 ml.). The reaction mixture acquires slight green colour and the stirring was continued for 2 hr. When it was thoroughly extracted with chloroform, washed with water and dried (MgSO\textsubscript{4}). Evaporation of the solvent provided 0.8 g (72.5%) of yellow coloured solid which was recrystallised from light pet-ether, m.p. 145-46°.

Found: C, 57.3; H, 2.9; N, 24.7; S, 13.8;
C\textsubscript{11}\textsubscript{H\textsubscript{8}}\textsubscript{N\textsubscript{4}}\textsubscript{S} requires C, 57.89; H, 3.50; N, 24.56; S, 14.03%.

IR \(\nu\)\textsubscript{KBr} max 2210 cm\textsuperscript{-1} (C=\textsubscript{N}).

NMR (CDCl\textsubscript{3}):
7.85 (1H, d, H-4); 7.30 (1H, d, H-5);
6.23 (1H, d, H-7); 5.43 (1H, q, H-8);
4.83 (1H, q, H-9); 3.30 (3H, s, N\textsubscript{6}-Me).
Methiodide of 9-cyano-1,2,5-thiadiazolo[3,4-f]quinoline (LV)

To 9-cyano-6,9-dihydro-6-methyl-1,2,5-thiadiazolo[3,4-f]quinoline (LIV; 0.6 g; 0.006 mole) taken in dry distilled pyridine (10 ml.) was added iodine (0.25 g.) in cold dry ethanol (10 ml.) at 0° during 30 min. and stirred at 0° for 8 hr. and left in a refrigerator as such for 48 hr. Distilled off the ethanol at water bath and the pyridine under reduced pressure and the residue, thus left, was dissolved in hot water and filtered. The filtrate was concentrated to 10 ml. and cooled in ice. The desired product crystallised as reddish coloured solid which melted at 207-208°, yield 0.8 g. (80%).

Found: C, 37.4; H, 1.8; N, 15.5; S, 8.7;
C₁₁H₇N₄SI requires C, 37.28; H, 1.97;
N, 15.81; S, 9.04%.

IR (KBr) max. 2190 cm⁻¹ (C≡N).

Attempted synthesis of 9-cyano-1,2,5-thiadiazolo[3,4-f]-quinoline (LVI) leading to the parent compound:

Above methiodide (LV; 0.7 g; 0.002 mole) was suspended in ethylbenzoate (5 ml.) and refluxed in an oil bath for 3 hr. The cooled mixture was added to ethereal hydrochloric acid and the precipitated solid was filtered and dissolved in water (20 ml.) and
basified with 10% sodium hydroxide solution. The product was thoroughly extracted with chloroform, the chloroform layer was washed with water and dried (MgSO₄). Evaporation of the solvent and crystallisation of the residue from benzene afforded the compound 1,2,5-thiadiazolo[3,4-f]quinoline instead of 9-cyano-1,2,5-thiadiazolo [3,4-f]quinoline, m.p. 112-13°. Its mixed m.p. with the authentic sample remained unpressed (112°). Its IR and NMR spectra were superimposable over that of the authentic sample.

7-Phenyl-6,7-dihydro-6-methyl-1,2,5-thiadiazolo[3,4-f]-quinoline (LVII):

To freshly prepared phenyl magnesium bromide was added methiodide (LIII; 0.65 g; 0.0025 mole) when a vigorous reaction ensued. After the vigour of the reaction subsided the reaction mixture was refluxed on a water bath for 1 hr., distilled off the solvent, then the residue was added into water (100 ml.) and the organic material was taken up in chloroform. The aqueous layer was washed with chloroform (2 x 250 ml.) and the combined chloroform extracts were washed with water and dried (Na₂SO₄). The solvent was stripped off and the residue, thus obtained, was purified by passing through a column of silica gel to obtain 0.3 g. (60%) of TLC pure white coloured compound with characteristic smell, m.p. 70-71°.
Found:

C, 68.6; H, 4.7; N, 14.9; S, 11.3;

C_{16}H_{13}N_{3}S requires C, 68.81; H, 4.66;
N, 15.05; S, 11.47%.

NMR (CDCl$_3$)

1.3 (3H, s, N$^6$-Me); 7.66 (1H, d, H-9);
7.61 (1H, d, H-4); 7.55 (1H, d, H-5);
7.23$\delta$(1H,dd, H-8); 7.50-7.30(6H, m, H-7+CH$_2$).

8-Nitro-1,2,5-thiadiazolo[3,4-f]quinoline-6N-oxide (LVIII):

Benzoyl chloride (0.56 g; 0.004 mole) in dichloromethane (10 ml.) was gradually added to the stirred solution of silver nitrate (1.0 g; 0.006 mole) in dry dichloromethane (10 ml.) and the mixture was vigorously stirred for another 15 min. The solution was quickly filtered and the filtrate was transferred to a separatory funnel and gradually added to an ice cold solution of 1,2,5-thiadiazolo[3,4-f]quinoline-6N-oxide (XLVIII; 0.40 g; 0.002 mole) in dry dichloromethane at such a rate so as to maintain the temperature below 0° and stirring was continued for 30 min. The reaction mixture was further stirred at room temperature for 2 hr. and finally refluxed on a water bath for another 30 min. After being cooled dry ammonia was passed until alkaline and filtered. The solvent was distilled off and residue, a yellow obtained, was finally passed through a column of silica gel, eluted with benzene. The eluent was stripped off
the solvent to procure 0.25 g. (54.3%) of yellow
coloured solid, m.p. 230°.

Found: C, 43.2; H, 1.4; N, 22.1; S, 12.7;

IR (KBr): 1520, 1340 cm⁻¹ (NO₂); 1220 cm⁻¹ (N→O).

NMR (DMSO-d₆): 8.30 (2H, q, H-4 and H-5).

6,7-Dihydro-7-oxo-1,2,5-thiadiazolo[3,4-f]quinoline (LX):

To the solution of N₆-oxide (XLVIII; 0.40 g; 0.002
mole) in dry methylene chloride (10 ml.) was gradually
added, sodium hydroxide (0.22 g; 0.004 mole) in water
(5 ml.) with cooling and stirring (ca. 1.5 hr.). After
completion of addition stirring was continued at room
temperature for further 2 hr. Water (100 ml.) was added
and the methylene chloride layer was separated. The
aqueous layer was extracted with two portions (2 x 50 ml.)
of methylene chloride and the combined methylene chloride
extracts were washed with water and dried (Na₂SO₄).
Evaporation of the solvent followed by chromatography afforded 0.25 g. (62.5%) of the desired compound which
melted at 196-97°.

Found: C, 51.8; H, 2.3; N, 20.7; S, 15.7;
C₉H₅N₃S° requires C, 53.20; H, 2.46; N, 20.69; S, 15.76%.

IR \text{KBr} \quad \nu \text{max.} \quad 1740 \text{ cm}^{-1} (\text{C}=\text{O}); 3200-3400 \text{ cm}^{-1} (\text{broad band OH}).

NMR (CDCl₃): 9.18 (1H, d, H-9); 8.35 (1H, dd, H-8); 8.12 (1H, d, NH); 7.64 (1H, d, H-4); 7.53 (1H, d, H-5).

7-Cyano-1,2,5-thiadiazolo[3,4-f]quinoline (LXII):

Potassium cyanide (0.39 g; 0.006 mole) in water (5 ml.) was added to N⁶-oxide (XLVIII; 0.4 g; 0.002 mole) in methylene chloride (10 ml.). Benzoyl chloride (0.42 g; 0.006 mole) in methylene chloride (10 ml.) was gradually added to the above vigorously stirred reaction mixture, stirring was continued for a period of 6 hr. The organic layer was separated, washed well with water and dried (Na₂SO₄). Evaporation of the solvent and usual chromatography over silica gel using benzene as a eluent afforded 0.25 g. (59.5%) of the white crystalline solid, m.p. 260-61°.

Found: C, 56.4; H, 1.6; N, 26.2; S, 15.2;
C₁₀H₄N₄S requires C, 56.60; H, 1.83; N, 26.41; S, 15.09%.

IR \text{KBr} \quad \nu \text{max.} \quad 2230 \text{ cm}^{-1} (\text{C}=\text{N}).
7-Ethoxycarbonyl-1,2,5-thiadiazolo[3,4-f]quinoline (LXIII):

The cyano compound (LXII; 0.21 g; 0.001 mole) was taken in concentrated sulphuric acid (8 ml.) and absolute alcohol (10 ml.) was added to it and the reaction mixture was refluxed on a water bath for 6 hr. Thereafter it was poured onto crushed ice and the organic material was taken up in chloroform and the aqueous layer was extracted twice (2 x 100 ml.) with chloroform and the combined extract was dried (MgSO\(_4\)). Usual work up provided 0.12 g. (48%) of white coloured crystals, m.p. 209-10\(^\circ\).

Found: 

C, 55.3; H, 3.6; N, 15.8; S, 12.4;

C\(_{12}\)H\(_9\)N\(_3\)S\(_2\) requires C, 55.59; H, 3.47; N, 16.21; S, 12.35%.

IR \(\frac{\text{KBr}}{\text{max.}}\) 1760 cm\(^{-1}\) (C=O).

7-Acetoxy-1,2,5-thiadiazolo[3,4-f]quinoline (LXI):

Acetic anhydride (5 ml.) in dry methylene chloride (5 ml.) was added to the vigorously stirred solution of N\(^6\)-oxide (XLVIII; 0.4 g; 0.002 mole) taken in dry methylene chloride (10 ml.) at room temperature (ca. 30 min.). Thereafter, the reaction mixture was refluxed on a water bath for another 8 hr. The reaction mixture was cooled and poured in ice-cold water, basified with liquor ammonia, separated the methylene
chloride layer, and extracted the aqueous layer twice with methylene chloride (2 x 100 ml.). The combined extract was washed with water and dried (Na₂SO₄). Evaporation of the solvent followed by column chromatography and sublimation in vacuum afforded 0.2 g. (40.8%) of the desired product which did not melt up to 300°.

Found: C, 53.6; H, 2.7; N, 17.3; S, 12.9;

\[ \text{C}_{11}H_{7}N_{3}SO_{2} \text{ requires C, 53.87; H, 2.85; N, 17.14; S, 13.06}. \]

IR (nujol) max. 1660 cm⁻¹ (C=O)

NMR (TFA): 9.85 (1H, d, H-9); 8.62 (1H, d, H-6);
8.50 (1H, d, H-4); 8.43 (1H, d, H-8);
1.35 (3H, s, C-Me).

9-Nitro-1,2,5-Thiadiazolo[3,4-f]quinoline-6N-oxide (LIX):

The N⁶-oxide (XLVIII; 0.4 g; 0.002 mole) was dissolved in minimum quantity of concentrated sulphuric acid (ca. 10 ml.) at 0° and to this well stirred and cooled solution was added fuming nitric acid (ca. 3 ml.) in small portions so as to maintain temperature at 0°. The stirring was continued for another 2 hr. at room temperature and finally the reaction mixture was refluxed on a water bath for 1 hr. Cooled the reaction mixture and
the contents were poured into iced-water (100 ml.).
The reaction mixture was basified with ammonia
solution and the organic material was taken up in
chloroform, usual workup including column chromato-
graphy provided 0.22 g. (44.8%) of light yellow coloured
compound which melted at 226-27°.

\[
\text{Found: } \begin{array}{cccc}
\text{C, } & 43.3; & \text{H, } & 1.5; \\
\text{N, } & 21.8; & \text{S, } & 12.5; \\
\end{array}
\]
\[
\text{\text{C}_9\text{H}_4\text{N}_4\text{S}_0_3 \text{ requires C, } 43.54; \text{H, } 1.61; \\
\text{N, } 22.58; \text{S, } 12.90%.}
\]

IR (KBr) \[
\text{max. } \begin{array}{c}
1560, 1350 \text{ cm}^{-1} (\text{NO}_2); \\
1220 \text{ cm}^{-1} (\text{N} \rightarrow \text{O}).
\end{array}
\]

NMR (CDCl\textsubscript{3}): 8.92 (1H, d, H-8); 8.72 (1H, d, H-5); 8.33 (1H, d, H-4); 8.30 (1H, d, H-7).

**5,7-Dichloro-1,2,5-thiadiazolo[3,4-f]quinoline (LXIV):**

The N\textsuperscript{6}-oxide (XLVIII; 0.40 g; 0.002 mole) was
refluxed with excess of phosphorus oxychloride (8 ml.)
for 3 hr. After cooling the reaction mixture was poured
into cold water and basified with ammonia (1:1). The
organic material was taken up in chloroform and the
aqueous layer was extracted twice with chloroform
(2 x 100 ml.). The combined chloroform extracts were
washed with water and dried (Na\textsubscript{2}SO\textsubscript{4}) and the solvent
was stripped off. The residue, thus obtained, was:
purified by passing it through a column of silica gel, elution with pet-ether (60-80°) + benzene (50:50), removal of the solvent gave 0.19 g. (37.2%) of the white coloured dichloro compound, m.p. 196-97°.

Found: C, 41.8; H, 1.2; N, 16.1; S, 12.3;

$C_9H_3N_3SCl_2$ requires C, 42.19; H, 1.17; N, 16.40; S, 12.50%.

NMR (CDCl₃): 9.05 (1H, s, H-4); 8.95 (1H, d, H-9);
7.72 (1H, d, H-8).

7-Nitroquinoline (LXIVa):

Glycerol (184 g.) was thoroughly mixed with an intimate mixture of finely powdered m-nitroaniline (69 g; 0.5 mole), arsenic pentaoxide (86 g.) and 80% sulphuric acid (120 ml.) was added with thorough stirring. The reaction mixture was heated at 195° (oil bath). When a vigorous exothermic reaction ensued the flask was removed from the oil bath and cooled with water to moderate the vigorous reaction. When the vigour of the reaction subsided the reaction mixture was maintained at 170° for 8 hr., cooled to room temperature and poured into iced-water. The reaction mixture was basified with ammonium hydroxide (1:1) and then the organic material was extracted with chloroform (4 x 100 ml.). The combined chloroform extracts were washed with water and dried (MgSO₄).
The solvent was stripped off and the blackish residue, thus obtained, showed two spots on TLC plate. After usual work up and column chromatography (silica gel; pet-ether) provided the desired compound, 30.0 g. (34.3%), which melted at 130°C. Lit. m.p. 132-33°C.213.

Found: C, 61.8; H, 3.3; N, 15.6;
C₇H₆N₂O₂ requires C, 62.06; H, 3.44; N, 16.09%.

**IR** KBr
\[ \text{max.} \ 1360, 1540 \text{ cm}^{-1} (\text{NO}_2). \]

Later on 5-nitroquinoline was also obtained from the column.

**8-Amino-7-nitroquinoline (LXIVb):**

To 7-nitroquinoline (5.2 g; 0.003 mole) in ethanol (75 ml.) was added hydroxylamine hydrochloride (6 g.) dissolved in hot 96% ethanol (25 ml.) and allowed to cool whilst being shaken so that the sparingly soluble nitroquinoline separated in very small crystals. Then 20% alcoholic potassium hydroxide (40 ml.) was added in one portion at room temperature. Potassium chloride separated out immediately and after brief shaking the 7-nitroquinoline dissolved imparting yellow coloration to the solution. The amino-nitroquinoline started precipitating out of solution,
forming a crystalline mass. Luke-warm water (200 ml.) was added and the yellow crystalline mass was filtered and drained well. The mother liquor was concentrated to give another crop of the product, the combined solid was recrystallised from ethanol to obtain 4.2 g. (75.0%) of silky needles, m.p. 184°. Lit. m.p. 185-86° 209.

Found: C, 57.1; H, 2.8; N, 22.1;

requires C, 57.14; H, 3.70;
N, 22.22%.

IR \( \sqrt{\text{KBr}} \)
max. 3480, 3360 cm\(^{-1}\) (\( \text{NH}_2 \)); 1330, 1560 cm\(^{-1}\) (\( \text{NO}_2 \)).

7,8-Diaminoquinoline (LXIVc):

To a boiling solution of 7-nitro-8-aminoquinoline (3.1 g; 0.0016 mole) in ethanol (50 ml.) was added Raney-Nickel (1.0 g, out of a total of 2.5 g.) by 100% hydrazine hydrate (3.0 ml. out of a total of 7.5 ml.) when a vigorous reaction ensued. After the vigour of the reaction subsided another instalment of Raney-Nickel (0.5 g.) and hydrazine hydrate (1.5 ml.) was added. The procedure was repeated until the additions were complete and refluxing was continued until the yellow colour disappeared. The reaction mixture was filtered hot and the solvent removed to give a dark residue of the
diamine (2.0 g.) which due to its oxidation property was used as such for the next step.

1,2,5-Thiadiazolo[3,4-b]quinoline (LXIVd):

7,8-Diaminoquinoline (1.6 g; 0.01 mole) was taken in dry benzene (30 ml.) and purified thionyl chloride (5 ml.) was added and the reaction mixture refluxed for 10 hr. Excess thionyl chloride and benzene were distilled off, water (100 ml.) was added to the residue and the organic material, thus obtained, was basified with liquor ammonia and then extracted thrice with chloroform (3 x 100 ml.). The combined chloroform extracts were washed with water, dried (MgSO₄). The solvent was distilled off and column chromatography over silica gel provided 0.5 g. (26.3%) of white coloured compound which melted at 139-40°. Lit. m.p. 141-42°.

Found: C, 58.2; H, 2.5; N, 22.5; S, 16.9;
C₉H₅N₃S requires C, 57.75; H, 2.67; N, 22.46; S, 17.11%.

NMR (CDCl₃): 9.00 (1H, dd, H-8); 8.87 (1H, dd, H-6);
8.02 (1H, d, H-5); 7.97 (1H, d, H-4);
7.47 (1H, q, H-7); J₇,8 = 4.0; J₆,8 = 2.0; J₆,7 = 8.5

4-Ethoxy-2-nitroacetanilide (LXV):

Fuming nitric acid (12.6 g; 0.2 mole) was added
dropwise to a well stirred and cooled solution of phenacetin (17.9 g; 0.1 mole) in acetic anhydride (80 ml.) at such a rate (ca. 30 min.) so as to maintain the temperature below 10-12°. Stirring was continued for another 30 min. and thereafter the reaction mixture was poured onto crushed ice (60 g.), the solid thus obtained, was filtered and the residue was washed with water, sodium bicarbonate solution and drained well. It was recrystallised from ethanol to obtain 12.2 g. (54.4%) of light yellow coloured crystals which melted at 104-05°. Lit. m.p. 104° 215°.

Found: C, 53.4; H, 5.1; N, 12.6;
C16H12O4N2 requires C, 53.57; H, 5.36;
N, 12.50%.

IR νmax. (Nujol) 1520, 1320 (NO2); 1710 (c=o); 3380 cm⁻¹(NH).

4-Ethoxy-2-nitroaniline (LXVI):

4-Ethoxy-2-nitroacetanilide (11.2 g; 0.05 mole) was taken up in 10% alcoholic potassium hydroxide (80 ml.) the reaction mixture was refluxed for 1 hr. It was poured into ice cold water (200 ml.), the bright red coloured precipitate of nitroamine was filtered, washed until free from acidic impurities, drained well and further purified by steam distillation to obtain 7.2 g. (79.1%) of bright red coloured needies of the desired product which melted at 112-13°. Lit. m.p. 113° 215°.
Found: C, 52.3; H, 5.2; N, 15.6;

C₈H₁₀N₂O₃ requires C, 52.74; H, 5.49; N, 15.38%.

IR ν<sub>max</sub> (nujol): 3340, 3460 (NH₂); 1350, 1510 cm⁻¹ (NO₂).

NMR (CDCl₃): 7.85 (1H, d, H-3); 7.17 (1H, dd, H-5);
6.90 (1H, d, H-6); 5.05 (2H, broad s, NH₂); J₅,₆ = 9.0.

2,2'-Diamino-5,5'-diethoxydihydroazabenzene (LXXI):

4-Ethoxy-2-nitroaniline (2.5 g; 0.013 mole) was taken up in 50 ml. of super dry methanol and magnesium turnings (1.0 g; out of the total of 3.8 g.) were added to warm solution, a vigorous reaction ensued. When the vigour of the reaction subsided, another instalment of magnesium turnings (0.5 g.) was added, the procedure was repeated until the additions were complete and the refluxing was continued until the red colour of the reaction mixture disappeared. The reaction mixture was cooled and the upper layer decanted, poured the supernatant liquid to a separatory funnel containing of 20% ammonium chloride (50 ml.) and it was shaken vigorously for 5 min. The mixture was extracted with chloroform and the chloroform extract was washed with water and dried (MgSO₄). Stripping off the solvent provided dark brown coloured residue of the hydroazobenzene derivative which was used as such for the next step.
2,2', 3,3'-Tetramino-6,6'-diethoxydiphenyl (LXXII):

The dark brown coloured residue obtained above was dissolved in ether contained in a separatory funnel with continuous stirring and to this was added a mixture of 50 ml. of concentrated hydrochloric acid, 10 ml. of water and crushed ice (20 g.). The solid benzidine hydrochloride did not separate out. The reaction mixture was basified with liquor ammonia extracted thrice with chloroform (3 x 100 ml.), dried (MgSO₄) and the solvent was distilled off. The dark residue of the tetramine (1.3 g), thus obtained, was used as such for the next step.

5,5'-Die thoxy-bis -benzo-2,1,3-thiadiazole (LXXIII):

To the ice cold solution of the tetramine (1.0 g.; 0.003 mole) in dry benzene (80 ml.), purified thionyl chloride (4 ml.) was added and the reaction mixture was refluxed on a water bath for 10 hr. with the exclusion of moisture. Benzene and excess of thionyl chloride were distilled off, water (50 ml.) was added to the residue and the organic material, thus obtained, was taken up in chloroform. The aqueous layer was washed thrice with 50 ml. portion of chloroform and the combined chloroform extracts were washed free from acidic impurities and dried (MgSO₄). The solvent was distilled off and the residue was dissolved in benzene and put on a column of silica gel which was eluted with a mixture of pet-ether
and benzene (70:30). After stripping off the solvent 0.3 g. (33.3%) of light yellow coloured crystals, melting point 144-150°, was obtained.

Found: 

\[ \text{C}_16\text{H}_{14}O_2\text{N}_4\text{S}_2 \] requires C, 53.63; H, 3.91; N, 15.64; S, 17.87%.

IR \[ \text{KBr} \] max. 

3020 (C-H, Str. in Het.); 1600, 1510 cm\(^{-1}\) (ring breathing).

NMR (CDCl\(_3\)):

7.87 & 7.47 (1H, d, H-7, H-7'); 7.43 (2H, d, H-6, H-6'); 4.34 (4H, q, CH\(_2\)); 1.55 (6H, t, C-Me); \[ \delta \]

2-Amino-4-ethoxyaniline (LXVII):

Raney-Nickel (1.0 g. out of the total of 2.5 g.) followed by 98% hydrazine hydrate (3 ml. out of a total of 7.5 mol) was added to a warm solution of 4-ethoxy-2-nitroaniline (LXVI; 9.1 g; 0.05 mole) in ethanol (150 ml.) when a vigorous reaction ensued. When the vigour of the reaction subsided another instalment of Raney-Nickel (0.5 g.) and hydrazine hydrate (1.5 ml.) was added and this procedure was repeated until the additions were complete and refluxing was continued until red colour disappeared. The reaction mixture was filtered hot and the solvent was distilled off, the dark brown coloured residue of the diamine (5.2 g.; 68.4%) was used as such for the next step.
5-Ethoxybenzo-2,1,3-thiadiazole (LXVIII):

Purified thionyl chloride (5 ml.) was gradually added to the ice cold solution of the diamine (4.5 g.; 0.03 mole) in dry benzene (70 ml.) and the reaction mixture was refluxed for 8 hr. Benzene and excess of thionyl chloride were distilled off, water (60 ml.) was added to the residue and the organic material, thus obtained, was taken up in chloroform. The aqueous layer was washed twice with two 50 ml. portions of chloroform and the combined chloroform extracts were washed free from acidic impurities and dried (MgSO₄). The solvent was distilled off and the residue dissolved in benzene and put on a column of silica gel which was eluted with pet-ether. The per-ether eluent was stripped off the solvent and the residue was crystallised from carbon tetrachloride to obtain 0.2 g. (37.0%) of the white coloured crystals, m.p. 33-34°.

Found: C, 53.1; H, 4.3; N, 15.5; S, 17.4;

C₁₁H₁₀ON₂S requires C, 53.33; H, 4.44;
N, 15.55; S, 17.77%.

IR νmax (nujol): 3080 (C-H, str. in het.); 1600, 1520 cm⁻¹ (ring breathing).

NMR (CDCl₃): 1.61 (3H, t, CH₃); 4.42 (2H, q, CH₂);
8.30 (1H, d, H-7); 7.36 (1H, d, H-4); 7.30 (1H, d, H-6)/J₆,₇ = 3.5 Hz; J₄,₅ = 3.5 Hz.
5-Ethoxy-4-nitrobenzo-2,1,3-thiadiazole (LXIX):

5-Ethoxybenzo-2,1,3-thiadiazole (LXVIII; 1.8 g; 0.01 mole) was dissolved in minimum quantity of concentrated sulphuric acid (ca. 10 ml.) at 0°. To this well stirred and cooled solution was added potassium nitrate (1.0 g; 0.01 mole) in small portions maintaining the temperature at 0° (ca. 0.5 hr.). The stirring was continued for another 2 hr. The contents were then poured into iced-water (50 ml.) and the thus obtained precipitates were filtered, washed free from acidic impurities and crystallised from pet-ether to procure 2.0 g (99.9%) of slight yellow coloured crystals m.p. 127-28°.

Found: C, 42.3; H, 3.1; N, 18.4; S, 14.2;

C₈H₇O₂N₃S requires C, 42.66; H, 3.11; N, 18.66; S, 14.22%.

IR

\[
\text{nujol max.} \quad 1620 \, (\text{C}=\text{N}); \quad 1530, \quad 1370 \, \text{cm}^{-1} \, (\text{NO}_2). 
\]

NMR (CDCl₃): 8.67+7.63 (1H, d, H-7; H-6); 4.5 (2H, q, -CH₂);

1.60 (3H, t, J₆,₇=10.0).

2-Methyl-1,2,5-thiadiazolo[5,4-e]benzoxazole (LXX):

5-Ethoxy-4-nitrobenzo-2,1,3-thiadiazole (LXIX, 1.1 g; 0.005 mole) was taken up in freshly prepared 48% hydrogen bromide (100 ml.). The reaction mixture was
refluxed for 5 hr., cooled and poured in iced-water (50 ml.). The organic layer was taken up in chloroform and the aqueous layer extracted with two 50 ml. portions of chloroform and the combined chloroform extracts were washed with water and dried (Na₂SO₄). The solvent was distilled off and the residue, thus obtained, was purified by column chromatography by using benzene as eluent. Removal of the solvent provided 0.3 g. (33.3%) of light yellow coloured solid which melted at 190-91°C.

Found: C, 50.3; H, 2.4; N, 22.1; S, 16.6; C₈H₅NO₃S requires C, 50.26; H, 2.61; N, 21.98; S, 16.75%.

IR (KBr) max. 1620 (C=N); 1580; 1500 cm⁻¹ (skeletal vib.).

NMR (CDCl₃) 8.15 (2H, q, H-7, H-8); 1.75 (3H, s, C₂-Me).

4-Ethylacetanilide (LXXIV):

p-Ethylaniline (24.2 g; 0.2 mole) was taken up in glacial acetic acid (50 ml.) and acetic anhydride (50 ml.) was added and the reaction mixture was refluxed (ca. 1 hr.). After being cooled the reaction mixture was poured into ice-cold water (300 ml.). Acetyl derivative, thus precipitated, was filtered, washed free from acidic impurities drained well and dried, to obtain 30.0 g. (92.0%) of white
coloured compound which melted at 92°. Lit. m.p. 94-95°

Found: C, 73.4; H, 7.8; N, 8.4;

\( \text{C}_{10}\text{H}_{13}\text{N}0 \) requires C, 73.62; H, 7.97;
N, 8.58%.

\[ \text{IR } \frac{\nu}{\text{KBr}} \text{ max. } 3300 \text{ cm}^{-1} (\text{NH}), 1620 \text{ cm}^{-1} (\text{C}=0). \]

4-Ethyl-2-nitroacetanilide (LXXV):

Fuming nitric acid (3.15 g; 0.025 mole) was added dropwise to a well stirred and cooled solution of p-ethyl-acetanilide (4.07 g; 0.025 mole) in acetic anhydride (80 ml.) at such a rate (ca. \( \frac{1}{2} \text{ hr.} \)) so as to maintain the temperature below 10-12°. Stirring was continued for another 30 min. and thereafter the reaction mixture was poured into iced-water (100 ml.), the precipitate thus obtained, was filtered, washed with water, 5% sodium bicarbonate solution and drained well. It was recrystallised from 50:50 aqueous ethanol to obtain 4.8 g. (92.3%) of light yellow coloured compound, m.p. 32°.

Found: C, 57.8; H, 5.6; N, 13.3;

\( \text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3 \) requires C, 57.69; H, 5.77;
N, 13.46%.

\[ \text{IR } \frac{\nu}{\text{KBr}} \text{ max. } 3400 \text{ (NH)}, 1645 \text{ (C}=0), 1360, 2530 \text{ cm}^{-1} (\text{NO}_3). \]
4-Ethyl-2-nitroaniline (LXXVI):

4-Ethyl-2-nitroacetanilide (10.4 g; 0.05 mole) was taken up in 10% alcoholic potassium hydroxide (100 ml.) the reaction mixture was refluxed for 1 hr. cooled and then poured onto crushed iced (120 g.). The thus obtained nitroamine was filtered, washed with water and drained well and recrystallised from dilute ethanol to procure 4.7 g. (56.6%) of the product which melted at 39-40°.

Found: C, 57.7; H, 6.2; N, 16.7;

\[ C_8H_{10}N_2O_2 \] requires C, 57.83; H, 6.02; N, 16.86%.

IR \( \nu_{\text{KBr}} \) max. 3400, 3510 (NH\(_2\)); 1350, 1530 cm\(^{-1}\) (NO\(_2\)).

NMR (CDCl\(_3\)) 1.24 (3H, t, Me); 2.71 (2H, q, CH\(_2\)); 8.43 (1H, d, H-3); 7.82 (1H, dd, H-5); 7.37 (1H, d, H-6); 6.59 (2H, s, NH\(_2\)); \( \delta = 10.0 ; J_{3,5} = 2.0 \)

2-Amino-4-ethylaniline (LXXVII):

Raney Nickel (1.0 g; out of the total of 2.5 g.) followed by 98% hydrazine hydrate (3 ml. out of the total of 7.5 ml.) was added to a warm solution of 4-ethyl-2-nitroaniline (8.3 g; 0.05 mole) in ethanol (150 ml.).
When the vigorous reaction subsided another instalment of Raney-Nickel (0.5 g.) and hydrazine hydrate (3 ml.) were added. This procedure was repeated until the additions were complete, and refluxing was continued until the reaction mixture became colourless. The reaction mixture was filtered hot and the solvent was distilled off from the filtrate and the thus obtained dark brown coloured residue of the diamine (5.1 g.) was used as such for the next step.

5-Ethyl-2,1,3-benzothiadiazole (LXXVIII):

The diamine (3.5 g; 0.0025 mole) was taken up in dry benzene (30 ml.), purified thionyl chloride (ca. 9 ml.) was added and the reaction mixture was refluxed (ca. 10 hr.). The excess of thionyl chloride along with benzene were distilled off, water (80 ml.) was added to the residue and the organic material was extracted with chloroform. The aqueous layer was washed twice with chloroform (2 x 50 ml.) and the combined chloroform extracts were successively washed with water, 5% sodium bicarbonate solution, water, and dried (MgSO₄). The solvent was distilled off and its column chromatography afforded 2.3 g. (56.0%) of liquid compound, b.p. 120-22°/10mm.

Found: C, 58.4; H, 4.7; N, 16.8; S, 19.7;
C₁₈H₁₄N₂S requires C, 58.53; H, 4.87;
N, 17.07; S, 19.51%.
NMR (CDCl$_3$) 1.77 (3H, t, Me); 3.35 (2H, q, CH$_2$); 8.83 (1H, d, H-7); 8.06 (1H, d, H-4); 8.02 (1H, dd, H-6); J$_{6,7}$ = 10.0; J$_{4,6}$ = 2.5.

4-Bromo-5-ethyl-2,1,3-benzothiadiazole (LXXIX):

The ethyl compound (LXXVIII; 1.64 g; 0.01 mole) in dry carbon tetrachloride (40 ml.) was taken in three-necked flask fitted with stirrer, condenser and a dropping funnel and placed on a boiling water bath. Benzoyl peroxide (0.25 g.) was added followed by gradual addition of N-bromosuccinimide (1.78 g; 0.01 mole) with stirring under irradiation, in such a way that the liberated bromine went on reacting and too large excess was not available. The contents were refluxed for further (ca. 1.5 hr.) and the hot contents were filtered to remove the succinimide formed. The filtrate was stripped off the solvent and usual chromatography provided a viscous TLC pure liquid, which could not be distilled due to extreme decomposition.

Found: C, 39.1; H, 2.7; N, 11.3; S, 13.4;
C$_8$H$_7$N$_2$SBr requires C, 39.50; H, 2.88; N, 11.52; S, 13.16%.

NMR (CDCl$_3$) 2.1 (3H, d, Me); 5.44 (1H, q, CH); 7.2 (1H, d, H-7); 7.90 (1H, d, H-4); 8.22 (1H, dd, H-6); J$_{6,7}$ = 10.0; J$_{4,6}$ = 2.0.
Attempted synthesis of 5-vinyl-2,1,3-benzothiadiazole leading to 5-polyvinyl-2,1,3-benzothiadiazole (LXXX):

Excess pyridine (ca. 6 ml.) was added to LXXIX (1.2 g; 0.005 mole) and the reaction mixture was refluxed (ca. 2 hr.). Thereafter, the contents were cooled and poured onto crushed ice (50 g.). The organic material was extracted with chloroform, washed with water and dried (Na$_2$SO$_4$). Removal of the solvent and column chromatography of the residue over silica gel column using benzene as eluent gave 0.84 g. of the polymer, as a white coloured amorphous compound, m.p. 125-30$^\circ$.

4-Acetylamino-3-bromo-5-nitrotoluene (LXXXII):

Fuming nitric acid (12.6 ml.) was added dropwise to a well stirred and cooled solution of 4-acetylamino-3-bromotoluene (22.8 g; 0.1 mole) in acetic anhydride (100 ml.) at such a rate (ca. 0.5 hr.) so as to maintain the temperature between 10-12$^\circ$. After stirring for another 30 min., the reaction mixture was poured onto crushed ice (50 g.) and the precipitate filtered, washed with water followed by 5% sodium bicarbonate solution and drained well. It was recrystallised from ethanol to give 20.5 g. (75.1%) of 4-acetylamino-3-bromo-5-nitrotoluene as light yellow crystals, m.p. 210-12$^\circ$. Lit. 213$^\circ$ 207.

Found: C, 39.3; H, 3.5; N, 10.4; Br, 29.1;
C$_{9}$H$_{9}$N$_{2}$O$_{3}$Br requires C, 39.56; H, 3.30; N, 10.26; Br, 29.30%.
IR (KBr) \( \nu \) max. 3250 (NH); 1670 (C=O); 1540, 1350 cm\(^{-1}\) (NO\(_2\)).

NMR (CDCl\(_3\)) 2.17 (3H, s, C\(_{\text{-Me}}\)); 2.26 (3H, s, -CO-CH\(_3\)); 7.06 (1H, d, H-2); 7.14 (1H, d, H-6); 7.32 (1H, broad s, NH; J\(_{2,6}\) = 1.5 Hz).

4-Amino-3-bromo-5-nitrotoluene (LXXXIII):

4-Acetylamino-3-bromo-5-nitrotoluene (13.65 g; 0.05 mole) was taken up in 1:1 dilute hydrochloric acid (100 ml.) and the reaction mixture refluxed for 1 hr. and poured in water (250 ml.). The yellow precipitate of nitroamine was filtered, washed free from acidic impurities drained well and recrystallised from dilute ethanol (1:1) to give 6.0 g. (52.2%) of bright yellow coloured plates of the desired product, m.p. 63-64\(^\circ\). Lit. m.p. 65\(^\circ\).

Found: C, 36.1; H, 3.2; N, 12.3; Br, 34.5; 
\( C_7H_7N_2O_2Br \) requires C, 36.36; H, 3.30; N, 12.13; Br, 34.63%.

IR \( \nu \) max. 3500, 3400, 3120 (-NH\(_2\)); 1640 (N-H band); 1550, 1340 cm\(^{-1}\) (-NO\(_2\)).

3-Bromo-4,5-diaminotoluene (LXXXIV):

To a warm solution of 4-amino-3-bromo-5-nitrotoluene (11.6 g; 0.06 mole) in ethanol (150 ml.) were added Raney Nickel (1.0 g. out of the total of 2.5 g.) and
then 98% hydrazine hydrate (3 ml. out of the total of 7.5 ml.) when a vigorous reaction ensued. After the vigour of the reaction subsided, another instalment of Raney Nickel (0.5 g.) and hydrazine hydrate (1.5 ml.) was added. The procedure was repeated until the additions were complete, and refluxing was continued until the yellow colour disappeared. The reaction mixture was filtered hot (the funnel was not allowed to dry so as to avoid catching fire by unreacted Raney Nickel) and the solvent removed to give a dark brown residue of the diamine (9.0 g.) which was used as such in the next step.

4-Bromo-6-methylbenzo-2,1,3-thiadiazole (LXXXV):

To a solution of 3-bromo-4,5-diaminotoluene (LXXXIV; 8.5 g; 0.04 mole) in dry benzene (120 ml.) was added purified thionyl chloride (10 ml.) and the reaction mixture refluxed for 8 hr. Excess thionyl chloride and benzene were removed, water (100 ml.) was added to the residue and the organic material, thus obtained, was taken up in chloroform. The aqueous layer was washed with chloroform (2 x 50 ml.) and the combined chloroform extracts were washed until free from acidic impurities. The solvent was distilled off and the residue was dissolved in benzene and adsorbed on a silica gel column which was eluted with pet-ether (60-80°). The eluent was stripped off, giving 5.2 g. (45.4%) of white crystals, m.p. 89-90°.
Found: C, 36.3; H, 2.4; N, 12.2; S, 13.6; 
\( \text{C}_7\text{H}_5\text{N}_2\text{SBr} \) requires C, 36.68; H, 2.18; 
N, 12.23; S, 13.97%.

**IR (nujol)** 

3050 (Heteroaromatic C-H str.); 1620 (C=N); 
1520, 1480 \( \text{cm}^{-1} \) (skelatal ring vib.).

**NMR (CDCl\(_3\))** 

2.26 (3H, s, \( \text{C}_6\)-Me); 7.726 (2H, degenerate 
quartet, H-5 and H-7).

4-Cyano-6-methylbenzo-2,1,3-thiadiazole (LXXXVII):

To a solution of the thiadiazole (LXXXV; 1.14 g; 
0.005 mole) in DMF (15 ml.) was added cuprous cyanide 
(0.54 g; 0.006 mole) and the reaction mixture refluxed for 
11 hr. After cooling it was poured onto crushed ice (200 g.) 
and the blackish complex filtered and stirred with a 
solution of potassium cyanide (5 g.) in water (50 ml.) 
for 1 hr. The organic material was taken up in chloroform 
and the aqueous layer extracted twice with 20 ml. portions 
of chloroform. The combined chloroform extracts were 
washed thoroughly with water and dried (MgSO\(_4\)). The solvent 
was removed and the residue on column chromatography over 
silica gel using pet-ether gave 0.2 g. (22.2%) of the 
desired product, m.p. 139-40\(^\circ\).

Found: C, 54.6; H, 3.2; N, 24.2; 
\( \text{C}_8\text{H}_5\text{N}_3\text{S} \) requires C, 54.86; H, 2.86; 
N, 24.00%.
1530 (C=C); 2210 cm$^{-1}$ (-C=N).

2.53 (3H, s, C$_6$-Me), 8.14 (1H, d, H-5); 7.87 (1H, d, H-7, $J_{5,7} = 2$ Hz.).

6-Methyl-4-N-morpholinobenzo-2,1,3-thiadiazole (LXXXVIII):

The bromo thiadiazole (LXXXV; 1.14 g; 0.005 mole) was refluxed with excess of morpholine (15 ml.) for 24 hr. After cooling the reaction mixture was poured into cold-water. The organic layer was taken up in chloroform and the aqueous layer extracted with chloroform (2x20 ml.). The combined chloroform extracts were washed with water and dried (Na$_2$SO$_4$). The solvent was stripped off and the residue, thus obtained, was purified by passing through a column of silica-gel (pet-ether) and benzene (50:50). Removal of the solvent gave 0.6 g. (51.3%) of white crystals, m.p. 67-68°.

Found: C, 56.3; H, 5.4; N, 17.7; S, 13.5;

$C_{11}H_{13}N_3S_0$ requires C, 56.17; H, 5.53; N, 17.87; S, 13.61%.

IR ν \text{nujol max.} 1610 (C=N), 1540, 1470 cm$^{-1}$ (ring breathing).

NMR (CDCl$_3$) 2.13 (3H, s, C$_6$-Me); 6.42 (1H, d, H-5); 7.19 (1H, d, H-7, $J_{5,7} = 2$ Hz.); 4.58-5.57 (4H, m, -CH$_2$); 3.16-3.50 (4H, m, -N(CH$_2$)$_2$).
4-Hydroxy-6-methylbenzo-2,1,3-thiadiazole (LXXXIX):

The thiadiazole (LXXXV; 0.57 g; 0.0025 mole) was treated with potassium hydroxide (0.5 g.) in ethanol (10 ml.) and the contents were refluxed on a water bath for 8 hr. After cooling, the reaction mixture was poured into the ice-cold water (100 ml.) and the aqueous layer extracted with chloroform to remove the unreacted compound and then rendered acidic to Congo red. The organic material was taken up in ether and the usual work up followed by chromatography afforded 0.15 g. (36.5%) of TLC pure compound as colourless crystals, m.p. 129-30°.

Found: C, 50.5; H, 3.5; N, 16.6; S, 19.1;
C₇H₅N₂SO requires C, 50.60; H, 3.61;
N, 16.87; S, 19.28%.

nujol IR ν max. 3360 cm⁻¹ (broad, bonded OH).

7-Bromo-5-methyl-4-nitrobenzo-2,1,3-thiadiazole (LXXXVI):

Compound (LXXXV; 1.14 g; 0.005 mole) was dissolved in minimum quantity of concentrated sulphuric acid (ca. 10 ml.) at 0°. To this well stirred and cooled solution was added sodium nitrate (2.15 g; 0.025 mole) in small portions so as to maintain the temperature at 0°.
(ca. 5 hr.). The stirring was continued for another 2 hr. and the contents were poured into iced-water (100 ml.), the precipitate, thus formed, was filtered, washed free from acidic impurities and recrystallised from dilute ethanol to give 6.5 g. (92.7%) of buff coloured crystals, m.p. 160-61°.

Found: C, 30.7; H, 1.3; N, 15.2; S, 11.5;

C₇H₄N₃O₂SBr requires C, 30.66; H, 1.46; N, 15.33; S, 11.68%.

IR ν\text{max.} KBr 2900, 1380 cm⁻¹ (aromatic -CH₃); 1360, 1540 cm⁻¹ (NO₂).

NMR (CDCl₃) 2.64 (3H, s, C₅-Me); 7.83 (1H, s, H-6).

7-Cyano-5-methyl-4-nitrobenzo-2,1,3-thiadiazole (XC):

The nitro compound (LXXXVI; 0.69 g; 0.0025 mole) was taken in DMF (15 ml.) and cuprous cyanide (0.22 g; 0.0025 mole) was added to it. The contents were refluxed for 15 hr. under anhydrous conditions. Thereafter it was cooled, poured into water (200 ml.) and the blackish complex, thus obtained, was filtered and decomposed by stirring at room temperature with potassium cyanide (5.0 g.) in water (50 ml.) for 1 hr. The organic material was taken up in chloroform and the usual work up gave 0.4 g. (80.0%) of the desired cyano compound, m.p. 240°.
Found: C, 43.5; H, 2.1; N, 25.3; S, 14.7; 
C\textsubscript{8}H\textsubscript{4}N\textsubscript{4}O\textsubscript{2}S requires C, 43.63; H, 1.82; 
N, 25.45; S, 14.54%.

IR ν\textsubscript{max} (nujol) 2200 (CN); 1560, 1330 cm\textsuperscript{-1} (NO\textsubscript{2}).

5-Methyl-7-N-morpholino-4-nitrobenzo-2,1,3-thiadiazole (XCI):

The nitro compound (LXXXVI; 0.69 g; 0.0025 mole) 
was taken up in morpholine (15 ml.) and the mixture was 
refluxed for 24 hr. The reaction mixture was cooled and 
poured into iced-water (200 ml.), the organic material was 
taken up in chloroform and usual workup including column 
chromatography provided 0.50 g. (83.3%) of bright yellow 
crystals of the desired compound (XCI), m.p. 204-05°.

Found: C, 47.5; H, 4.3; N, 19.69; S, 11.1; 
C\textsubscript{11}H\textsubscript{12}N\textsubscript{4}O\textsubscript{3}S requires C, 47.14; H, 4.28; 
N, 20.00; S, 11.43%.

IR ν\textsubscript{max} (nujol) 1540, 1360 cm\textsuperscript{-1} (NO\textsubscript{2}).

NMR (CDCl\textsubscript{3}) 2.62 (3H, s, C\textsubscript{5}-Me); 6.44 (1H, s, H-6); 
3.63-4.08 (4H, m, N<CH\textsubscript{2} and 4H, m, 
0<CH\textsubscript{2}).
7-Hydrazino-5-methyl-4-nitrobenzo-2,1,3-thiadiazole (XCII):

The nitro compound (LXXXVI; 0.69 g; 0.0026 mole) was taken up in dry DMF (10 ml.) and 98% hydrazine hydrate (25 ml.) was added to it. The contents were refluxed for 2 hr., cooled and poured into water (100 ml.), the organic material was extracted with chloroform and usual work up afforded 0.30 g. (37.5%) of the yellow coloured product (XCII), m.p. 90-91°.

Found: C, 37.5; H, 3.3; N, 31.0; S, 14.2;

C₇H₅N₀₂S requires C, 37.33; H, 3.11;
N, 33.11; S, 14.22%.

nujol IR max
3370, 3180 (NH₂ Str.); 1630 cm⁻¹ (-NH bending).

7-Hydroxy-5-methyl-4-nitrobenzo-2,1,3-thiadiazole (XCIII):

To nitro compound (LXXXVI; 0.69 g; 0.0025 mole) in ethanol (25 ml.) was added potassium hydroxide (0.5 g.) in ethanol (10 ml.), the reaction mixture refluxed for 3 hr. cooled, poured into water (150 ml.) and extracted with chloroform. The aqueous phase was acidified with dilute hydrochloric acid, extracted with chloroform, washed free from acidic impurities and dried (MgSO₄). The usual workup gave 0.3 g. (60.0%) of yellow coloured crystals which did not melt upto 250°.
The nitro compound (LXXXVI; 0.69 g; 0.0025 mole) in dry carbon-tetrachloride (30 ml.) was taken in a three-necked flask fitted with a stirrer condenser, and a dropping funnel and placed on a boiling water bath. Benzoyl peroxide (0.25 g.) was added followed by N-bromosuccinimide (0.48 g; 0.0025 mole) with stirring under irradiation with a 200W lamp in small instalments of 0.1 g. each (ca. 1 hr.) in such a way that the liberated bromine went on reacting and too large excess was not available. The reaction mixture was stirred under reflux for further 1 hr. and the hot contents were filtered to remove the succinimide formed. The filtrate was stripped off the solvent and the residue was crystallised from carbon-tetrachloride to give 0.70 g. (77.7%) of TLC pure product (XCIV), m.p. 139-40°C.

Found: C, 23.9; H, 1.0; N, 11.7; Br, 45.5;
\[ \text{C}_7\text{H}_3\text{N}_3\text{O}_2\text{SBr}_2 \text{ requires C, 23.79; H, 0.85; N, 11.89; Br, 45.32%.} \]

IR \( \nu \text{nujol max.} \) 1530, 1320 cm\(^{-1}\) \((-\text{NO}_2\)).
7-Cyano-5-cyanomethyl-4-nitrobenzo-2,1,3-thiadiazole (XCV):

The bromomethyl compound (XCVI; 0.88 g; 0.0025 mole) was taken in dry DMF in (15 ml.) and cuprous cyanide (0.44 g.; 0.0025 mole) was added to it. The reaction mixture was refluxed for 8 hr. under dry conditions, cooled, poured in water and the blackish complex, thus obtained, was filtered and decomposed by stirring with potassium cyanide (5.0 g.) in water (50 ml.) for 1 hr. The organic material was taken up in chloroform and the usual work up followed by column chromatography gave 0.31 g. (53.5%) of the desired product, m.p. 250°.

Found: C, 43.9; H, 1.3; N, 28.7; S, 12.7;

C$_9$H$_3$NS$_2$ requires C, 44.08; H, 1.22;
N, 28.57; S, 13.06%.

nujol
IR V$_{max.}$ 2200 (CN); 1560, 1330 cm$^{-1}$ (-$\text{NO}_2$).