CHAPTER II

STUDIES IN FRIES' REARRANGEMENT

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Condensation of phenols with succinyl chloride
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The present work and discussion

It is remarkable to note that succinyl chloride when reacted with phenols under Friedel-Crafts condition does not give keto-acids or diketones but give exclusively esters. Phenol, o-cresol, m-cresol, p-cresol, p-chlorophenol, p-chloro-m-cresol has been condensed with succinyl chloride in presence of AlCl₃ at 0°-5° giving the corresponding esters instead of the diketones or keto acids. The esters are formed in very good yield and not a trace of keto-acid or diketone is formed.

Phenol reacts with succinyl chloride in presence of AlCl₃ using nitrobenzene as a solvent or succinic acid in presence of phosphorus oxychloride to give diphenyl succinate (1).

\[
\begin{align*}
\text{O-CO-} & \quad \text{O-CO-} \\
\text{C₆H₄} & \quad \text{C₆H₄}
\end{align*}
\]
The condensation product of o-cresol and succinyl chloride in presence of anhydrous AlCl₃ and nitrobenzene are solvent is di-o-toluyl succinate (2).

\[ \text{C₆H₅-CH-CO-(CH₂)₂-CO-C₆H₅} \]

M-cresol reacts with succinyl chloride giving di-(m-toluyl) succinate (3).

\[ \text{H₂C-C₆H₄-CO-(CH₂)₂-CO-C₆H₄CH₃} \]

Di-(o-chlorophenyl) succinate is obtained from the condensation of o-cresol and succinyl chloride in presence of anhydrous AlCl₃ (4).

\[ \text{Cl-C₆H₄-CO-(CH₂)₂-CO-C₆H₄Cl} \]
Eugenol reacts with succinic acid in presence of phosphorus oxychloride and gives di-(4-allyl-2 methoxy phenyl) succinate (5).

α-naphthol reacts with succinic acid in presence of phosphorus oxychloride to give di-(α-naphthyl) succinate (6).

2-chloro-5-hydroxy toluene reacts with succinyl chloride in presence of anhydrous AlCl₃ or succinic acid in presence of phosphorus oxychloride resulting in di-(4-chloro-3-methyl phenyl) succinate (7).
The condensation of p-chloro-phenol and succinyl chloride in presence of anhydrous AlCl₃ or p-Cl-phenol and succinic acid in presence of phosphorus oxychloride produces di-p-chlorophenyl succinate (8).

p-cresol reacts with succinyl chloride in presence of anhydrous AlCl₃ or succinic acid in presence of phosphorus oxychloride to give di-(p-toluyl) succinate (9).
p-bromo phenol and succinic acid in presence of phosphorus oxychloride give di-(p-bromo phenyl) succinate (10).

Chloro-xylenol reacts with succinic acid in presence of phosphorus oxychloride to give di-(4-chloro-3,5 dimethyl phenyl) succinate (11).
4-chloro-1-naphthol and succinic acid in presence of phosphorus oxychloride give di-(4-chloro-1-naphthyl) succinate (12).

The diphenyl succinates thus obtained by the condensation of phenols with succinyl chloride have proved valuable intermediates for the synthesis of 1:4 diketone by Fries' rearrangement.
The double Fries' rearrangement of diaryl ester of aliphatic dicarboxylic acid was reported as early as 1902 by Bischoff et al [Ber., 35, 4085, 1902]. These workers prepared 1,5-bis (2-hydroxy phenyl) 1,5 pentane dione by subjecting diphenyl glutarate to Fries' rearrangement in presence of AlCl₃.


Thomas II, Sharma and Fernelius [J.Amer.Chem.Soc., 1958, 80, 5864] have prepared di-p-tolyl esters of aliphatic
dicarboxylic acids and have submitted them to double Fries' rearrangement. They found that the di-p-tolyl esters of the aromatic acids isophthalic and terephthalic acid successfully rearrange in the presence of anhydrous AlCl₃ to their corresponding bis-(o-hydroxy ketones). Attempted rearrangement of the di-p-tolyl esters of oxalic, malonic and phthalic acids did not result in the formation of bis-(o-hydroxy ketones).
Condensation of phenols with malonyl chloride

Double Fries' rearrangement of diphenyl malonates

Formation of 1:3 diketone

The present work and discussion

The formation of diphenyl succinate and the Fries' rearrangement of the diphenyl succinate led us to the study of the condensation of malonic acid or its chloride with phenols and the Fries rearrangement of the diphenyl malonate to 1:3-diketones.

In the literature there is no reference to double Fries' rearrangement of diphenyl malonate.

Gina [Gina, Atti Accad. Lincei (6) 2, 343 (1925)], [C.A., 20, 1233 (1926)] obtained di-β-naphthyl malonate (13) while attempting to prepare 4-hydroxy-6,7-benzocoumarin by condensing β-naphthol with malonyl chloride in the presence of AlCl₃.

\[
\begin{align*}
\text{PhOH} & + \text{CH₂COCl} \\
\text{Ph} & \xrightarrow{\text{anhيدروك}} \\
\text{Ph} & \xrightarrow{\text{AlCl₃}} \\
\end{align*}
\]

(13)
Zeigler and Junek have prepared several 4-hydroxy coumarins by the action of aluminium chloride on the appropriate malonic ester [(a) E. Zeigler and H. Junek, Monatsh., 86, 29 (1955); (b) 86, 506 (1955); (c) 87, 212, 218 (1956); (d) E. Ziegler and H. Majer, this journal, 89, 143 (1958)].

The di-p-tolyl ester of oxalic acid was prepared but the ester did not give the corresponding bis-(o-hydroxy ketones) when subjected to the conditions of the Fries rearrangement. Attempted rearrangement of di-p-tolyl oxalate resulted in the formation of a small amount of 2-hydroxy-5-methyl benzoic acid (14).

Thomas II, Shamma and Fernelius [J. Amer. Chem. Soc., 1958, 80, 5864] condensed p-cresol with malonic acid and p-cresyl malonate (I) thus obtained yielded 4-hydroxy coumarin (II) instead of the diketone (III) on treatment with AlCl₃ using chlorobenzene as solvent.
The present author has found that malonic acid condenses smoothly with p-cresol leading to the formation of the diaryl ester (I) at 115-120° in presence of phosphorus.
The di-p-cresyl malonate (I) has been subjected to double Fries' rearrangement in presence of AlCl₃ at 130-140° yielding the 1:4 diketone III.

P-chloro phenol reacts with malonic acid in presence of phosphorus oxychloride to give di-p-chloro-phenyl malonate (15).

Di-p-chloro phenyl malonate undergoes Fries rearrangement when heated in presence of anhydrous AlCl₃ and gives 1,3 bis-(2-hydroxy-5-Cl-phenyl) propane 1,3 dione (16).

P-chloro-m-cresol and malonic acid give di-p-chloro-m-cresyl malonate in presence of phosphorus oxychloride (17).
Di-4-chloro-m-cresyl malonate when heated in presence of anhydrous AlCl₃ gives 1,3 bis (2-hydroxy-6-methyl-5-chloro-phenyl) propane 1,3 dione (18a) or (2-hydroxy-4-methyl-5-chlorophenyl) propane 1,3 dione. (18b).
Di-chloro-xylenyl malonate is produced from the condensation of Cl-xylenol and malonic acid in presence of phosphorus oxychloride (19).

Di-chloro-xylenyl malonate undergoes Fries rearrangement in presence of anhydrous AlCl₃ and gives 1,3 bis (2-hydroxy-5-Cl-4,6-dimethyl phenyl) propane 1,3 dione (20).
β-naphthol reacts with malonic acid in presence of phosphorus oxychloride to give di-β-naphthyl malonate (21).

![Chemical structure of di-β-naphthyl malonate](image1)

When di-β-naphthyl malonate is heated with anhydrous AlCl₃ 1,3 bis (2-hydroxynaphthyl) propane 1,3 dione is produced (22).

![Chemical structure of 1,3 bis (2-hydroxynaphthyl) propane 1,3 dione](image2)

These 1:3-diketones have been found to be valuable intermediates for the synthesis of heterocyclic compounds (Chakravarti and Sarkar, Science & Culture, 1966, 32, p.592).
Condensation of Succinyl chloride with phenols

Preparation of succinyl chloride


Succinic acid (15 g.) was refluxed with acetic anhydride (25 ml.) in a sand-bath for 4 hours. It was chilled suddenly when succinic anhydride separated, filtered and dried.

Succinyl chloride (Morrel, J.Chem.Soc., 1914, 1933)

The above succinic anhydride (25 g.) was intimately mixed with PCl₅ (50 g.) and heated in an oil-bath for 3 hours at a temperature of 120°C. It was distilled under reduced pressure.

Diphenyl succinate

A solution of freshly distilled phenol (2.4 g.) in 30 ml. nitrobenzene was cooled in a 250 ml. three-necked flask, equipped with stirrer, dropping funnel and a gas outlet tube.
Aluminium chloride (7.5 g.) was added and the solution was cooled to 0-5°. A solution of succinyl chloride (3.9 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. It was left at room temperature for 18 hours. After decomposing by ice and hydrochloric acid it was distilled in steam to remove nitrobenzene. The crude product solidified on cooling was insoluble in Na₂CO₃ and NaOH solution. It was crystallised from dilute alcohol as needles, m.p. 125°, yield 2 g. (Weselsky, Ber., 2, 519. Reported m.p. 118°.

The above diphenyl succinate was also obtained as follows:

(1) Succinic acid (11 g.) and phenol (20 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from dilute ethanol, m.p. 124°.

(2) When a solution of succinyl chloride and phenol was heated in a water-bath for 3 hours, it gave an ester, m.p. 125°. No depression in mixed m.p. with the compound prepared as above.
Di-(o-tolyl) succinate:

(1) A mixture of freshly distilled o-cresol (2.7 g.) in 20 ml. nitrobenzene was cooled in a 250 ml. three-necked flask, equipped with stirrer, dropping funnel and a gas outlet tube. Aluminium chloride (7.5 g.) was added and the solution was cooled to 0-5°. A solution of succinyl chloride (3.9 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. It was left at room temperature for 13 hours. After decomposing by ice and hydrochloric acid it was distilled in steam. The liquid product was insoluble in Na₂CO₃ or NaOH solution. Extracted with ether, dried and distilled, b.p. 240°/5 m.m., yield 2 g. (B.V. Hedenstrom, Ber., 35, 4079. Reported b.p. 238-240° at 5 m.m.).

(2) When a solution of o-cresol and succinyl chloride was heated in water-bath for 3 hours it gave an ester, b.p. 240°/5 m.m. which was identical with the ester prepared as above.
Di-(m-toluyl) succinate:

(1) A solution of freshly distilled m-cresol (2.7 g.) in 20 ml. nitrobenzene was cooled in a 250 ml. three-necked flask, equipped with stirrer, dropping funnel and a gas outlet tube. Aluminium chloride (7.5 g.) was added and the solution was cooled to 0-5°. A solution of succinyl chloride (3.9 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. It was left at room temperature for 18 hours. After decomposing by ice and hydrochloric acid it was distilled in steam. The crude product was insoluble in Na₂CO₃ or NaOH solution. It was crystallised from dilute alcohol as rectangular plates, m.p. 60°.

(B.V. Hedenstrom, Ber., 35, 4080, reported m.p. 60°)

(2) When a solution of m-cresol and succinyl chloride was heated on a water-bath for 3 hours it gave an ester, m.p. 60°. No depression in mixed m.p. with the compound prepared as above.
Di-(o-chlorophenyl) succinate:

A solution of o-chloro phenol (3.2 g.) in 25 ml. nitrobenzene was taken in a 250 ml. three-necked flask, fitted with stirrer, dropping funnel and a gas outlet tube. Aluminium chloride (7.5 g.) was added and the solution was cooled to 0-5°. A solution of succinyl chloride (3.9 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. The mixture was left for 18 hours at room temperature. After decomposing by ice and hydrochloric acid it was distilled in steam. The crude product was insoluble in Na₂CO₃ or NaOH solution, crystallised from alcohol as rectangular plates, m.p. 90°.

[Found: C, 56.65; H, 3.42; C₁₆H₁₂O₄Cl₂ requires C, 56.63; H, 3.54%]

Di-(4-allyl-2-methoxy phenyl) succinate:
Succinic acid (11 g.) and eugenol (16 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from dilute alcohol, m.p. 87°.

[Found: C, 70.13; H, 5.92; C_{24}H_{20}O_6 requires C, 70.24; H, 6.34%]

Di-(α-naphthyl) succinate:

Succinic acid (11 g.) and eugenol (16 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from alcohol, m.p. 160°.

[Found: C, 77.07; H, 4.87; C_{24}H_{18}O_4 requires C, 77.34; H, 4.86%]
Di-(p-tolyl) succinate:

Method A

A solution of freshly distilled p-cresol (2.1 g.) in 30 ml. nitrobenzene was cooled in a 250 ml. three-necked flask, equipped with stirrer, dropping funnel and a gas outlet tube. Aluminium chloride (4 g.) was added and the solution was cooled to 0-5°. A solution of succinyl chloride (2 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. It was left at room temperature for 18 hours. After decomposing by ice and HCl it was distilled in steam to remove excess nitrobenzene. The crude product solidified on cooling was insoluble in Na₂CO₃ and NaOH solution. It was crystallised from alcohol as needles, m.p. 121°C.

[Hedenstrom, Ber., 35, 4080. Reported m.p. 121°]

Method B

Succinic acid (11 g.) and p-cresol (21 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was
poured into ice, filtered, dried and crystallised from dilute alcohol, m.p. 120°.

Method C

When a solution of succinyl chloride and p-cresol was heated in a water-bath for 3 hours, it gave an ester, m.p. 121°. No depression in mixed m.p. with the compound prepared as above.

[Found: C, 72.12; H, 6.14; C₁₈H₁₈O₄ requires C, 72.48; H, 6.84%]

Synthesis of 1,4 bis(2-hydroxy-5 methyl phenyl) butane 1,4 dione by Double Fries' Rearrangement

Di-(p-toluyl) succinate (3 g.) and aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with thermometer and air condenser fitted with a calcium chloride guard tube. The flask with the contents were heated to 130-140° for 3-4 hours. After the reaction was completed it was allowed to cool, decomposed by ice and conc. hydrochloric acid and was kept overnight. The decomposed product was then extracted with ether. The product obtained after removal of ether was dissolved in 5% alkali solution.
The alkali solution on acidification gave crystalline product, crystallised from ethyl alcohol, m.p. $189^\circ$ [Reported m.p. $187^\circ$. K. Fries and K. Bartens, Ann. 422, 270 (1924)].

[Found : C, 72.32; H, 6.24; $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 72.48; H, 6.04%]

The 2:4 Di-D.N.P. crystallised from acetic acid, m.p. 239°.

[Found : N, 16.3; $\text{C}_{30}\text{H}_{26}\text{O}_{10}\text{N}_8$ requires N, 17.0%]

Di-oxime prepared as usual was crystallised from dilute alcohol, m.p. 269°.

[Found : N, 7.80; $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$ requires N, 8.53%]

**Di-(p-bromophenyl) succinate**

Succinic acid (11 g.) and p-bromo phenol (25 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised
from dilute ethanol solution, m.p. 112°.

When a solution of succinyl chloride and p-bromo-phenol was heated on a water-bath for 3 hours it gave an ester, m.p. 111°. No depression in mixed m.p. with the compound prepared as above.

[Found : C, 44.75 ; H, 2.83 ; C16H12O4Br2 requires C, 44.86 ; H, 2.80%]

Synthesis of 1,4 bis (2-hydroxy-5-bromo phenyl) butane 1,4 dione by Double Fries' Rearrangement

Di-(p-bromo phenyl) succinate (3 g.) and anhydrous aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with thermometer and air-condenser fitted with a calcium chloride guard tube. The flask with the contents were heated to 130-140° for 3-4 hours. After the reaction was completed it was allowed to cool decomposed by ice and concentrated hydrochloric acid and was kept overnight. The decomposed product was then extracted with ether. The brownish product obtained after removal of ether was dissolved in 5% alkali solution. The alkali solution on acidification
Method A

A solution of freshly distilled p-chlorophenol (2.5 g.) in 30 ml. nitrobenzene was cooled in a 250 ml. three-necked flask, equipped with stirrer, dropping funnel and a gas outlet tube. Aluminium chloride (4 g.) was added and the solution was cooled to 0-5°C. A solution of succinyl chloride (2 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. It was left at room temperature for 18 hours. After decomposing by ice and hydrochloric acid it was distilled in steam to remove nitrobenzene. The crude product solidified on cooling was insoluble in Na₂CO₃ and NaOH solution. It was crystallised from alcohol as needles, m.p. 105°C.
Method B

Succinic acid (11 g.) and p-Cl-phenol (25 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from dilute ethanol, m.p. 104°.

Method C

When a solution of succinyl chloride and p-Cl-phenol was heated in a water-bath for 3 hours, it gave an ester, m.p. 105°. No depression in mixed m.p. with the compound prepared as above.

[Found: C, 56.52; H, 3.24; C16H12O4Cl2 requires C, 56.63; H, 3.54%]

Synthesis of 1,4 bis (2-hydroxy-5-chloro phenyl) butane 1,4 dione by Double Fries' Rearrangement

Di-p-chlorophenyl succinate (3 g.) and aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with thermometer and air-condenser fitted with a calcium chloride guard tube. The flask with the contents were
heated to 130-140° for 3-4 hours. After the reaction was completed it was allowed to cool, decomposed by ice and conc. HCl and was kept overnight. The decomposed product was then extracted with ether. The product obtained after removal of ether was dissolved in 5% alkali. The alkali solution on acidification gave crystalline product, crystallised from dilute alcohol, m.p. 182°.

[Found : C, 56.60; H, 3.68; C_{16}H_{12}O_{4}Cl_{2} requires C, 56.63; H, 3.56%]

It gave violet colouration with FeCl₃ solution.


[Found : N, 16.59; C_{28}H_{20}O_{10}N_{8}Cl_{2} requires N, 16.0%]

Di oxime crystallised from dilute alcohol, m.p. 175°.

[Found : N, 7.0; C_{16}H_{14}O_{4}Cl_{2}N_{2} requires N, 7.59%]

Di-(4-chloro-3,5 dimethyl phenyl) succinate
Succinic acid (11 g.) and Cl-xylenol (31 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from dilute alcohol, m.p. 120°.

When a solution of succinyl chloride and Cl-xylenol was heated on a water-bath for 3 hours, it gave an ester, m.p. 120°. No depression in mixed m.p. with the compound prepared as above.

[Found : C, 60.64 ; H, 4.99 ; C₂₀H₂₀O₄Cl₂ requires C, 60.75 ; H, 5.06%]

Synthesis of 1,4 bis (2-hydroxy-5-chloro-4,6 dimethyl phenyl) butane 1,4 dione by Double Fries' Rearrangement

Di-(4-chloro-3,5 dimethyl phenyl) succinate (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with thermometer and air-condenser fitted with a calcium chloride guard tube. The flask with the contents were heated to 130-140° for 3-4 hours. After the reaction was completed it was allowed
to cool, decomposed by ice and concentrated hydrochloric acid and was kept overnight. The decomposed product was then extracted with ether. The product obtained after removal of ether was dissolved in 5% alkali solution. The alkali solution on acidification gave crystalline product, crystallised from dilute alcohol, m.p. 250°.

[Found : C, 60.44 ; H, 4.69 ; C_{20}H_{20}O_{4}Cl_{2} requires C, 60.75 ; H, 5.06%]

The 2:4 Di-D.N.P. crystallised from benzene, m.p. 220°.

[Found : N, 14.0, C_{32}H_{28}O_{10}N_{8}Cl_{2} requires N, 14.8%]

Di(4-chloro-1-naphthyl) succinate :

Succinic acid (11 g.) and chloro naphthol (40 g.) was taken in a 200 ml. round-bottomed flask equipped with thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from alcohol, m.p. 140°.
When a solution of succinyl chloride and chloronaphthol was heated in a water-bath for 3 hours, it gave an ester, m.p. 140°. No depression in mixed m.p. with the compound prepared as above.

[Found: C, 65.45; H, 3.57; \( \text{C}_{24}\text{H}_{16}\text{C}_{12}\text{O}_{4} \) requires C, 65.60; H, 3.64%]

**Double Fries' rearrangement of di (4-chloro-1-naphthyl) succinate**

Di-(4-chloro-1-naphthyl) succinate (3 g.) and anhydrous aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with thermometer and air condenser fitted with a calcium chloride guard tube. The flask with the contents were heated to 130-140° for 3-4 hours. After the reaction was completed it was allowed to cool, decomposed by ice and concentrated hydrochloric acid and was kept overnight. The decomposed product was then extracted with ether. The product obtained after removal of ether was dissolved in 5% alkali solution. The alkali solution on acidification gave crystalline product, crystallised from ethyl alcohol, m.p. 200°.

[Found: C, 65.15; H, 3.57; \( \text{C}_{24}\text{H}_{16}\text{O}_{4}\text{Cl}_{2} \) requires C, 65.60; H, 3.64%]

The position of the acyl group has not yet been definitely proved.
The 2:4 Di-D.N.P. crystallised from alcohol, m.p. 240°.

[Found : N, 13.95 ; C_{36}H_{24}O_{12}N_{2}Cl_{2} requires N, 14.0%]

**Di-(4-chloro-3-methyl phenyl) succinate**

Method A

A solution of 2-chloro-5-hydroxy toluene (3.5 g.) in 25 ml. nitrobenzene was cooled in a 250 ml. three-necked flask, equipped with stirrer, dropping funnel and a gas outlet tube. Aluminium chloride (7.5 g.) was added and the solution was cooled to 0-5°. A solution of succinyl chloride (3.9 g.) in 10 ml. nitrobenzene was added through the dropping funnel during 30 minutes. It was kept for 18 hours at room temperature. After decomposing by ice and hydrochloric acid it was distilled in steam. The crude product was insoluble in Na_2CO_3 or NaOH solution. It was crystallised from alcohol as rectangular plates, m.p. 91°.

Method B

Succinic acid (11 g.) and 2-chloro-5-hydroxy toluene (28.5 g.) in a 200 ml. round-bottomed flask equipped with
thermometer and a reflux condenser protected by a guard tube was heated for 2-3 hours at 115-120° with the addition of phosphorus oxychloride (10 g.) dropwise. The cold reaction mixture was poured into ice, filtered, dried and crystallised from dilute alcohol, m.p. 90°.

Method C

When a solution of succinyl chloride and 2-chloro-5-hydroxy toluene was heated in a water bath for 3 hours, it gave an ester, m.p. 90°. No depression in mixed m.p. with the compound prepared above.

[Found : C, 58.75 ; H, 4.32 ; C_{18}H_{11}O_{4}Cl_{2} requires C, 58.85 ; H, 4.36%]

Synthesis of 1,4 bis (2-hydroxy-5-chloro-6 methyl phenyl) butane 1,4 dione

or,

1,4 bis (2-hydroxy-5 chloro-4 methyl phenyl) butane 1,4 dione by Double Fries’ Rearrangement
Di-(4-chloro-3 methyl phenyl) succinate (3 g.) and anhydrous aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with thermometer and air condenser fitted with a calcium chloride guard tube. The flask with the contents were heated to 130-140° for 3-4 hours. After the reaction was completed it was allowed to cool, decomposed by ice and conc. HCl and was kept overnight. The decomposed product was then extracted with ether. The brownish product obtained after removal of ether was dissolved in 5% alkali solution. The alkali solution on acidification gave crystalline product. It was crystallised from dilute alcohol, m.p. 194°.

[Found : C, 58.99 ; H, 4.01 ; C₁₈H₁₆O₄Cl₂ requires C, 58.85 ; H, 4.37%]

The 2:4 Di-D.N.P. crystallised from alcohol, m.p. 280°.

[Found : N, 15.75 ; C₂₆H₂₄N₆O₆S₂ requires N, 15.40%]
Condensation of malonic acid with phenols and substituted phenols

Di-p-cresyl malonate

Malonic acid (5.25 g.) and p-cresol (12.7 g.) were placed in a 200 ml. round-bottomed flask equipped with a thermometer and a reflux condenser protected by a drying tube. The flask was heated to 115-120° in an oil-bath. Phosphorus oxychloride (10 g.) was added dropwise to the hot mixture. Towards the end of the addition the vigorous bubbling due to the evolution of HCl subsided, and on continued heating only a negligible amount of bubbling was observed. After heating for 2-3 hours at 115°-120°, the dark reaction mixture was allowed to cool, whereupon a reddish brown material containing crystals was obtained. The crystalline material was scraped away from the black resin and mixed with 250 g. of a 1:1 mixture of ice and water. The dark orange crystals were then filtered, dried and recrystallised from ethanol, m.p. 69°.

[Found : C, 71.5 ; H, 6.4 ; C_{17}H_{16}O_{4} requires C, 71.83 ; H, 5.63%]
1,3 bis (2-hydroxy-5-methyl phenyl) propane 1,3 dione

Di-p-cresyl malonate (3 g.) aluminium chloride (3 g.) were placed in a 100 c.c. round bottomed flask equipped with a thermometer and a air condenser fitted with a CaCl$_2$ guard tube. The flask with the contents were heated to 130-140° for 3-4 hours. After the reaction was complete it was allowed to cool, decomposed by ice and conc. hydrochloric acid and was kept overnight. The decomposed product was then extracted with ether. The yellowish product obtained was soluble in 5% NaOH solution. It was filtered and acidified and crystallised from dilute ethanol, m.p. 260° C. It gave deep red colouration with FeCl$_3$ solution.

[Found : C, 71.5 ; H, 6.4 ; C$_{17}$H$_{16}$O$_4$ requires C, 71.83 ; H, 5.63%]

The 2:4 D.N.P. crystallised from alcohol, m.p. 262°.

[Found : N, 16.3 ; C$_{25}$H$_{24}$O$_{10}$N$_8$ requires N, 17.4%]
Di-p-chloro-phenyl malonate

Malonic acid (5.25 g.) and p-Cl-phenol (12.8 g.) were placed in a 200 ml. round-bottomed flask equipped with a thermometer and a reflux condenser protected by a drying tube. The flask was heated to 115-120° in an oil-bath. Phosphorus oxychloride (10 g.) was added dropwise to the hot mixture. Towards the end of the addition the vigorous bubbling due to the evolution of HCl subsided, and on continued heating only a negligible amount of bubbling was observed. After heating for 2-3 hours at 115°-120° the dark reaction mixture was allowed to cool, poured into ice water. It was filtered, dried and crystallised from alcohol, m.p. 122°.

[Found: C, 55.72; H, 3.51; C₁₅H₁₀₀₄Cl₂ requires C, 55.38; H, 3.08%]
1,3 bis (2-hydroxy-5-Cl-phenyl) propane 1,3 dione

Di-p-Cl-phenyl malonate (3 g.) aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with a thermometer, condenser and a CaCl$_2$ guard tube. The mixture was heated to 130°-140° for 3-4 hours. It was decomposed with ice and conc. HCl and allowed to stand for overnight. It was then extracted with ether. The product obtained was soluble in 5% NaOH solution. It was filtered and acidified and crystallised from dilute alcohol, m.p. 268°. It gave violet colouration with FeCl$_3$ solution.

[Found : C, 55.81; H, 3.16; C$_{15}$H$_{10}$O$_4$Cl$_2$ requires C, 55.38; H, 3.08%]

The 2:4 D.N.P. crystallised from acetic acid, m.p. 220°.

[Found : N, 16.8; C$_{27}$H$_{18}$O$_{10}$NSCl$_2$ requires N, 16.3%]
Di-Cl-xylenyl malonate

Malonic acid (5.25 g.) and Cl-xylenol (15.6 g.) were taken in a 200 ml. round-bottomed flask equipped with a thermometer and a condenser with guard tube. The flask was heated to 115-120° in an oil-bath. Phosphorus oxychloride (10 g.) was added dropwise to the hot mixture. Towards the end of the addition the vigorous bubbling due to the evolution of HCl subsided, and on continued heating only a negligible amount of bubbling was observed. After heating for 2-3 hours at 115°-120° it was allowed to cool, and poured into ice water. It was filtered, dried and crystallised from alcohol, m.p. 127°.

[Found : C, 59.73 ; H, 4.71 ; Cl₉H₁₈O₄Cl₂ requires C, 59.84 ; H, 4.72%]
1,3 bis (2-hydroxy-5-Cl-4-6-dimethyl phenyl) propane 1,3 dione

Di-Cl-xylenyl malonate (3 g.), aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with a thermometer, condenser and a CaCl₂ guard tube. The mixture was heated to 130-140° for 3-4 hours. It was decomposed with ice and HCl and allowed to stand for overnight. It was then extracted with ether. The product obtained was soluble in 5% NaOH solution. It was filtered and acidified and crystallised from ethanol, m.p. 120°.

[Found : C, 59.63 ; H, 4.51 ; C₁₉H₁₈O₄Cl₂ requires C, 59.84 ; H, 4.72%]

The 2:4 D.N.P. crystallised from benzene, m.p. 250°.

[Found : N, 7.00 ; C₃₁H₂₆O₁₀Cl₂N₈ requires N, 7.11%]
Di-β-naphthyl malonate:

\[
\text{C}_7\text{H}_4\text{C} = \text{O} - \text{C} = \text{O} - \text{C} = \text{O} - \text{C} = \text{O} - \text{C} = \text{O}
\]

Malonic acid (5.25 g.) and β-naphthol (17 g.) were taken in a 200 ml. round-bottomed flask equipped with a thermometer and a condenser with guard tube. The flask was heated to 115-120° in an oil-bath. Phosphorus oxychloride (10 g.) was added dropwise to the hot mixture. Towards the end of the addition the vigorous bubbling due to the evolution of HCl subsided, and on continued heating only a negligible amount of bubbling was observed. After heating for 2-3 hours at 115°-120° it was allowed to cool, and poured into ice water. It was filtered, dried and crystallised from alcohol, m.p. 145°.

[Found: C, 77.20; H, 4.43; \(\text{C}_{23}\text{H}_{16}\text{O}_4\) requires C, 77.55; H, 4.49%]
1.3 bis (2-hydroxy-naphthyl) propane 1,3 dione

Di-β-naphthyl malonate (3 g.), aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with a thermometer, condenser and a CaCl₂ guard tube. The mixture was heated to 130-140° for 3-4 hours. It was decomposed with ice and HCl and allowed to stand for overnight. It was then extracted with ether. The product obtained was soluble in 5% NaOH solution. It was filtered and acidified and crystallised from ethyl alcohol, m.p. 250°.

[Found : C, 4.33; H, 77.30; C₂₃H₁₆O₄ requires C, 77.5%; H, 4.49%]

The 2:4 D.N.P. crystallised from dilute alcohol, m.p. 289°.

[Found : N, 5.5; C₃₅H₂₄O₁₀N₈ requires N, 5.64%]
Preparation of di-p-Cl-m-cresyl malonate

Malonic acid (5.25 g.) and $p$-Cl-m-cresol (14.2 g.) were taken in a 200 ml. round-bottomed flask equipped with a thermometer and a condenser with guard tube. The flask was heated to 115-120° in an oil-bath. Phosphorus oxychloride (10 g.) was added dropwise to the hot mixture. Towards the end of the addition the vigorous bubbling due to the evolution of HCl subsided, and on continued heating only a negligible amount of bubbling was observed. After heating for 2-3 hours at 115°-120° it was allowed to cool, and poured into ice water. It was filtered, dried and crystallised from dilute alcohol, m.p. 95°.

[Found : C, 57.58 ; H, 3.85 ; $C_{17}H_{14}O_4Cl_2$ requires C, 57.78 ; H, 3.96%]
1,3 bis (2-hydroxy-4-methyl-5-Cl-phenyl) propane 1,3 dione

or,

1,3 bis (2-hydroxy-6-methyl-5-Cl-phenyl) propane 1,3 dione

Di-4-Cl-m-cresyl malonate (3 g.), aluminium chloride (3 g.) were placed in a 100 c.c. round-bottomed flask equipped with a thermometer, condenser and a CaCl₂ guard tube. The mixture was heated to 130°-140° for 3-4 hours. It was decomposed with ice and HCl and allowed to stand for overnight. It was then extracted with ether. The product obtained was soluble in 5% NaOH solution. It was filtered and acidified and crystallised from ethanol, m.p. 250°. It gave deep red colouration with FeCl₃ solution.

[Found : C, 57.71 ; H, 3.84 ; Cl₁₇H₁₄O₄Cl₂ requires C, 57.78 ; H, 3.96%]

The 2:4 D.N.P. crystallised from acetic acid, m.p. 260°.

[Found : N, 15.8 ; C₂₉H₂₂O₁₀Cl₂N₂ requires N, 15.7%]