EXPERIMENTAL PART II.

SECTION II.

General Method for the preparation of:

(1) Substituted Benzyl Malonic Esters:

In a 500 c.c. r.b. flask fitted with a reflux condensor, an ethanolic solution of sodium ethylate was prepared by the addition of metallic sodium (4.6 gm., 0.2 gm. atom) to absolute alcohol (50 c.c.). After cooling the solution to room temp., Ethyl malonate (35.2 gm., 0.22 mol.) is added and this is followed by the dropwise addition of appropriate substituted benzyl halide (0.20 mol.) with cooling. The resulting mixture was refluxed and after it became neutral (2 to 2.5 hrs.), alcohol was distilled off. The residue was treated with water and the organic layer separated, dried over anhydrous MgSO₄ and distilled under reduced pressure. Yield 80 per cent (based on malonic ester).

(Leuchs, Ber., 1911, 44, 1509.)

(ii) Substituted Benzyl Methyl Malonic Esters:

Above substituted benzyl malonic ester (0.1 mol.) was methylated in presence of sodium ethylate (0.1 gm. atom Na in 25 c.c. ethanol) by Methyl iodide (0.12 mol., 17.05 gm.) by the usual procedure. The product was distilled under reduced pressure. Yield 80 per cent (based on ester).
General Method for the preparation of:

(i) 5-Methyl-5'- (substituted benzyl)-Barbituric Acids and
(ii) 5-Methyl-5'- (substituted benzyl)-2-Thiobarbituric Acids:

In a 250 c.c. r.b. flask, equipped with a reflux condenser and a CaCl₂ guard-tube, is placed anhydrous ethanol (80 c.c.) and in it is dissolved finely cut metallic sodium (6.9 gm., 0.3 gm. atom). Appropriate substituted benzyl methyl malonic ester (0.1 mol.) is now added with shaking and then anhydrous urea (12 gm., 0.2 mol.) or thiourea (15.2 gm., 0.2 mol.) is added rapidly. The mixture is refluxed in an oil bath at 120° for 12 hours. The reaction mixture is then heated on a water bath to remove alcohol and the residue treated with 100-150 c.c. of water. It is filtered and the filtrate acidified with conc. HCl. On keeping overnight, the barbituric acid or thiobarbituric acid precipitates out, which is filtered and crystallised from alcohol. Yield 25 to 30 per cent.

In the following pages, the substituted benzyl malonic esters, substituted benzyl methyl malonic esters, barbiturates and thiobarbiturates are respectively described.
o-Chlorobenzyl malonic ester:

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and o-Chlorobenzyl chloride (32.2 gm.) by the procedure described above. Colourless liquid, b.p. 140-48°/12 mm., $N_D^{27}$: 1.4880.

Found Cl, 12.38 per cent.

$C_{14}H_{17}O_4Cl$ requires Cl, 12.47 per cent.

o-Chlorobenzyl-methyl malonic ester:

Above ester (28.5 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 30 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 140°/9 mm., $N_D^{27}$: 1.4960.

Found Cl, 11.81 per cent.

$C_{15}H_{19}O_4Cl$ requires Cl, 11.89 per cent.

5-Methyl-5'-(o-Chlorobenzyl)-Barbituric Acid:

It was prepared in 30 per cent yield from o-Chlorobenzyl-methyl malonic ester (7.46 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrorous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 170°.

Found N, 10.41 per cent.

$C_{12}H_{11}N_2O_5Cl$ requires N, 10.50 per cent.
5-Methyl-5'-(o-Chlorobenzyl)-2-Thiobarbituric Acid:

It was prepared in 30 per cent yield from o-Chlorobenzyl-methyl malonic ester (7.46 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 112°.

Found N, 9.89 per cent.
C_{12}H_{11}N_{2}O_{2}Cl requires N, 9.91 per cent.

p-Chlorobenzyl malonic ester:

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and p-Chlorobenzyl chloride (32.2 gm.) by the procedure described above. Colourless liquid, b.p. 188-90°/16 mm., \( \mu_{D}^{27} \): 1.4975.

Found Cl, 12.43 per cent.
C_{14}H_{17}O_{4}Cl requires Cl, 12.47 per cent.

p-Chlorobenzyl-methyl malonic ester:

Above ester (28.5 gm.) was methylated in presence of sodium ethylate (2.8 gm. Na in 30 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 195°/ 16 mm., \( \mu_{D}^{27} \): 1.4918.

Found Cl, 11.86 per cent.
C_{15}H_{19}O_{4}Cl requires Cl, 11.89 per cent.
5-Methyl-5′-(p-Chlorobenzyl)-Barbituric Acid:

It was prepared in 30 per cent yield from p-Chlorobenzyl-methyl malonic ester (7.46 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 197°.

Found N, 10.48 per cent.

\[ \text{C}_{12}\text{H}_{11}\text{N}_{2}\text{O}_{5}\text{Cl} \text{ requires N, 10.50 per cent.} \]

5-Methyl-5′-(p-Chlorobenzyl)-2-Thiobarbituric Acid:

It was prepared in 30 per cent yield from p-Chlorobenzyl-methyl malonic ester (7.46 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless platelets, m.p. 220°.

Found N, 9.89 per cent.

\[ \text{C}_{12}\text{H}_{11}\text{N}_{2}\text{O}_{2}\text{SCl} \text{ requires N, 9.91 per cent.} \]

do-Bromobenzyl malonic ester:

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and o-Bromobenzyl bromide (50 gm.) by the procedure described above. Yellowish liquid, b.p. 180°/12 mm., \( \rho \text{D}^{27} : 1.4940 \).
Found Br, 24.20 per cent.

\[ \text{C}_{14}\text{H}_{17}\text{O}_{4}\text{Br} \text{ requires Br, 24.31 per cent.} \]

**o-Bromobenzyl-methyl malonic ester:**

Above ester (32.9 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 30 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is an yellowish liquid, b.p. 196°/15 mm., \( \delta_{D}^{5}: 1.5120 \).

Found Br, 32.89 per cent.

\[ \text{C}_{15}\text{H}_{19}\text{O}_{4}\text{Br} \text{ requires Br, 32.92 per cent.} \]

5-Methyl-5′-(o-Bromobenzyl)-Barbituric Acid:

It was prepared in 30 per cent yield from o-Bromobenzyl-methyl malonic ester (8.57 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 151-52°.

Found N, 8.98 per cent.

\[ \text{C}_{12}\text{H}_{11}\text{N}_{2}\text{O}_{3}\text{Br} \text{ requires N, 9.00 per cent.} \]

5-Methyl-5′-(o-Bromobenzyl)-2-Thiobarbituric Acid:

It was prepared in 30 per cent yield from o-Bromobenzyl-methyl malonic ester (8.57 gm.),
sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 109-10°C.

\[ \text{Found } N, 8.51 \text{ per cent.} \]
\[ C_{12}H_{11}N_{2}O_{2}BrS \text{ requires } N, 8.56 \text{ per cent.} \]

**m-Bromobenzyl malonic ester:**

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and m-Bromobenzyl bromide (50 gm.) by the procedure described above.

Yellowish liquid, b.p. 175-80°/7 mm., \( n_D^{38.5} = 1.5289 \).

\[ \text{Found } Br, 24.26 \text{ per cent.} \]
\[ C_{14}H_{17}O_{4}Br \text{ requires } Br, 24.31 \text{ per cent.} \]

**m-Bromobenzyl-methyl malonic ester:**

Above ester (32.9 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 30 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is an yellowish liquid, b.p. 198-200°/7 mm., \( n_D^{38.6} = 1.5327 \).

\[ \text{Found } Br, 32.86 \text{ per cent.} \]
\[ C_{15}H_{19}O_{4}Br \text{ requires } Br, 32.92 \text{ per cent.} \]
5-Methyl-5'-(m-Bromobenzyl)-Barbituric Acid :

It was prepared in 30 per cent yield from m-Bromobenzyl-methyl malonic ester (8.57 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 159-60°.

Found N, 8.93 per cent.

\[ \text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_3\text{Br} \] requires N, 9.00 per cent.

5-Methyl-5'-(m-Bromobenzyl)-2-Thiobarbituric Acid :

It was prepared in 28 per cent yield from m-Bromobenzyl-methyl malonic ester (8.57 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless plates, m.p. 115°.

Found N, 8.53 per cent.

\[ \text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2\text{BrS} \] requires N, 8.56 per cent.

p-Bromobenzyl malonic ester :

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and p-bromobenzyl chloride (41.2 gm.) by the procedure described above. Yellowish liquid, b.p. 185-86°/ 10 mm., \( \eta^2_0^2 \) : 1.5090.
Found Br, 24.29 per cent.

C\textsubscript{14}H\textsubscript{17}O\textsubscript{4}Br requires Br, 24.31 per cent.

\textbf{p-Bromobenzyl-methyl malonic ester :}

Above ester (32.9 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 30 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is an yellowish liquid, b.p. 196°/11 mm., N\textsubscript{D}\textsuperscript{27} 1.5062.

Found Br, 32.88 per cent.

C\textsubscript{15}H\textsubscript{19}O\textsubscript{4}Br requires Br, 32.92 per cent.

\textbf{5-Methyl-5'-{(p-Bromobenzyl)}-Barbituric Acid :}

It was prepared in 30 per cent yield from p-Bromobenzyl-methyl malonic ester (8.57 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 204°.

Found N, 9.96 per cent.

C\textsubscript{12}H\textsubscript{11}N\textsubscript{2}O\textsubscript{3}Br requires N, 9.00 per cent.

\textbf{5-Methyl-5'-{(p-Bromobenzyl)}-2-Thiobarbituric Acid :}

It was prepared in 30 per cent yield from p-Bromobenzyl-methyl malonic ester (8.57 gm.),
sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless platelets, m.p. 131-32°.

Found N, 8.49 per cent.

\[ \text{C}_{12}\text{H}_{11}\text{N}_{2}\text{O}_{2}\text{BrS} \] requires N, 8.56 per cent.

**o-Methylbenzyl malonic ester:**

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and o-Methylbenzyl bromide (37.0 gm.) by the procedure described above. Colourless liquid, b.p. 168-70°/10 mm., \( \text{N}_D^{27} : 1.4920 \).

Found C, 68.00 per cent.; H, 7.53 per cent.

\[ \text{C}_{15}\text{H}_{20}\text{O}_4 \] requires C, 68.18 per cent.; H, 7.57 per cent.

**o-Methylbenzyl-methyl malonic ester:**

Above ester (26.4 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 182°/ 9 mm., \( \text{N}_D^{27} : 1.4812 \).

Found C, 69.00 per cent.; H, 7.89 per cent.

\[ \text{C}_{16}\text{H}_{22}\text{O}_4 \] requires C, 69.09 per cent.; H, 7.91 per cent.
5-Methyl-5'-((o-Methylbenzyl)-Barbituric Acid:

It was prepared in 50 per cent yield from o-Methylbenzyl-methyl malonic ester (6.95 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless platelets, m.p. 134°.

Found N, 11.26 per cent.

\[ \text{C}_{13}\text{H}_{14}\text{N}_{2}\text{O}_3 \] requires N, 11.38 per cent.

5-Methyl-5'-((o-Methylbenzyl)-2-Thiobarbituric Acid:

It was prepared in 50 per cent yield from o-Methylbenzyl-methyl malonic ester (6.95 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 116°.

Found N, 10.58 per cent.

\[ \text{C}_{13}\text{H}_{14}\text{N}_{2}\text{O}_2\text{S} \] requires N, 10.68 per cent.

m-Methylbenzyl malonic ester:

It was obtained in 60 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and m-Methylbenzyl bromide (37.0 gm.) by the procedure described above. Colourless liquid, b.p. 180°/30 mm., \( \text{N}^2_{D} \): 1.5052.
Found C, 68.10 per cent.; H, 7.50 per cent.

\[ \text{C}_{15}\text{H}_{20}\text{O}_4 \text{ requires C, 68.18 per cent.; H, 7.57 per cent.} \]

**m-Methylbenzyl-methyl malonic ester:**

Above ester (26.4 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 180°/10 mm., \( n^2_{D} \): 1.5420.

Found C, 95.93 per cent.; H, 7.79 per cent.

\[ \text{C}_{16}\text{H}_{22}\text{O}_4 \text{ requires C, 96.06 per cent.; H, 7.91 per cent.} \]

**5-Methyl-5'-(m-Methylbenzyl)-Barbituric Acid:**

It was prepared in 28 per cent yield from m-Methylbenzyl-methyl malonic ester (6.95 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 127-28°.

Found N, 11.33 per cent.

\[ \text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3 \text{ requires N, 11.38 per cent.} \]

**5-Methyl-5'-(m-Methylbenzyl)-2-Thiobarbituric Acid:**

It was prepared in 25 per cent yield from m-Methylbenzyl-methyl malonic ester (6.95 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described...
previously. It crystallised from alcohol in colourless needles, m.p. 115°.

Found N, 10.62 per cent.

\[ \text{C}_1\text{H}_{1\text{4}}\text{N}_2\text{O}_2\text{S} \] requires N, 10.68 per cent.

\textbf{p-Methylbenzyl malonic ester}:

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and \( p \)-Methoxybenzyl bromide (37.0 gm.) by the procedure described above. Colourless liquid, b.p. 208°/20 mm., \( \textit{N}^\text{27}_\text{D} \): 1.5049.

Found C, 68.00 per cent.; H, 7.50 per cent.

\[ \text{C}_{15}\text{H}_{20}\text{O}_4 \] requires C, 68.18 per cent.; H, 7.57 per cent.

\textbf{p-Methylbenzyl-methyl malonic ester}:

Above ester (26.4 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 76 per cent. It is a colourless liquid, b.p. 220°/20 mm., \( \textit{N}^\text{25}_\text{D} \): 1.5328.

Found C, 95.99 per cent.; H, 7.88 per cent.

\[ \text{C}_{16}\text{H}_{22}\text{O}_4 \] requires C, 96.06 per cent.; H, 7.91 per cent.
5-Methyl-5'-\((p\text{-}Methylbenzyl)\)-Barbituric Acid:

It was prepared in 30 per cent yield from p-Methylbenzyl-methyl malonic ester (6.95 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It did not crystallise from any solvent, wax-like.

5-Methyl-5'-\((p\text{-}Methylbenzyl)\)-2-Thiobarbituric Acid:

It was prepared in 30 per cent yield from p-Methylbenzyl-methyl malonic ester (6.95 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 114°.

Found N, 10.53 per cent.

\( \text{C}_{13}\text{H}_{14}\text{N}_{2}\text{O}_{2}\text{S} \) requires N, 10.68 per cent.

3,4-Dimethylbenzyl malonic ester:

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and 3,4-Dimethylbenzyl chloride (30.9 gm.) by the procedure described above. Colourless liquid, b.p. 200°/60 mm., \( \rho_{D}^{20} \): 1.4809.

Found C, 69.00 per cent.; H, 7.88 per cent.;

\( \text{C}_{16}\text{H}_{22}\text{O}_{4} \) requires C, 69.06 per cent.; H, 7.91 per cent.;
3,4-Dimethylbenzyl-methyl malonic ester:

Above ester (27.8 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 222°/50 mm., \( N_D^{27} \): 1.4932.

Found C, 69.80 per cent.; H, 8.18 per cent.

\( C_{17}H_{24}O_4 \) requires C, 69.86 per cent.; H, 8.21 per cent.

5-Methyl-5'-(3,4-Dimethylbenzyl)-Barbituric Acid:

It was prepared in 30 per cent yield from 3,4-Dimethylbenzyl-methyl malonic ester (7.3 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 175°.

Found N, 10.69 per cent.

\( C_{14}H_{16}N_2O_3 \) requires N, 10.76 per cent.

5-Methyl-5'-(3,4-Dimethylbenzyl)-2-Thiobarbituric Acid:

It was prepared in 30 per cent yield from 3,4-Dimethylbenzyl-methyl malonic ester (7.3 gm.), sodium ethylate (1.73 gm. Na\(^2\) in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described.
previously. It crystallised from methyl alcohol in
colourless needles, m.p. 100°.

Found N, 10.00 per cent.

\[ \text{C}_{14}\text{H}_{16}\text{N}_{2}\text{O}_{2}\text{S} \text{ requires } \text{N}, 10.14 \text{ per cent.} \]

**2,4-Dimethylbenzyl malonic ester**:  
It was obtained in 80 per cent
yield from ethyl malonate (35.2 gm.), sodium ethylate
(4.6 gm. Na in 50 c.c. ethanol) and 2,4-Dimethoxybenzyl
chloride (30.9 gm.) by the procedure described above.

Colourless liquid, b.p. 180-85°/20 mm., \( \text{N}_{D}^{27} \): 1.4932.

Found C, 68.95 per cent.; H, 7.82 per cent.

\[ \text{C}_{16}\text{H}_{22}\text{O}_{4} \text{ requires } \text{C}, 69.06 \text{ per cent.; H}, 7.91 \text{ per cent.} \]

**2,4-Dimethylbenzyl-methyl malonic ester**:  
Above ester (27.8 gm.) was
methylated in presence of sodium ethylate (2.3 gm. Na
in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the
usual procedure. Yield 75 per cent. It is a colourless
liquid, b.p. 206-08°/32 mm., \( \text{N}_{D}^{38.5} \): 1.5108.

Found C, 69.80 per cent.; H, 8.19 per cent.

\[ \text{C}_{17}\text{H}_{24}\text{O}_{4} \text{ requires } \text{C}, 69.86 \text{ per cent.; H}, 8.21 \text{ per cent.} \]

**5-Methyl-5'-(2,4-Dimethylbenzyl)-Barbituric Acid**:

It was prepared in 30 per cent
yield from 2,4-Dimethylbenzyl-methyl malonic ester (7.3 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from methyl alcohol in colourless needles, m.p. 118°.

Found N, 10.68 per cent.

C_{14}H_{16}N_{2}O_{3} requires N, 10.76 per cent.

5-Methyl-5′-(2,4-Dimethylbenzyl)-2-Thiobarbituric Acid:

It was prepared in 30 per cent yield from 2,4-Dimethylbenzyl-methyl malonic ester (7.3 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 120°.

Found N, 10.10 per cent.

C_{14}H_{16}N_{2}O_{2}S requires N, 10.14 per cent.

2,5-Dimethylbenzyl malonic ester:

It was obtained in 80 per cent yield from ethyl malomate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and 2,5-Dimethylbenzyl chloride (30.9 gm.) by the procedure described above. Colourless liquid, b.p. 174-76°/ 12 mm., N\(_D^{27}\): 1.4890.
Found C, 69.00 per cent.; H, 7.90 per cent.  
\[ \text{C}_{16}\text{H}_{22}\text{O}_4 \text{ requires C}, 69.06 \text{ per cent.; H, 7.91 per cent.} \]

**2,5-Dimethylbenzyl-methyl malonic ester:**

Above ester (27.8 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 182°/10 mm., \( \varepsilon_{27}^5 \): 1.4880.

Found C, 69.83 per cent.; H, 8.17 per cent.  
\[ \text{C}_{17}\text{H}_{24}\text{O}_4 \text{ requires C}, 69.86 \text{ per cent.; H, 8.21 per cent.} \]

**5-Methyl-5'-[(2,5-Dimethylbenzyl)]-Barbituric Acid:**

It was prepared in 28 per cent yield from 2,5-Dimethylbenzyl-methyl malonic ester (7.3 gm.), sodium ethylate (1.75 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from benzene in colourless needles, m.p. 78°.

Found N, 10.69 per cent.  
\[ \text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3 \text{ requires N}, 10.76 \text{ per cent.} \]

**5-Methyl-5'-[(2,5-Dimethylbenzyl)]-2-Thiobarbituric Acid:**

It was prepared in 28 per cent
yield from 2,5-Dimethylbenzyl-methyl malonic ester (7.3 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from dil. alcohol in colourless needles, m.p. 116°.

Found N, 10.06 per cent.

\[ \text{C}_{14}\text{H}_{16}\text{N}_{2}\text{O}_{2}\text{S} \text{ requires } \text{N}, 10.14 \text{ per cent.} \]

o-Methoxybenzyl malonic ester:

It was obtained in 78 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and o-Methoxybenzyl chloride (31.3 gm.) by the procedure described above. Colourless liquid, b.p. 194°/13 mm., \( N_D^{38.5} : 1.4950 \).

Found C, 64.18 per cent.; H, 7.09 per cent.

\[ \text{C}_{15}\text{H}_{20}\text{O}_{5} \text{ requires } \text{C}, 64.28 \text{ per cent.}; \text{H}, 7.14 \text{ per cent.} \]

o-Methoxybenzyl-methyl malonic ester:

Above ester (28.0 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 196°/15 mm., \( N_D^{38.5} : 1.4918 \).

Found C, 65.26 per cent.; H, 7.42 per cent.

\[ \text{C}_{16}\text{H}_{22}\text{O}_{5} \text{ requires } \text{C}, 65.30 \text{ per cent.}; \text{H}, 7.48 \text{ per cent.} \]
5-Methyl-5'-(o-Methoxybenzyl)-Barbituric Acid:

It was prepared in 25 per cent yield from o-Methoxybenzyl-methyl malonic ester (7.35 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from dil. alcohol in colourless flakes, m.p. 168°.

Found N, 10.62 per cent.

\[ C_{13}H_{14}N_2O_4 \] requires N, 10.68 per cent.

5-Methyl-5'-(o-Methoxybenzyl)-2-Thiobarbituric Acid:

It was prepared in 25 per cent yield from o-Methoxybenzyl-methyl malonic ester (7.35 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from dil. alcohol in colourless needles, m.p. 115°.

Found N, 10.00 per cent.

\[ C_{13}H_{14}N_2O_3S \] requires N, 10.07 per cent.

p-Methoxybenzyl malonic ester:

It was obtained in 80 per cent yield from ethyl malonate (35.2 gm.), sodium ethylate (4.6 gm. Na in 50 c.c. ethanol) and p-Methoxybenzyl chloride (31.3 gm.) by the procedure described above. Colourless liquid, b.p. 202°/25 mm., \( n_D^{27} : 1.4946 \).
Found C, 64.08 per cent.; H, 7.10 per cent.

\[ C_{15}H_{20}O_5 \] requires C, 64.28 per cent.; H, 7.14 per cent.

**p-Methoxybenzyl-methyl malonic ester:**

Above ester (28.0 gm.) was methylated in presence of sodium ethylate (2.3 gm. Na in 25 c.c. ethanol) by methyl iodide (17.0 gm.) by the usual procedure. Yield 80 per cent. It is a colourless liquid, b.p. 220°/25 mm., \( N_{D}^{20} = 1.5132. \)

Found C, 65.23 per cent.; H, 7.41 per cent.

\[ C_{16}H_{22}O_5 \] requires C, 65.30 per cent.; H, 7.48 per cent.

**5-Methyl-5'-(p-Methoxybenzyl)-Barbituric Acid:**

It was prepared in 25 per cent yield from p-Methoxybenzyl-methyl malonic ester (7.35 gm.), sodium ethylate (1.73 gm. Na in 25 c.c. ethanol) and anhydrous urea (3.0 gm.) by the procedure described previously. It crystallised from alcohol in colourless needles, m.p. 252°.

Found N, 10.60 per cent.

\[ C_{15}H_{14}N_{2}O_{4} \] requires N, 10.68 per cent.

**5-Methyl-5'-(p-Methoxybenzyl)-2-Thiobarbituric Acid:**

It was prepared in 25 per cent
yield from p-Methoxybenzyl-methyl malonic ester (7.35 gm.), sodium ethylate (1.75 gm. Na in 25 c.c. ethanol) and anhydrous thiourea (3.8 gm.) by the procedure described previously. It crystallised from dil. alcohol in colourless needles, m.p. 116°.

Found N, 9.98 per cent.

\[ \text{C}_{15}\text{H}_{14}\text{N}_{2}\text{O}_{3}\text{S} \text{ requires N, 10.07 per cent.} \]