THE MECHANISM OF HYDROLYSIS
OF
CARBOXYLIC ESTERS.
THE WORK DESCRIBED IN THIS THESIS WAS CARRIED OUT BY ME IN THE CHEMICAL LABORATORIES OF BATTERSEA POLYTECHNIC, UNDER THE SUPERVISION OF DR. J. KENYON, F.R.S., TO WHOM I DESIRE TO RECORD MY SINCERE THANKS FOR HIS KINDLY ENCOURAGEMENT AND HELP.

II. Alkyl-Oxygen Fission in Derivatives of:
   (a) p-Methyl p'-methoxybenzhydrol
   (b) p-Isopropyl-p'-methoxybenzhydrol
   (c) α-Naphthyl-α-methoxyphenyl Carbimol.

Being a Thesis submitted to the University of London for the degree of Doctor of Philosophy, by Alfred Alexander Evans, B.Sc. (Lond.), A.I.C.

May, 1944.
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Although the hydrolysis of carboxylic esters in acid or in alkaline media usually takes place by mechanism I, there has become available, during recent years, ample evidence that mechanism II does also occur, especially when the alkyl group $R_{11}$ has strong electron-releasing properties.

![Chemical structures](image)

**Mechanism I**

Mechanism II, which implies the liberation of the carbonium cation, $R_{11}^+$, during some stage of the reaction, can be observed in the case of optically active esters by the racemisation of the products of the reaction. It has been shown that the optically pure hydrogen phthalic esters of certain substituted allyl alcohols, when submitted to hydrolysis with only a slight excess of alkali, yield the partly racemised alcohols; but when larger proportions of alkali are used optically pure alcohols are obtained (Arcus and Kenyon, J.C.S., 1939, 1912). The most complete demonstration of mechanism II has been provided in the case of optically active $p$-methoxybenzhydrally hydrogen phthalate — the most powerful electron-release of the $p$-methoxyl group causing the ester to dissociate with great ease (Bingle, Boughly, Kenyon and Popelett, J.C.S., 1942, 605). In the present investigation it has been shown that the following secondary alcohols and their derivatives react chiefly by mechanism II:
1. \(\alpha\)-Naphthylanisyl carbinol.
2. \(\mu\)-Methyl \(p\prime\)-methoxy benzhydrol.
3. \(p\)-Isopropyl-\(p\prime\)-methoxybenzhydrol.
4. \(\alpha\)-Naphthyl-\(\omega\)-methoxyphenyl carbinol.

\(\alpha\)-Naphthylanisyl carbinol has been resolved into its (+) and (-) forms by the fractional crystallisation of alkaloidal salts of its hydrogen phthalic and hydrogen succinic esters. The hydrogen of these optically active acid esters, when carried out under suitable experimental conditions, has been shown to proceed by alkyl-oxygen fission. This receives strong confirmation from the other reactions of the optically active carbinol and its esters, in all of which mechanism II is the usual mode of reaction.

The reactions of the esters of \(\mu\)-methyl-\(p\prime\)-methoxybenzhydrol, \(p\)-iso-propyl-\(p\prime\)-methoxybenzhydrol, and \(\alpha\)-naphthyl-\(\omega\)-methoxyphenyl carbinol are similar to those of the esters of \(\alpha\)-naphthylanisyl carbinol and alkyl-oxygen fission may also be assumed in the reactions of these compounds.
THE MECHANISM OF HYDROLYSIS OF CARBOXYLIC ESTERS.

INTRODUCTION.

The hydrolysis of carboxylic esters, as was pointed out by van't Hoff as far back as 1899 (Lecture, Part II, 1899), can be concisely formulated in either of two ways:

\[
\text{R. CO} \left[ \text{O} + \text{H}_2\text{O} \right] \text{R} \quad \text{R. CO} \text{OH} + \text{R}_2\text{OH} \quad (\text{i})
\]

and

\[
\text{R. CO} \left[ \text{O} + \text{H}_2\text{O} \right] \text{R} \quad \text{R. CO} \text{OH} + \text{R}_2\text{OH} \quad (\text{ii})
\]

Should the hydrolysis proceed according to (i), where the acyl-oxyl bond of the ester molecule is ruptured, the liberated alcohol would necessarily derive its oxygen from the ester itself; but should it proceed according to (ii), where the alkyl-oxyl bond is ruptured, the alcohol would derive its oxygen exclusively from the aqueous medium. It is necessary to determine which of the alternatives, (i) or (ii), correctly represents the reaction.

This problem was discussed by Ferns and Lapworth in 1912 (J.C.S., 1912, 101, 273). In a research on the preparation and properties of sulphonyl esters, they drew attention to the fact that sulphonyl, unlike carboxylic, esters behave in many of their reactions as alkylating agents; and, therefore, concluded that (i) whereas sulphonyl esters react with fission of the alkyl-oxyl bond, (ii) carboxylic esters do so with fission of the acyl-oxyl bond. In the majority of cases hitherto investigated, the conclusion (ii) has been fully confirmed as the following experimental results show:

(1) Should the alkyl-oxyl bond of an optically active ester,
R.COOR₁ (the asymmetric carbon atom being the one linking R₁ to O) be ruptured during any stage of the hydrolysis, then the liberated carbonium ion, R⁺, being effectively planar, would racemise immediately on formation and give rise to an optically inactive alcohol; but should this bond remain undisturbed throughout the reaction, the alkyl radical would maintain its configuration and give rise to an optically active alcohol. Experimental evidence for the optical instability of carbonium ions has been obtained by Kenyon and Phillips (J.C.S., 1930, 1679) and more recently by Wallis and Adams (J.A.C.S., 1933, 55, 3838). In 1912 Holmberg applied the above mentioned considerations to the hydrolysis of L-\textit{N}-acetylmalic acid both in alkaline and non-alkaline aqueous media (Ber., 1912, 45, 2997). The results of the experiments showed that there was an almost complete retention of the rotatory power of the liberated malic acid, from which it must be inferred that these hydrolyses took place with acyl-oxygen fission. A similar result was reported by Hughes, Ingold and Westerman (J.C.S., 1939, 346) who found that the direct esterification of \textit{\beta}-n-octyl alcohol with acetic acid gave an ester in which the configuration of the \textit{\beta}-n-octyl radical had been fully preserved; esterification in the presence of sulphuric acid led to only a small amount of racemisation.

(2) Mainly on the basis of these investigations of Burton and Ingold (J.C.S., 1928, 904, 1650), it is now accepted that reversible isomeric change in systems of the type:

\[ RCHX \cdot CH \rightleftharpoons R CH \cdot CHXR₁ \]

involves an intermediate stage consisting in the ionisation of the molecule followed by the mesomerisation of the ionisation of the
liberated kation as in:

\[ \text{RCH}_{-} \cdot \text{CH}: \text{CHR} \quad \rightarrow \quad \text{RCH}: \text{CH} \cdot \text{CHR} \quad + \]

\[ \text{RCH}, \text{CH} : \text{CHR}, \quad \rightarrow \quad \text{RCH}: \text{CH} \cdot \text{CHR} \quad + \quad \text{OH} \]

It follows that if the alkyl group of a carboxylic ester \((X = \text{acyloxy})\) is such that during hydrolysis it gives a mesomeric positive ion, then alkyl-oxygen fission will be revealed by the liberation of a mixture of isomeric alcohols:

\[ \text{CH}_{3} \cdot \text{CH} \cdot \text{CH} : \text{CH}_{2} \quad + \quad \text{OH} \]

Now Frévost had already shown that crotyl acetate and \(\alpha\)-methylallyl acetate, on hydrolysis \(\text{w}t\) in both acid or alkali media, yielded exclusively their own alcohols (Ann. Chim. 1929, 10, 147). These hydrolyses could not, therefore, have involved at any stage the liberation of the mesomeric ion: \(\text{CH}_{3} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_{2}\)

and again, it must be concluded that the hydrolyses took place with the rupture of the acyl-oxygen bond. A similar result was reported by Ingold and Ingëd with 0.5N alkali (J.C.S., 1938, 756) in the hydrolysis of \(\alpha\)-methyl-allylacetate.

(3) This, the most recent method, takes advantage of the fact that, if a neopentyl radical be set free during a reaction, it
invariably rearranges to tert-amyl, with the simultaneous formation of
unsaturated derivatives (Whitmore and Rothrock, J.A.C.S., 1922, 54,
3431; Whitmore, Little and Hopkins, J.A.C.S., 1932, 54, 3931; Whitmore,
Little and Hopkins, J.A.C.S., 1933, 55, 61, 1986). In 1940, Cnayle and
Horton (J.A.C.S., 1940, 62, 1170) esterified, by the standard methods, neopentyl alcohol with a series
of acids of widely varying strength; namely acetic, chloracetic,
dichloracetic, and trichloracetic acids. The resulting esters were
unaccompanied by the unsaturated compounds which are usually formed
during the rearrangement of the neopentyl radical, and when
hydrolysed with aqueous alkali, they yielded neopentyl alcohol
exclusively. The results clearly indicate that at no stage of the
esterification and hydrolytic processes was the neopentyl ion
kinetically free, and that it was the acyl-oxy bond that was ruptured.

(4) It was by the method of Polanyi and Szabo (Trans. Faraday
Soc., 1934, 30, 508) that hydrolysis with acyl-oxygen fission first
received its most direct demonstration. The method involves no
assumptions, and employs as the hydrolytic agent water containing an
enriched proportion of the heavier oxygen isotopes. Primary acyl-
acetoate was hydrolysed in alkaline solution, the water used having a
density 1.00033 as compared with ordinary water at the same temperature.
The liberated alcohol was dehydrated, and the water thus obtained was
found, after purification, to have a normal density. Had the oxygen
of the hydrolysing medium entered into the liberated alcohol, the
density of the water would have been higher than normal. It is
evident that in this instance too the ester molecule was ruptured at
the acyl-oxy bond. A similar conclusion was reached in the acid
hydrolysis of methyl hydrogen succinate (Bette, Hey and Inold, J.A.C.S.
In the esterification of benzoic acid with methyl alcohol containing an enhanced proportion of the heavier oxygen isotope, it was found that the liberated water did not contain an unusual proportion of heavy oxygen (Roberts & Hiley, J.A.C.S., 1939, 60, 2391).

Although, as the foregoing experimental results have shown, the hydrolysis of carboxylic esters usually takes place with acyl-oxygen fission, there has, during recent years, become available some evidence in support of the alternative mechanism. Alkyl-oxygen fission in carboxylic esters was first observed during the hydrolysis in very weak alkaline solutions, of some optically active $\alpha$-di-substituted allyl hydrogen phthalates, when it was found that the liberated alcohols had been considerably racemised. For example, it was reported that the hydrolysis of $\alpha$-dimethylallyl hydrogen phthalate in aqueous sodium acetate (Hills, Kenyon and Phillips, J.C.S., 1936, 576) and of $(+)$-phenyl-$\alpha$-methylallyl hydrogen phthalate in aqueous sodium carbonate (Kenyon, Partidge and Hills, J.C.S., 1936, 86) gave in each case a racemic alcohol. Hydrolysis in 5% aqueous alkali, however, gave the optically pure alcohols. These results suggest that, whereas acyl-oxygen fission of the esters in question is operative when the hydrolysis is conducted in concentrated aqueous alkali, alkyl-oxygen fission comes increasingly into play as the hydroxide concentration of the solution is reduced, as in solutions of sodium carbonate and sodium acetate.

Hydrolysis with alkyl-oxygen fission of the esters of substituted allyl alcohols, involving as it does the formation of a racemic ketone, should lead to isomerisation. But in asymmetrically substituted
esters, such as \( \alpha \gamma \)-dimethylallyl hydrogen phthalate, this effect cannot be observed on account of the symmetrical nature of the allyl residue. In the hydrolysis of optically active \( \alpha \)-phenyl-\( \gamma \)-methallyl hydrogen phthalate, with a slight excess of alkali, it was found that the liberated alcohol was a mixture from which, highly recrystallised \( \gamma \)-phenyl-\( \alpha \)-methylallyl alcohol was obtained. (Kenyon, Partridge and Phillips, J.C.S., 1937, 207). Clearly the allyl-oxy bond of the ester is ruptured during the reaction:

\[
\begin{align*}
\text{C}_6\text{H}_5\cdot\text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 + \text{OOC} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH} & \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 \cdot \text{COOH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 \\
\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 \cdot \text{OH} & \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 \cdot \text{COOH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 \\
\end{align*}
\]

On hydrolysis with alcoholic alkali, the ester in question yielded its own alcohol exclusively.

One of the most convincing demonstrations of hydrolysis with alkyl-oxygen fission was recently reported in the case of \( \gamma \)-methoxybenzhydryl hydrogen phthalate (Balfour, Loughby, Kenyon and Spoonett, J.C.S., 1942, 605). Sodium

It was shown that even when 10 N aqueous hydroxide was used for the hydrolysis of this ester extensive racemisation occurred. The alcohol of highest rotatory power was obtained when the hydrolysis was carried out in alcoholic potash containing about 2% of water.

Hydrolysis with alkyl-oxygen fission received strong confirmation from the other reactions of the ester and of the alcohol, the most striking being:
(1) the ease and completeness of formation of 3,5-\textit{p}-methoxybenzhydryl chloride by the action of dilute concentrated hydrochloric acid on the alcohol, its esters and others.

(II) the formation of 3,5-\textit{p}-methoxybenzhydryl-\textit{p}-tolyl sulphone when acid \textit{p}-toluenesulphinate was added to an aqueous solution of the sodium salt of 3,5-\textit{p}-methoxybenzhydryl hydrogen phthalate.

(iii) the separation of the neutral ester, 3,5-\textit{p}-methoxybenzhydryl phthalate, from a solution of the acid phthalic ester in an equimolecular proportion of dilute sodium hydroxide.

The optically active alcohol, on trituration with cold concentrated hydrochloric acid or on treatment with thionyl chloride and pyridine, gave by either procedure the \textit{dl}-chloride; and on heating with water became racemised without undergoing chemical decomposition.

The optically active hydrogen phthalate, on trituration with cold concentrated hydrochloric acid, gave the \textit{dl}-chloride; on warming with methyl alcohol, it gave \textit{dl}-\textit{p}-methoxybenzhydryl methyl ether; and on dissolving in an equimolecular proportion of dilute sodium hydroxide, it reacted with an aqueous solution of sodium \textit{p}-toluenesulphinate to give \textit{dl}-\textit{p}-tolyl-\textit{p}-methoxybenzhydryl sulphone. The racemisation involved in all these reactions is clear evidence that alkyl-oxygen fission had occurred.

It was further reported that when the optically active hydrogen phthalate was dissolved in 0.15M sodium hydroxide (1 Vol.) there separated from the solution an oil which was separated into \textit{p}-methoxybenzhydryl of low dehydrogenation and dehydrogenation \textit{dl}-\textit{p}-methoxybenzhydryl phthalate. Hydrolysis of this neutral ester with alcoholic sodium hydroxide gave dehydrogenation \textit{dl}-\textit{p}-methoxybenzhydryl
with approximately half the rotatory power of the optically pure alcohol. From these results, it appears that one of the p-methoxy-benzhydrol radicals has been through a phase of ionic-fission during the formation of the neutral ester:

$$2 \overset{\text{COOR}(\text{Na})}{\text{COONa}} = \overset{\text{COOR}(\text{Na})}{\text{COOR} + \text{COONa}}$$

On the basis of the available experimental data, it is now evident that hydrolysis of carboxylic esters is no simple reaction; for in several instances two distinct and concurrent mechanisms can be observed, each predominating under certain experimental conditions. These two mechanisms have been discussed in a recent authoritative review of the subject by Day and Ingold (Trans. Faraday Soc., 37, 656). Throughout the discussion the terms "Unimolecular" and "Bimolecular" refer exclusively to the mechanism of the controlling stage of the reaction concerned and not to the overall kinetics.

The mechanism of bimolecular basic hydrolysis was first discussed in detail by Lowry (J.C.S., 1925, 127, 1330), who formulated the reaction thus:

$$R-C-OR_1 + OH^- \rightarrow R-C-OR_1 \quad (\text{i})$$

$$R-C-OR_1 + H_2O \rightarrow R-C-OR_1 + OH^- \quad (\text{ii})$$

$$R-C+OR_1 \rightarrow R-COOH + R_1OH \quad (\text{iii})$$

$$R-COOH + OH^- \rightarrow R-CO^- + H_2O \quad (\text{iv})$$
The postulated mechanism is in harmony with the view that initial attack is by hydroxyl ion on the unsaturated carbon atom of the ester molecule; von Eechmann (Ber., 1898, 31, 503) actually isolated a binary addition-product of ethyl benzoate and sodium methoxide, which he formulated thus:

\[
\text{ONa} \\
\text{C}_6\text{H}_5 - \text{C} - \text{OCH}_3 \\
\text{O} \text{C}_2\text{H}_5
\]

The binary addition-product is assured to react with a molecule of water to form a bipolar ion, which then breaks down in the manner indicated in stage (II'). This involves the rupture of the middle bond of the bipolar ion, the covalency being converted into an electrovalency with the simultaneous neutralisation of the changes on the two residues. The final stage consists in the neutralisation of the alkali with the acid formed in the preceding stage of the hydrolysis. In principle reversible, the reaction is carried to completion in the forward direction on account of the stability of the carboxylate ion. The reaction is visualised as the slow addition of hydroxyl ion to the unsaturated carbon atom of the ester, followed by the rapid addition of a proton to the binary addition-product, and finally the instantaneous rupture of the bipolar ion into the acid and alcohol. It will be observed that at no stage of the hydrolysis is the C-H bond of the ester disturbed, so that if R is asymmetric at the point of attachment its configuration remains unchanged. One of the distinguishing features of this mechanism is
that both the alkali and the water are represented as taking part in
the reaction. The hydroxyl ion acts as a catalyst, for in stage (i)
it functions as a reagent, while in stage (ii) as a product of the
reaction.

Admirably as this view offers an explanation of the observed
facts, it is nevertheless open to some criticism; for, whereas in
acid hydrolysis a molecule of water must be represented in the
equation, basic hydrolysis can be formulated as the reaction of the
ester and alkali only. There is, in addition, no experimental
evidence available to show that the alkali does in fact play the
part of a catalyst rather than of a reagent. Accordingly Foy &
Ingold propose to formulate the mechanism in the following simple
way:

\[
\begin{align*}
RCOOR' + OH & \underset{\text{slow}}{\longrightarrow} RCOOH + OR' \quad (i) \\
RCOOR' + OH & \underset{\text{fast}}{\longrightarrow} RCOOH + OR' \quad (ii) \\
(RCOOH + OR') & \underset{\text{fast}}{\longrightarrow} RCO + R'OH \quad (iii)
\end{align*}
\]

This mechanism is in agreement with all the observed experimental
facts, but leaves out the hypothetical role played by water in the
Leyry mechanism.

It is interesting to note that bimolecular basic hydrolysis
with acyl-oxygen fission can also be regarded as a simple
substitution reaction:
The reaction is visualised as the addition of hydroxyl ion to the ester molecule, with the simultaneous removal of the alkyl-oxy anion. 

The attacking reagent approaches the ester molecule along the line of its axis on the remote side, and simultaneously the alkyl-oxy anion recedes. As the $O - R_1$ bond of the ester is not disturbed, the alkyl radical retains its configuration. Different as this conception appears, on a superficial view, from the preceding one, there is in reality no material difference between them; for, as Iky and Ingold point out, the identity becomes apparent when the expressions (i) and (ii) for the most intensively intermediate states are examined:

\[
\begin{align*}
\text{(i)} & : \quad \underset{\text{HO}}{\underset{\text{C}}{\text{O}}} \quad \text{OR}_1 \\
\text{HO} & : \quad \text{C} \quad \text{OR}_1 \\
\text{(ii)} & : \quad \underset{\text{OH}}{\underset{\text{C}}{\text{O}}} \quad \text{OR}_1
\end{align*}
\]

"These structures differ only in electron distribution and are to be regarded as imperfect representations of a mesomeric system having an intermediate electronic arrangement."

The alternative mechanism, namely hydrolysis with alkyl-oxy anion fission, necessarily involves as a preliminary step the liberation of the planar carbonium cation, $R_1^+$, which then reacts with a molecule of water or with a hydroxyl ion to produce the alcohol:

\[
\begin{align*}
R_1 + H_2O & \quad \xrightarrow{\text{slow}} \quad R_1^+ + H_2O \\
R_1^+ + \text{OH} & \quad \xrightarrow{\text{fast}} \quad R_1^+ \text{OH}_2
\end{align*}
\]
(The various factors that control the mechanism of hydrolysis are considered in detail at a later stage of this discussion). As bond fission usually controls the rate of a reaction, the controlling stage in the above two mechanisms is probably unimolecular. Fission occurs at the alkyl-oxy bond, so that if \( R \) is asymmetric at the point of attachment, the liberated carbanion kation, \( R^+ \), will be effectively planar and racemised in consequence, if \( \beta \)-unsaturated it will be mesomerised. In this type of compound additional support for the unimolecular mechanism is found in the investigation of Burton and Ingold (loc. cit.) in which the tendency of the alkyl group to pass into cationic forms has been demonstrated.

The investigations discussed in this thesis are in continuation of those on \( p \)-methoxybenzydrol and its derivatives. In the reactions of the following secondary alcohols and their derivatives,
in all instances been demonstrated. \(\alpha\)-Naphthylcarbinol has studied in greater detail than the other three alcohols and its resolution into optically active forms by two methods has been described.
Alkyl-Oxygen Fission in Derivatives of α-Naphthylisyl Carbinal.

α-Naphthylisyl carbinal, prepared from a Grignard reagent, is a colourless crystalline solid, soluble in a variety of organic solvents; and its resolution into optically active components, by two methods involving the fractional crystallisation of alkaloidal salts of its hydrogen phthalate and hydrogen succinic esters,\textsuperscript{12} was now described. From the preparative point of view, resolution via the fractional Kistilvaz crystallisation of the alkaloidal salts of the hydrogen succinic ester is to be preferred, the yields of optically active ester being about 65%. Rotatory powers are recorded in Table II.

Optically active α-naphthylisyl carbinal can be readily separated, by fractional crystallisation, from its mixtures with the racemic carbinal. It was found that on recrystallising the partially active carbinal from ether-light petroleum, the optically active form first separates in its characteristic crystalline form of cotton wool-like clusters of needles; on standing the mother liquor the racemic carbinal is then deposited in prismatic crystals. When the procedure is followed carefully, a sharp separation is obtained.

The acid esters (hydrogen phthalate and hydrogen succinates) of the carbinal were prepared by the usual reaction of a molecular proportions of carbinal and acid anhydride in the presence of pyridine. The procedure adopted was a slight modification of that generally employed; for it was found that if the reaction mixture were heated on the steam-bath extensive decomposition of the acid ester occurred, resulting in extremely poor yields. The same remark applies to the other three carbinals examined. Thus molecular proportions of
carbinol, acid anhydride and pyridine when heated on the steam-bath yielded in the case of α-naphthylisocarbinol practically no acid ester, and in the case of γ-methyl-β-formoxybenzhydrol only a 30% yield. It was found that when the reaction is allowed to proceed at room temperature for a period of about 3 days, in the presence of a suitable solvent such as benzene, practically quantitative yields of unrecrystallised esters are obtained, which in spite of their indefinite melting points give perfectly clear solutions in dilution dilute alkali. By recrystallisation, pure esters are obtained in yields of 80% and upwards.

Particular interest attached to optically active α-naphthylisocarbinyl hydrogen phthalate, on account of its great instability. Obtained at first as an oil on decomposing with dilute acid a solution of its brine salt in acetone, it gradually hardens on keeping in the refrigerator, and can then be pulverised to a white powder. This material cannot be recrystallised, even from inert solvents, without undergoing extensive racemisation. At ordinary temperatures it undergoes a remarkable change. It was observed that after a period that varied between two and ten days from one specimen to another, there appeared throughout the powder certain spots of a pasty character that steadily increased in size until the entire mass of phthalate had become affected; the pasty mass then gradually hardened. Throughout this period there was a steady loss in rotatory power, until a value $\left[\alpha\right]_{549}^\circ +4^\circ$ in acetone was reached, after which it remained fairly constant over a period of about 2 months.

It was shown that these changes in its physical appearance were accompanied by the dismutation of the hydrogen phthalate into phthalic
acid and the dipthalate ester, according to the equation:

\[
2 \text{COOR} + \text{COOH} = 2 \text{COOR} + \text{COOH}
\]

The phthalic acid could be isolated by treating the product with chloroform in which phthalic acid remained insoluble; the di-phthalate could be isolated by extracting the product with dilute alkali which dissolved the phthalic acid and any unchanged hydrogen phthalate, leaving the insoluble di-phthalate. (The formation of these di- or neutral esters is discussed elsewhere in this thesis). The rate at which the change occurred varied from one specimen to another. The observations are interesting in that they demonstrate the stability of the migrating cation, \( R^+ \), and the readiness with which it is detached from the molecule of the acid ester. A similar type of phenomenon was reported in the case of \((\pm)\alpha\)-phenyl-\(\gamma\)-methyldiallyl hydrogen phthalate (Kenyon, Partridge, and Phillips, J.C.S., 1937, 207) which at ordinary temperatures and under diminished pressure slowly changed to a pasty mass which resolidified after about 10 days the hydrogen phthalate being at the same time converted into \((\pm)\gamma\)-phenyl-\(\alpha\)-methyldiallyl hydrogen phthalate and its di-analogue. As expected \((\pm)\alpha\)-naphthylisocarbonyl hydrogen phthalate resorbed readily in a variety of organic solvents at room temperature. The results are recorded in Table IV.

The results of the hydrolysis of the optically active acid esters of \(\alpha\)-naphthylisocarbonyl benzoate are summarised in the table below:
From these results it must be concluded that both the acid esters in question undergo hydrolysis with acyl-oxygen fission in alcoholic solution, but that the alternative mechanism comes increasingly into play as the hydrolysing medium becomes more aqueous and less alkaline. The results are therefore in full agreement with those of esters such as p-methoxybenzhydryl hydrogen phthalate, that undergo alkyl-oxygen fission with ease. Hydrolysis with alkyl-oxygen fission is possible, only in esters in which the alkyl group is not very firmly held, and this mechanism therefore receives strong confirmation from the other reactions of the esters and of the carbonyl, in all of which the liberation of the alkyl radical as a carbonium ion has been demonstrated. These reactions are discussed later.

There are several factors that determine whether the hydrolysis of carboxylic esters in alkaline solution will proceed according to the bimolecular or the unimolecular mechanism. For the sake of ready reference these mechanisms are again set out below:

<table>
<thead>
<tr>
<th>Ester</th>
<th>Hydrolysing Medium</th>
<th>Rotatory Power of Carbonyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-) Hydrogen Phthalate</td>
<td>Alcoholic alkali</td>
<td>(-60.6)</td>
</tr>
<tr>
<td>(-) Hydrogen Phthalate</td>
<td>10N aqueous sodium hydroxide</td>
<td>(-29.2)</td>
</tr>
<tr>
<td>(-) Hydrogen Phthalate</td>
<td>0.3N sodium carbonate</td>
<td>(-14.4)</td>
</tr>
<tr>
<td>(+) Hydrogen Sussinate</td>
<td>Alcoholic alkali</td>
<td>60.9</td>
</tr>
<tr>
<td>(+) &quot;</td>
<td>5N aqueous sodium dioxide</td>
<td>25.5</td>
</tr>
</tbody>
</table>

Bi-molecular Hydrolysis with Acyl-Oxygen Fission.
Fimolecular Hydrolysis with Acyl-Oxygen Fission.

\[
\text{R.CO.O}_1 + \text{OH} \xrightarrow{\text{slow}} \text{R} - \text{C} - \text{OH} \xrightarrow{\text{fast}} \text{R.CO}^- + \text{R}_1 \quad \text{(i)}
\]

\[
\text{R} - \text{C} - \text{OH} \xrightarrow{\text{fast}} \text{R.CO}^- + \text{R}_1 \quad \text{(ii)}
\]

\[
\text{R.CO}^- + \text{R}_1 \xrightarrow{\text{fast}} \text{R.CO}^- + \text{R}_1 \text{OH} \quad \text{(iii)}
\]

Unimolecular Hydrolysis with Alkyl-Oxygen Fission.

\[
\text{R.CO}^- \xrightarrow{\text{slow}} \text{R.CO}^- + \text{R}_1 \quad \text{(i)}
\]

\[
\text{R}_1 + \text{H}_2 \xrightarrow{\text{fast}} \text{R}_1 \text{OH} \xrightarrow{\text{slow}} \text{R}_1 \text{OH} \quad \text{(ii)}
\]

\[
\text{R.CO}^- + \text{R}_1 \text{OH} \xrightarrow{\text{fast}} \text{R.CO}^- + \text{R}_1 \text{OH} \quad \text{(iii)}
\]

or

\[
\text{R.CO}^- \xrightarrow{\text{slow}} \text{R.CO}^- + \text{R}_1 \quad \text{(i)}
\]

\[
\text{R}_1 + \text{OH} \xrightarrow{\text{fast}} \text{R}_1 \text{OH} \quad \text{(ii)}
\]

Let it be assumed that, in all instances, the three mechanisms can operate simultaneously - though at different speeds. It is only to be expected that attack by hydroxyl ion on the unsaturated carbon
atom of the ester molecule (as in stage (1) of mechanism I) would exert a powerful influence on the course of the hydrolysis; and in the case of simple aliphatic esters this attack is predominant under all experimental conditions, so that bimolecular basic hydrolysis involving acyl-oxygen fission is the rule. Should the hydroxyl ion concentration of the hydrolysing medium be reduced, so also will the speed of the bimolecular process; and provided the structure of the ester molecule is suitable (as in the esters of $\alpha$-naphthylmethyl carbonyl) might eventually fall below the rate of ionisation of the ester as represented in stages (1) of each of the two possible unimolecular mechanisms. When this happens the unimolecular mechanism becomes predominant and the hydrolysis takes place chiefly according to mechanisms II and III simultaneously. In a neutral solution the mechanism III alone is possible. The importance of the strength of the alkaline solution used is therefore obvious with regard to the mechanism of hydrolysis.

Another factor which influences the mechanism is the nature of the hydrolysing medium. The unimolecular mechanism will clearly be inhibited, and at the same time the bimolecular mechanism will be facilitated, by a solvent which impedes the ionisation of the ester. The precise effect of the solvent upon reaction velocity has not yet been determined, but it will depend in part upon the dielectric constant of the solvent and its power to solvate the ions of the ester. It is likely that water with its high dielectric constant would favour the unimolecular mechanism, while alcohol with its lower dielectric constant would favour the bimolecular mechanism.

These conclusions are in agreement with the experimental results here obtained.
The basic hydrolysis of an insoluble neutral ester is a two phase reaction in which the hydroxyl ion attacks the surface of the ester; the mechanism is necessarily bimolecular and involves acyl-oxygen fission. The unimolecular mechanism implies no such attack by the hydroxyl ion on the ester, which undergoes spontaneous fission; if the ester is stable per se, it is therefore necessary that the hydrolysis be conducted in a medium which dissolves at least some of the ester. From these considerations, it is apparent that in the basic hydrolysis of acid esters, such as those of α-naphthyl isyl carbinal, the function of the hydroxyl ion is not merely that which is indicated in the various mechanisms already discussed: the hydroxyl ion also serves to bring these esters into solution. Two opposing effects may here be noticed, the first of which arises from the difference between the values of the first and the second dissociation constants of dibasic acids. When an acid ester is dissolved in aqueous potassium, e.g.

\[
\begin{align*}
\text{COOR}_\text{COOH} + \text{OH}^- & \rightarrow \text{COOR}_\text{COO}^- + \text{H}_2\text{O} \\
(i) & \quad (ii)
\end{align*}
\]

One result is that the ester (i) of an acid having a certain dissociation constant is converted into ester (ii) of an acid having a lower dissociation constant; that is, the tendency of the radical, R, to ionise is lessened to some extent. The effect is, of course, to favour acyl-oxygen fission. On the other hand, by bringing the ester into solution in a medium such as water, which has a high dielectric constant and solvating power, the tendency towards ionisation of the
radical, $R$, is thereby increased. The effect of this is to favour alkyl-oxygen fission. Which of these two opposing effects is the greater depends largely upon the structure of the alkyl group. In the case of the acid esters of $\alpha$-naphthylethenyl carbinoi experimental results show that the latter effect is the greater.

Essential to the unimolecular mechanism is a sufficient electron-release from the alkyl group of the ester, so as to bring about the necessary weakening of the alkyl-oxy bond and thereby permit the dissociation. Helpful in this respect are $o$- and $p$-substituted alkyl groups, and the methoxy in particular. The readiness with which the methoxy group increases the electron availability at the $o$-position is illustrated in the case of $p$-anisic acid, for example, which has a relatively low dissociation constant as compared with that of benzoic acid. The average value for the dissociation constant ($10^{-5}$) of benzoic acid as recorded by Dippie (Chem. Reviews, 1935, 25, 151) is 6.38, while that of $p$-anisic acid is 3.5.

The strong electron release of the $p$-methoxy group is unfavourable to the dissociation of the acid, thus assisting the left hand side of the equilibrium:

\[
\text{CH}_3\text{O}^-\text{CH}_2\text{O}^\cdot\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{O}^-\text{CH}_2\text{OH}^+ + \text{COO}^- + \text{H}_2\text{O}
\]

But when substituted in the alkyl-group of an ester, the methoxy group will confer greater stability upon the alkyl radical, thus favouring the right hand side of the equilibrium:

\[
\text{CH}_3\text{O}^-\text{CH}_2\text{O}^\cdot\text{OC}^-\text{R} \rightleftharpoons \text{CH}_3\text{O}^-\text{CH}_2\text{OH}^+ + \text{R}^-\text{COO}^- + \text{H}_2\text{O}
\]
Hence, it is that the most conspicuous instances of alkyl-oxygen fission hitherto reported have been encountered in esters, the alkyl groups of which contain suitably placed methoxy groups. Saturated aliphyl groups are usually of a weak electron-repulsive character, as is illustrated in the dissociation constants of the monocarboxylic acids (Dipps, loc. cit.). It has been found (Kharasch and Elenner, J.A.C.S., 54, 674) that this inductive effect of aliphyl groups (to which reference will again be made) is increased by a lengthening of the aliphyl chain and also by progressive substitution of methyl by further methyl groups. Should an aliphyl group be linked to an aromatic system (as in the substituted benzenols herein studied) electronic displacements will be set up and the effect relayed to the 0- and 0- position.

A summary of the reactions of optically active α-naphthlenisyl carbinal and its acid esters is given in the accompanying diagram.

The hydrogen phthalate and hydrogen succinate of α-naphthlenisyl carbinal dissolve in a slight excess of dilute aqueous alkali (0.3N) giving clear solutions, which on standing at room temperature gradually turn turbid and deposit di-α-naphthlenisylearbinyl phthalate and di-α-naphthlenisylearbinyl succinate respectively, as fine bulky crystalline compounds. The dissociation, which takes place according to the equation:

\[
2 COO\text{R} + COONa \rightarrow COO\text{R} + COONa
\]

is one of the most interesting and unusual reactions of the esters of
THE REACTIONS OF 8-NAPHTHYLANISYL CARBINOL

\[ R = \text{structure diagram} \]

\[ \text{dl-ROH} \]

\[ \text{mp } 31^\circ \]

\[ \text{COOR} \]

\[ \text{mp } 151^\circ \]

\[ \text{dl-CH}_2\text{COOR} \]

\[ \text{mp } 125^\circ \]

\[ \text{dl-CH}_2\text{COOH} \]

\[ \text{mp } 62^\circ-63^\circ \]

\[ \text{dl-ROH} \]

\[ \text{mp } 114^\circ-115^\circ \]

\[ \text{dl-ROH} \]

\[ \text{mp } 180^\circ \]

\[ \text{dl-R} \text{OEt} \]

\[ \text{mp } 87^\circ-88^\circ \]

\[ \text{dl-R} \text{OH} \]

\[ \text{mp } 87^\circ-88^\circ \]

\[ \text{dl-ROH} \]

\[ \text{mp } 61^\circ-61.5^\circ \]

\[ \text{dl-R} \text{OME} \]

\[ \text{mp } 58^\circ \]

\[ \text{dl-ROH} \]

\[ \text{mp } 160^\circ-161^\circ \]

\[ \text{dl-ROH} \]

\[ \text{mp } 57^\circ-58^\circ \]

\[ \text{dl-ROH} \]

\[ \text{mp } 144^\circ \]

\[ \text{(-) + dl-ROH} \]

\[ \text{(-) + dl-ROH} \]
secondary alcohols that undergo alkyl-oxygen fission with readiness.

Similar results have been reported in the hydrogen phthalates of \( \mu \)-methoxybenzyipol, \( \alpha \)-methoxybenzhydro, and methyl- and phenyl-piperonyl carbinols. All the neutral esters hitherto prepared by this reaction, however, have been viscous liquids, difficult to obtain in an analytically pure condition. In these investigations attempts have been made to obtain solid neutral esters, capable of purification through recrystallisation. This has been achieved, and the identity of these compounds thereby established conclusively. For the successful preparation of neutral esters, it is essential that very pure materials be used, as small amounts of impurities carried into the unrecrystallised neutral esters inhibit the process of recrystallisation very considerably. In cases where recrystallisation proves troublesome, preliminary extraction with a poor solvent (e.g. light petroleum) is an effective means of eliminating impurities.

The formation of neutral esters from aqueous solutions of the sodium salts of acid esters provides one of the most convincing demonstrations of the unimolecular mechanism in hydrolysis and esterification. This statement might, at first, seem surprising, since the connection between hydrolysis and esterification on the one hand and neutral ester formation on the other might not appear obvious. But an inspection of the equation:

\[
2 \text{COOR} \quad = \quad \text{COOR} + \quad \text{COONa}
\]

suggests that it is essentially the nature of a partial hydrolysis and partial esterification; and the study of neutral ester formation.
from optically active acid esters not only confirms this view
shows that the mechanism is probably unimolecular. Experiments
results show that neutral esters, obtained from the optically
pure acid esters of \( \alpha \)-naphthylanisyl carbinal, yield on
hydrolysis in alcoholic solution, a carbinal the specific
rotation of which is approximately one half of that of the fully
active carbinal. From \((-\alpha\)-naphthylanisyl carbinal hydrogen
phthalate there was obtained a neutral ester with \([\alpha]_{\text{D}}^5 = 24.6^\circ\)
(132; c, 1) in carbon disulphide, which on hydrolysis in alcoholic solution gave a carbinal with \([\alpha]_{\text{D}}^5 = 28.2^\circ\) (1,2; c, 1.5) in carbon
disulphide. Similarly the optically active neutral succinate,
\([\alpha]_{\text{D}}^5 = 28.0^\circ\) (1,2; c, 1.5) in benzene, obtained from \((-\alpha\)-naphthylanisyl carbinal hydrogen succinate, gave on hydrolysis
in alcoholic solution, a carbinal with \([\alpha]_{\text{D}}^5 = 28^\circ\) (1,2; c, 1.5)
in the carbon disulphide. The rotatory powers of these carbinals
is approximately half of that of \((-\alpha\)-naphthylanisyl carbinal
\([\alpha]_{\text{D}}^5 = 60.9^\circ\) (1,2; c, 1.5) in carbon disulphide. From these
results it is inferred that one of the alkyl radicals of each of the
neutral ester molecules concerned has been racemised during the
course of the reaction, and has therefore been through a phase of
ionic fission. The mechanism of the reaction might therefore
be formulated thus:

\[
\begin{align*}
\text{COOR} & \quad \text{COOR} \\
\text{COOH} & \quad \text{COOH}
\end{align*}
\]

\( \text{COOR} + [\text{R}^+] \quad \Rightarrow \quad \text{COOR} \quad \text{COOR}
\]

\[\text{COOR} + [\text{R}^+] \quad \Rightarrow \quad \text{COOR} \quad \text{COOR}\]
and similarly with the hydrogen succinate. The first stage is an equilibrium involving the ionisation of acid ester anion of the sodium salt; the liberated carbonium kation then combines (step 1) with a second acid ester anion to give the neutral ester. The reaction is carried to completion in the forward direction on account of the insolubility of the final product in the aqueous medium. Where R is asymmetric at the point of attachment, the liberated carbonium kation will adopt a planar configuration and become racemised in consequence; hence the neutral ester will contain only one alkyl radical that has retained its configuration, and on hydrolysis in alcoholic solution should give a carbinal with a specific rotation one half of that of the fully active carbinal. If this postulated mechanism is correct, then it at once becomes apparent that the reaction is in effect a partial hydrolysis and partial esterification, the mechanism of each being of the unimolecular type; stage III (i) represents the initial stage of a unimolecular hydrolysis, while stage (ii) represents the final stage of a unimolecular esterification.

Esterification in alkaline solution does appear to be enormous, but it must be remembered that the alkalinity of the solution in these reactions is only slight, so that its influence on the course of the reaction is small in comparison with the other controlling factors, namely the readiness with which the acid esters ionise and the insolubility of the neutral esters in water.

Di-o-naphthylmesysisocarbonyl phthalate is also formed when o-naphthylmesysisocarbonyl hydrogen phthalate is dissolved in chloroform. From the clear solution, at ordinary temperatures, phthalic acid rapidly separates, and after the reaction is complete the neutral ester can be recovered from the chloroform solution. The reaction proceeds according to the equation:
It was found that in the case of the optically active hydrogen phthalate, the recovered neutral ester was optically inactive, as was also the carbimol obtained by the hydrolysis in alcoholic solution of the neutral ester. These results bear interesting comparison with those just described, in which it was shown that, when the reaction was allowed to proceed in aqueous solutions of the sodium salts of the acid esters, only one of the alkyl groups of the neutral ester had been recrystallised. From the aqueous medium the neutral ester is precipitated when only one of the alkyl radicals has been through a phase of ionic fission, and phthalic acid remains in solution as the sodium salt; from chloroform phthalic acid is precipitated, while the neutral ester remains in solution; and both the alkyl radicals undergo ionic fission on account of the continued ionisation of the neutral ester in solution, according to the equilibrium:

\[ \text{COOR} \xrightarrow{\text{COOR}} \text{COOH} + \text{COOH} \]

The formation of the di-\(\alpha\)-naphthylideneindolinyl phthalic in chloroform solution is probably a two stage process, similar to that in aqueous solution, and might be formulated thus:
The reaction is carried to completion in the forward direction on account of the insolubility of phthalic acid in chloroform.

One of the most characteristic reactions of the acid esters of secondary alcohols that undergo alkyl-oxygen fission with readiness is the formation of sulphones. In theoretical yield, on mixing aqueous solutions of the sodium salts of the acid esters and at least one molecular proportion of sodium \( \alpha \)-toluenesulphonate,

\[
\text{COOR} + \text{CH}_3\text{C}_6\text{H}_4\text{SOONa} = \text{CH}_3\text{C}_6\text{H}_4\text{-S-R} + \text{COONa}.
\]

Both the hydrogen phthalate and the hydrogen succinate of \( \alpha \)-naphthyl anisyl carbinol yield \( \alpha \)-toly-\( \alpha \)-naphthylanisyl sulphone by this reaction. It is a sharp melting crystalline solid, which can be recovered unchanged from hot glacial acetic acid after heating with concentrated hydrochloric acid. The optically active hydrogen phthalates and hydrogen succinates of \( \alpha \)-naphthylanisyl carbinol yield optically inactive sulphones, and the inference is that those esters undergo ionic fission in the course of the reaction, involving the transitory existence of the planar carbonium cation. It is possible that the initial product of the reactions is the sulphone, which immediately undergoes an intermolecular rearrangement to the sulphone.
Some support for this view is found in the investigation of Kenyon and Phillips (J.C.S., 1930, 1670) on the rearrangement of (-)phenylmethylcarbinyl p-toluene sulphinic acid into dl-p-tolylphenylmethyl sulphone. The optically active p-toluene sulphonate, a clear liquid prepared by the interaction of l-phenylmethyl carbinol and p-toluene sulphinyl chloride in the presence of pyridine, on heating under reflux with ethyl alcohol containing potassium carbonate, yielded the original carbinol unchanged in rotatory power. But on standing in a closed glass vessel for a few days at room temperature it deposited crystals of the dl-sulphone. The transformation occurs spontaneously and in the absence of reagents. On the other hand, it seems more likely that the liberated \( \alpha \)-naphthylmethylcarbinyl carbinium kation would migrate directly to the lone pair of electrons of the sulphonate ion:

\[
\left[ \begin{array}{c}
\text{R}^+ \\
0
\end{array} \right] + \left[ \begin{array}{c}
\text{O} \\
\text{S} \\
\text{C}_6\text{H}_4\text{CH}_3
\end{array} \right] = \text{CH}_3\text{C}_6\text{H}_4\text{S} : \text{O} : \\
\text{O} : \\
\]

The reaction is complete on account of the insolubility of the sulphone in the aqueous medium and also because of the poor structural stability of these sulphones. The formation of sulphones by the above reaction is similar to the well-known reaction of ethyl halides or methyl sulphates with the salts of sulphinic acids:

\[
\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot\text{Na} + \text{CH}_3\text{X} = \text{CH}_3\cdot\text{C}_6\text{H}_4\text{S} : \text{O} : \\
\text{O} : \\
\text{CH}_3 + \text{NaX}
\]
Methyl halides and methyl sulphate are known to react with fission of the alkyl-halide bond and the alkyl-oxy bond respectively.

The principles underlying the mechanism of replacement, in aliphatic compounds, of groups containing an asymmetric carbon atom have been laid down by Kenyon and Phillips (Trans. Faraday Soc., 1939, 35, 45) and by Hughes, Ingold, et alii (J.C.S., 1937, 1852). Should the entering group become attached to the asymmetric carbon atom before the displaced group becomes detached, then there is inversion of configuration with a small amount of racemisation:

\[ A - X + Y \rightarrow Y + A - X = A - Y + X \]

Inversion results because the attacking reagent approaches the asymmetric carbon atom on the side remote from the group that is displaced. The controlling stage is unimolecular. Should, however, the displaced group become detached before the entering group gets attached, then racemisation is considerable:

\[ A - X \rightarrow A^+ + X^- \]
\[ A^+ + Y^- \rightarrow A - Y \]

This is a two stage process, and the controlling stage is unimolecular.

Any retention of optical activity due to the shielding action of the reacting group would, in this instance, lead to inversion. The unimolecular mechanism is not possible when the bond, \( A - X \), is sufficiently strong.

Thus the occurrence or absence of racemisation provides an important criterion of reaction mechanism.
It has been shown that when $\alpha$-naphthylmethyl carbinol is triturated with concentrated hydrochloric acid optically inactive $\alpha$-naphthylmethyl methyl chloride is obtained. The reaction therefore takes place by the unimolecular mechanism involving the transitory existence of the planar carbonium cation. This is in contrast to the interaction of $1-\beta$-cetanol with hydrogen chloride, for example, to form $\alpha-\beta$-chloro-esters - a reaction which must necessarily proceed according to the bimolecular mechanism:

\[
\text{\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} & \rightarrow \text{CH}_3\text{CH}_2\text{O}^\cdot + \text{HCl}^+ \\
\text{CH}_3\text{CH}_2\text{O}^\cdot + \text{CH}_3\text{CH}_2\text{O}^\cdot & \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{CH}_3\text{CH}_2\text{O}.
\end{align*}}
\]

The acid and neutral esters (phthalates and succinates) readily yield crystalline ethyl and methyl ethers by reaction with ethyl and methyl alcohol respectively. The optically active forms of the esters give optically inactive ethers. Here again it must be inferred that the mechanism of the reaction involves ethyl-oxygen fission with the formation of the planar, resonated carbonium cation:

\[
\text{R.CO.OR}_1 \quad \Rightarrow \quad \text{R.CO}^- + \text{R}_1^+ \\
\text{R}_1^-\cdot\text{O} + \text{R}_1^+ \quad \Rightarrow \quad \text{R}_1^- - \text{O} - \text{H} \\
\text{R.CO}^- + \text{R}_1^- - \text{O} - \text{H} \quad \Rightarrow \quad \text{R}_1^-\text{O}.\text{R}_1 + \text{R.CO.OH}
\]

The equilibrium is displaced in the forward direction because of the excess of alcohol used.
Alkyl-Arylene Fission in Derivatives of \(p\)-Methyl-\(p\)'-methoxybenzhydrol, 
\(p\)-Isopropyl-\(p\)'-methoxybenzhydrol, and \(\alpha\)-Naphthyl-\(o\)-methoxy phenyl carbinal.

\(p\)-Methyl-\(p\)'-methoxybenzhydrol, a crystalline solid, m.p. 61-62°, was prepared by the interaction of anisaldehyde and \(p\)-isopropylmagnesium bromide, and decomposition of the resulting complex with cold ammonium chloride solution. It readily forms a hydrogen phthalic and hydrogen succinic ester, in yield of 90% or more, when allowed to react under mild conditions with the appropriate acid anhydrides in the presence of pyridine. Decreased yields result at higher temperatures, as is shown by the fact that if the reaction mixture is heated on the water-bath, only a 30% yield of the hydrogen phthalic ester is obtained.

The following diagram contains a survey of the reactions of the carbinal and of its esters:

\[ R = \text{[Diagram with molecular structures]} \]
The sodium salt of the hydrogen phthalic ester readily deposits the neutral ester in aqueous solution, the separation being complete after about 20 minutes. It also yields a sulphone by reaction with sodium p-toluene sulphonate in aqueous solution. As both these reactions have been observed only in esters that undergo alkyl-oxygen fission with ease, such as the acid esters of α-naphthylamisyl carbinal, it must be inferred that the ester in question belongs to the same category. In the case of p-methoxybenzhydryl hydrogen phthalate (Hill, Doughty, Venyon and societ, loc. cit.) it was reported that the separation of the neutral ester was complete after about 18 hours, as compared with 20 minutes for p-toly methyl p'-methoxybenzhydryl hydrogen phthalate. When the added effect of the electron-release of the p-methyl group in the latter compound is taken into consideration, the greater speed of reaction of this ester is not unexpected.

The action of dilute aqueous sodium hydroxide (0.3N) on the hydrogen succinate gave a surprising result; for in this instance it was not the neutral ester, but the carbinal, that was deposited on triturating the solid ester with the calculated amount of dilute alkali, at no stage was a clear solution obtained; before the ester had had time to dissolve the crystalline carbinal began rapidly to separate - so readily does hydrolysis take place. This phenomenon has in the meantime been observed by other workers at Battersea Polytechnic. In both neutral ester formation and in hydrolysis in weakly alkaline solution the first stage is presumably inner fission of the ester. But it is difficult to understand why in some instances, the liberated carbonium ion should migrate to give the
neutral ester, while in other instances it should, on formation, react with water to give the monoaacetate and methyl carbinal. Whatever the explanation for these anomalies may be, however, it is very likely that the hydrolysis of the hydrogen succinate of $p$-methyl $p'$-methoxy benzhydryl hydrogen succinate, proceeding as it does in very weakly alkaline solutions and under mild experimental conditions, takes place by the unimolecular mechanism.

Further evidence of alkyl-oxygen fission is obtained by the readiness with which $p$-methoxy methyl-$p'$-methoxybenzhydryl gives the corresponding chloride when titrated with cold concentrated hydrochloric acid, and the corresponding di-ether when heated.

Attempts to resolve the carbinal proceeded on the whole unsatisfactorily. The hydrogen succinate gave a well defined crystalline salt with cinchonidine, which after four recrystallisations from acetone followed by decomposition with dilute acid, yielded an optically inactive hydrogen succinate. The ester did not give crystalline alkaloidal salts with quinine or brucine. The hydrogen phthalate gave a crystalline quinidine salt from acetone which after several recrystallisations and decompositions with dilute acid, yielded a hydrogen phthalic ester of low rotatory power. Further attempts to effect a resolution by this means showed that the separation was irregular and partial. Failure to effect a satisfactory resolution of this carbinal might be ascribed to two causes. It is possible that in the case of the hydrogen succinate, cinchonidine combines with both emetitomorphs to give crystalline salts in which the difference in solubility in acetone is appreciable; while in the case of the quinidine salt or the hydrogen phthalic ester, the difference in
solubility between the two forms is only slight. On the other hand the \( \gamma \)-methyl-\( \alpha \)-methoxybenzhydryl radical may be so labile, that the failure may be due to the continued ionisation and consequent resolution of this radical during the very process of fractional crystallisation of the alkaloidal salts. The resolution of \( \gamma \)-naphthylacryloxybenzhydryl hydrogen phthalate in the solid state has already been noted, and it is not unlikely that the problem of resolving many of these secondary alcohols containing strong electron releasing groups is similar to that of resolving the tertiary alcohols. The ease with which the hydrogen phthalate of \( \gamma \)-methyl-\( \alpha \)-methoxybenzhydryl undergoes alkyl-oxygen fission is confirmed by the readiness with which the partially active ester re-crystallises in various solvents at room temperature. These results are recorded in the table on page 14 of the experimental section.

\( \gamma \)-Isopropyl-\( \alpha \)-methoxybenzhydryl, prepared from a Grignard reagent in a similar way to \( \gamma \)-methyl-\( \alpha \)-methoxybenzhydryl, is a crystalline solid resembling the latter compound in its physical properties. It gives a good yield of the hydrogen phthalic ester when the reaction is allowed to proceed under the mild conditions already described. Alkyl-oxygen fission is shown by (a) the formation of a neutral ester when an aqueous solution of the sodium salt of the hydrogen phthalic ester is kept at ordinary temperature, (b) the formation of a sulfone by the usual reaction of the sodium salt of the hydrogen phthalic ester and sodium toluene sulfinate in aqueous solution, and (c) the ready formation of the corresponding di-ether when the compound is heated.
It is convenient at this stage to examine the effects of the substituted aliphatic groups in the $n$-methyl-$o$-methoxybenzyl and $n$-iso-propyl-$o$-methoxybenzyl reactants. The values of the dipole moments of the earlier nitration of the various homologous series of aliphatic compounds (halides, nitriles, alcohols, etc.) as given by Groves and Sugden (J.C.S., 1937, 152) indicate that aliphyl groups exhibit weak electron-repulsion. The inductive effect of the aliphyl group increases by progressive replacement of hydrogen by further methyl groups, and eventually reaches a limit which varies with the attached group of each homologous series. The results are generally in agreement with the dissociation constants of the saturated aliphatic acids as recorded by Biny (Chem. Reviews, 1939, 25, 151) and with Kharasch and Flanner's comparison (J.A.C.S., 1932, 54, 671) of aliphatic groups extending from methyl to $n$-heptyl, which gave the following order for increasing electron repulsion:

$$\text{CH}_3 < \text{C}_2\text{H}_5 < \text{n-C}_9\text{H}_{17} < \text{n-C}_8\text{H}_{17} < \text{n-C}_7\text{H}_{13}$$

$$\text{iso-C}_8\text{H}_{17} < \text{BR} < \text{C}_9\text{H}_{16}.$$

It has, however, been noticed that when directly linked to an aromatic system the groups, methyl, ethyl, iso-propyl, and tert-butyl often depart from the normal order of their inductive effects - methyl exhibiting a capacity for electron-repulsion superior to that of the other groups. Perhaps the best known examples of this anomalous behaviour of methyl are found in the studies of Le Fevre and collaborators, who have shown that the mono-nitration (J.C.S., 1933, 290) - sulphonation (J.C.S., 1934, 1901) and - halogenation (loc. cit.) of
In a discussion of this subject Laker and Nathan (J.C.S., 1935, 1944) have found it necessary to postulate a new mechanism of electron-release of alkyl groups attached to a conjugate or enolistic system, a mechanism that is distinct from and additional to that which arises from the normal inductive effect. It is suggested that the duplicates of electrons linking carbon to hydrogen in one of the groups, \(-\text{CH}_3\), \(-\text{CH}_2\), and \(-\text{CH}_2\text{H}_2\), come under the influence of the adjacent carbon atom of a conjugate system, giving rise to displacements represented thus:

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}
\]

This effect cannot therefore operate when the attached group is \(-\text{CR}_3\), since this has no hydrogen atom of the necessary type, and it is obviously greater for the methyl group than for the isopropyl, since the former has three hydrogen atoms that can come under the influence of the adjacent carbon atom of a conjugate system, as compared with two hydrogen atoms of the latter. The quantitative laws governing the postulated effect are at present unknown, but from the available experimental data it is concluded that the total electron-release (i.e., inductive effect + postulated effect) is greater in the case of methyl than in the case of isopropyl.

In agreement with these recent conclusions concerning the electron release of alkyl groups attached to an enolistic nucleus, it has also been found in the present investigations that the electron release of the methyl group is greater than that of the isopropyl. The time for the complete separation of the neutral ester from an aqueous solution...
of the sodium salt of \( \mu \)-methyl-\( \mu' \)-methoxybenzhydryl hydrogen phthalate is about 20 minutes, while in the case of \( \mu \)-isopropyl hydrogenbenzhydryl-\( \mu' \)-methoxybenzhydryl hydrogen phthalate it is about 3 hours. As bond-fission usually controls the rate, the controlling stage in neutral ester formation is probably unimolecular; and the greater speed of this stage in the case of \( \mu \)-methyl-\( \mu' \)-methoxybenzhydryl hydrogen phthalate can only be due to the greater electron-release of the \( \mu \)-substituted methyl group in this ester. The method adopted for comparing the speeds of the two reactions concerned can only be regarded as qualitative; difference in the times for the complete separation of the neutral esters is, nevertheless, very noticeable.

\( \alpha \)-\( \alpha \)-dimethoxyphenyl cinnamal is a crystalline solid, prepared by the interaction of \( \alpha \)-methoxybenzaldehyde and \( \alpha \)-naphthyl-\( \beta \)-naphthene bromide and decomposition of the resulting complex with ammonium chloride solution. It gives 95% yields of the hydrogen phthalic and hydrogen succinic esters on reaction, under mild conditions, with the respective acid anhydrides in the presence of pyridine. Both these acid esters yield a crystalline sulphone on reaction with sodium p-toluenesulphinate in aqueous solution. The hydrogen succinate behaves in a manner similar to \( \mu \)-methyl-\( \mu' \)-methoxybenzhydryl hydrogen succinate when dissolved in dilute aqueous alkali, for this treatment leads essentially to hydrolysis and the neutral ester is not the main product of the reaction. The readiness with which the hydrolysis takes place in a practically neutral solution suggests that the mechanism is unimolecular. The hydrogen phthalate gives a neutral ester when dissolved in dilute alkali. The cinnamal gives the corresponding
di-ether when heated, and the chloride on reaction with cold concentrated hydrochloric acid. The chloride reacts with sodium p-toluene sulphonate in aqueous acetone to yield the sulphone. The reaction of the carbinol and its derivatives which are summarised in the accompanying scheme are therefore, in full agreement with those of the other alcohols and their derivatives, which react with alkyl-oxygen fission.

\[
R = \text{Scheme Image}
\]

On the basis of the available experimental data, carboxylic esters may now be divided into four classes. To the first of these belong the simple aliphatic esters which react with acyl-oxygen fission only. Next are esters, such as the substituted alkyl esters, which react with alkyl-oxygen fission under appropriate conditions. In the esters of the silylalkyl carbinols the tendency to acyl alkyl-oxygen fission is very pronounced and this is the usual mechanism involved in their reactions. Finally come the esters of tertiary alcohols...
which probably react with alkyl-oxygen fission only. The classification is only an approximate one, and the distinction between the members of one class of ester and of another is often blurred. Thus the esters of phenylmethyl carbinal and α-naphthylmethyli carbinal tend to react with alkyl-oxygen fission though to a less extent than the esters of the allyl alcohols; they would, therefore, occupy a position between those of the simple aliphatic esters and the esters of the allyl alcohols. Another borderline case is that of benzhydryl hydrogen phthalate which gives a sulphone on reaction with sodium n-toluene sulphinate in aqueous solution, though it does not give a neutral ester when dissolved in dilute alkali; it is probable that this ester would occupy a position between those of the esters of the allyl-alcohols and of the esters of the α-phenylacyl carbinals.
EXPERIMENTAL.

\(-\)-Bromonaphthalene. To a well stirred mixture of 256g. (2 mols.) of naphthalene and 138g. (35c.c.) of carbon tetrachloride, heated on the steam-bath to gentle boiling, was gradually added 354g. (110c.c., 2.2 mols.) of bromine. This required about 8 hours, care being taken that practically no bromine was carried over with the liberated hydrogen bromide. When the addition was complete, the mixture was further heated, with stirring, until the evolution of hydrogen bromide ceased. The carbon tetrachloride was then removed, by distillation from the steam-bath, under slightly diminished pressure. The residue was mixed with 20g. of powdered sodium hydroxide and stirred at 90-100° for 4 hours. After this treatment, the liquid was distilled under diminished pressure, \(-\)-bromonaphthalene passing over at 145-148°/20m.m. Colourless liquid. Yield 295g., 70% of the theoretical amount. The preparation is described in Organic Synthesis, Coll. Vol. I., p. 121.

\(d\)-\(-\)-Naphthylensyl carbinal; A Grignard reagent was prepared by adding a solution of \(-\)-bromonaphthalene (207g.) in ether (400c.c.) to magnesium (24g.) covered with a layer of ether (100c.c.) To get the reaction to start within a reasonable time it was found necessary to use about 1 g. of iodine. Once started, the reaction was maintained at a brisk rate, the addition of the halide taking about 3 hours. To complete the reaction, the
reaction flask was gently heated for a further half hour. The Grignard reagent, which separated as a heavy oil, was brought into solution by the addition of dry benzene (535 c.c.); and to this, after cooling in a freezing mixture, was added during 4 hours, a solution of anisaldehyde (122 c.c. = 0.9 mols.) in ether (200 c.c.) The resulting complex, which remained in solution, was hydrolysed by the slow addition of a cold, saturated solution of ammonium chloride (150 c.c.), the end of the hydrolysis being indicated by the sudden clearing of the solution in the reaction flask. The separated ether-benzene layer was dried with anhydrous potassium carbonate, concentrated to small bulk, and mixed with light petroleum.

_ß_-Naphthylanisyl carbiny1 (152 g. = 60% yield) separated in prisms, m.p. 87°. It can, if necessary, be recrystallised from ether-light petroleum. (Shurakowski, J. Russ. Phys. Chem. Soc., 1909, 41, 1682, gives m.p. 87°).

dl- _ß_-Naphthylanisyl carbiny1 hydrogen phthalate. Finely powdered phthalic anhydride (15 g.) was added to a solution of _ß_-naphthylanisyl carbiny1 (26.5 g.) in benzene (30 c.c.) and pyridine (10 c.c.), and brought into solution by stirring and gently warming. After standing at room temperature for 3 days, the solution which should not have developed a pronounced yellow colour, was diluted with an equal volume of acetone and washed with dilute hydrochloric acid until free from pyridine. From the dried benzene solution, by addition of light petroleum, the acid ester was precipitated as an oil, which rapidly sets to an crystalline mass on keeping in the refrigerator (about 40 g., m.p. 142°-143°). Recrystallisation from benzene yields prisms, m.p. 151° (37 g. = 90% exact yield). Found
by rapid titration with 0.1N NaOH, M=410; C_{26}H_{20}O_{5} requires M=412.

By recrystallisation from acetone, it was obtained in clusters of well-formed prismatic rods, m.p. 85\(^\circ\), which contained one molecular proportion of acetone. (Found by rapid titration, M=473; molecular proportion of acetone. (Found by rapid titration, M=473; C_{29}H_{26}O_{6} requires M=470) The presence of acetone was confirmed by the formation of a 2:4-dinitrophenyl hydrazone (m.p. 128\(^\circ\), alone or mixed with an authentic specimen) when a saturated solution of 2:4-dinitrophenyl hydrazine in alcohol was added to a solution of the ester in alcohol. The m.p. of the crystalline ester, contained in a loosely closed vessel, slowly rose and after some 10 weeks reached 151\(^\circ\).

For the successful preparation of the hydrogen phthalic ester it is essential that the reaction be allowed to proceed under as mild conditions as possible. If the reactants are heated on the steam-bath and the product worked up in the usual manner, there is obtained a mixture which can be separated, by extraction with chloroform, into \(\text{L-\text{-naphtylanisyl phthalic acid and di-\text{-naphtylanisyl phthalate.}}\) It is not possible to purify crude \(\text{-naphtylanisyl hydrogen phthalate.}\) % by extraction with dilute ammonia which brings about immediate dismutation into \(\text{-naphtylanisyl phthalate and phthalic acid.}\)

\((-)\text{L-naphtylanisyl Hydrogen Phthalate:} \) To a solution of the di-ester (103g.) in a mixture of acetone (100c.c.) and ethyl acetate (200c.c.) was added brucine (117g.), and a clear solution obtained by gentle warming and stirring. After standing for two days at room temperature, the brucine salt of the \((-)\)-ester was
deposited as a mass of fine crystals. This was filtered off, and after four recrystallisations from acetone-ethyl acetate was obtained in fine, hard, irregular crystals (100 g., m.p. 129°-130° decomp.). This salt, mixed with twice its weight of acetone, was decomposed with cold dilute hydrochloric acid, when the (−)-acid ester was precipitated as an oil. On keeping it in the refrigerator for some hours, it set to a hard mass, which was pulverised to a fine powder, washed several times with water, and dried in vacuo. The active phthalate so obtained had m.p. 62-63°. (Found by rapid titration with 0.1N, NaOH, Δ-415). Rotatory powers are recorded in Table I. It was not found practicable to recrystallise this ester owing to the readiness with which it racemised in solution.

Racemisation of (−)-C-Naphthylanisyl carbonyl Hydrogen Phthalate in Various Solvents at Room Temperature. The ester is soluble in a variety of organic solvents in which it racemises readily. The results are recorded in Table IV.

Racemisation of (−)-C-Naphthylanisyl carbonyl Hydrogen Phthalate at Room Temperature. The (−)-hydrogen phthale, obtained as a fine white powder on decomposing the brud ner salt, was kept in a stoppered bottle and the specific rotation taking periodically. The following observations were made:

<table>
<thead>
<tr>
<th>Solvent, acetone (1:2; c,2.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (days)</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>14</td>
</tr>
<tr>
<td>39</td>
</tr>
</tbody>
</table>
On the seventh day it was observed that certain parts of the powdered phthalate had assumed a pasty appearance. The parts so affected steadily increased in size until the change had spread throughout the entire mass of the phthalate and only a paste remained. During this period, as the above observations show, there was steady recrystallisation. After four months a specimen of the product was treated with chloroform; it was partially soluble, leaving phthalic acid undissolved. Treatment with dilute alkali, left an insoluble residue, which on hydrolysis yielded dl-α-naphthylanisyl carbimol.

(--)-α-Naphthylanisyl Carbimol. To a solution of the (-)hydrogen phthalate 2g., \([\alpha]_{589}^\circ -58^\circ (1,2; c,1)\) in carbon disulphide—in cold absolute ethanol (120 c.c.) was added sodium hydroxide (0.5c.c., of 50%) and the whole rapidly heated on the steam-bath. After 3 mins, a bulky crystalline precipitate of sodium phthalate had separated. Addition of water resulted in a clear solution from which, on standing overnight, (--)-α-naphthylanisyl carbimol separated in prisms, m.p. 113°-114°. Recrystallisation ether-light petroleum yielded cotton wool-like clusters of needles, m.p. 114-115° (1.1g.); \([\alpha]_{589}^\circ -60.5^\circ (1,2; c,1.5)\) in carbon disulphide.

Hydrolysis of (--)-α-Naphthylanisyl carbimyl Hydrogen Phthalate with Concentrated Aqueous Sodium Hydroxide. The (--)-ester (3g.) was triturated with sodium hydroxide (10c.c. of 10N). The resulting pasty solid was dried in vacuo and extracted with ether. The ether solution was concentrated to small bulk, and completely precipitated with light petrolæum. The light resulting crystalline material (15g. m.p. 80-98°, had \([\alpha]_{589}^\circ -29.2^\circ (1,2; c,1.0)\) in carbon disulphide.
Hydrolysis of (-)-C-Naphthylamisyl carbamyl Hydrogen Phthalate with Dilute Aqueous Sodium Carbonate. The (-)-ester (3g.) was heated under reflux for 30 minutes, with an excess of 0.3N aqueous sodium carbonate. The resulting pasty mass was dried in vacuo, and extracted with ether. The ethereal solution was concentrated to small bulk and completely precipitated with light petroleum. The resulting crystalline material (1.0g), m.p. 72-83°C, had $[\alpha]_{D}^{20}$ -14.4 (1,2; c,1) in carbon disulphide.

(+)-C-Naphthylamisyl Carbinol. The more soluble fractions of the brucine salt on decomposition with dilute hydrochloric acid yielded a highly dextrorotatory hydrogen phthalate as an oil, which on keeping in the refrigerator gradually turned solid (62g.) m.p. 52-54°C. To a solution of this ester (2g.) in absolute ethanol (120c.c.) was added sodium hydroxide (0.5c.c.) and the whole rapidly heated on the steam-bath. After 3 minutes the bulky precipitate of sodium phthalate which had separated was dissolved by the addition of an excess of water. The precipitated carbinol, m.p. 73-76°C, had $[\alpha]_{D}^{20} +42$ (1,2; c,1) in carbon disulphide. It was twice recrystallised from ether-light petroleum, from which it separates in cotton wool like clusters of needles (0.5g.) m.p. 114-115°C, $[\alpha]_{D}^{20} +60.2$ (1,2; c,1.5) in carbon disulphide. The ether-light petroleum mother liquors deposited a second crop of crystals; prisms (0.4g.) m.p. 87°C, which were optically inactive.

Recrystallisation of Dextrorotatory C-Naphthylamisylcarbimyl Hydrogen Phthalate at Room Temperature. The highly dextrorotatory hydrogen phthalate obtained by decomposition of the more soluble fractions of the brucine salt in the experiment just described,
was kept in a stoppered bottle and the specific rotations taken periodically. The following observations were made:

<table>
<thead>
<tr>
<th>Solvent, acetone</th>
<th>(1,2: c,2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (days)</td>
<td>[x]s97</td>
</tr>
<tr>
<td>0</td>
<td>+13.4°</td>
</tr>
<tr>
<td>15</td>
<td>6.8</td>
</tr>
<tr>
<td>43</td>
<td>4.2</td>
</tr>
<tr>
<td>114</td>
<td>4.0</td>
</tr>
</tbody>
</table>

After the second day the powdered hydrogen phthalate had assumed a pasty appearance, and thereafter it gradually hardened. After 4 months a portion of the product when treated with chloroform partly dissolved, leaving phthalic acid insoluble. On treating another portion of the product with dilute aqueous alkali, a part remained insoluble, which on hydrolysis yielded d-naphthylanisyl carbonyl, m.p. 87°.

**dl-α-Naphthylanisylcarbonyl Hydrogen Succinate.** Finely powdered succinic anhydride (10g.) was added to a solution of dl-α-naphthylanisyl carbinol (26.5g.) in benzene (25c.c.) and pyridine (10c.c.) and brought into solution by stirring and gently warming. After standing at room temperature for 3 days, the solution was diluted with an equal volume of acetone and washed with dilute hydrochloric acid until free from pyridine. From the benzene solution the hydrogen succinate rapidly crystallized on cooling in the refrigerator; fine crystals m.p. 120-121° (about 34g., 95% yield). By recrystallization from benzene-light petroleum, dl-α-naphthylanisylcarbonyl hydrogen succinate separates in clusters of prisms,
m.p. 125° (Found by rapid titration with 0.1N NaOH, M, 362; C_{22}H_{20}O_{5}, requires M, 362.4).

(+)-α-Naphthylisylcarbinyl Hydrogen Succinate: Brucine (46g.) was dissolved in a warm solution of the dl-acid succinate (38g.) in acetone (70c.c.) On cooling the clear solution, the brucine salt of (+)-α-naphthylisylcarbinyl hydrogen succinate (39g; m.p. 116-117°) rapidly separated; it was filtered off and thrice recrystallised from the minimum amount of acetone, from which it was obtained in clusters of prisms (30g., m.p. 122-123° decomp.) From the acetone mother-liquors, a further 4g. of the pure salt was obtained. The combined material (34g.), mixed with twice its weight of acetone, was decomposed with dilute hydrochloric acid; addition of water precipitated the (+)-acid succinate as an oil. After extraction with ether and drying _in vacuo_ it was obtained as a hard white mass (12g.) m.p. 55-57°; Found by rapid titration with 0.1N NaOH, M, 367) Specific rotatory powers are recorded in Table II.

(-)-α-Naphthylisylcarbinyl Hydrogen Succinate. Decomposition with dilute acid of the more soluble fractions of the brucine salt yielded an highly laevorotatory acid succinic ester (23g.) To a warm solution of this in acetone (70c.c.), was dissolved cinchonidine (19g.); and from the resulting clear solution, on standing, there rapidly separated a fine crystalline material (40g., m.p. 148-149°). Three recrystallisations from acetone yielded the cinchonidine salt of (-)-α-naphthylisylcarbinyl hydrogen succinate as a mass of fine irregular prisms (30g., m.p. 160°);
the acetone mother-liquors yielded an additional 4g., of the pure salt. This salt (31g.) was decomposed with dilute hydrochloric acid, when \((-\beta)\)-\(\alpha\)-naphthylamisyl carbamyl hydrogen succinate (13g.) was obtained as a paste. This set to a hard mass on cooling in the ice-box. It was then finely powdered, washed with water, and dried in vacuum m.p. 53-55\(^\circ\), \(\mathbf{\text{K.sq.s}}\)-49.9\(^\circ\) (1.2; c,1) in benzene.

Found by rapid titration with 0.1N Na\(\text{OH}\), M 388.

\((\pm)\)-\(\alpha\)-Naphthylamisyl Carbinal. To a solution of the \((\pm)\)-acid succinate (3.6g.) in cold absolute alcohol (150c.c.), sodium hydroxide (2c.c. of 50%) was added and the whole rapidly heated on the steam-bath. After 3 minutes, a bulky precipitate of sodium succinate had separated. Addition of water resulted in a clear solution from which, on standing overnight, \((\pm)\)-\(\alpha\)-naphthylamisyl naphthylamisylcarbinol separated in clusters of prisms, m.p. 112-113\(^\circ\). After three recrystallisations from ether-light petroleum, it was obtained in cotton wool-like clusters of needles, (2.2g.), m.p. 114-115\(^\circ\). After Rotatory powers are recorded in Table III.

\((-\beta)\)-\(\alpha\)-Naphthylamisyl Carbinal. To a solution of the\((-\beta)\)-acid succinate (3.6g.) in cold absolute alcohol (150c.c.), sodium hydroxide (2c.c. of 50%) was added, and the whole rapidly heated on the steam-bath. The bulky precipitate of sodium phthalate which rapidly separated, was dissolved by the addition of water, and from the clear solution so obtained \((-\beta)\)-\(\alpha\)-naphthylamisyl carbinal separated in prisms, m.p. 113-114\(^\circ\). Recrystallisation from ether-
light petroleum yielded cotton-wool like clusters of needles (2.1g.) m.p. 114-115°C.

Hydrolysis of (+)-α-Naphthylcarbonyl Hydrogen Succinate with 5.N Sodium Hydroxide. The (+) ester (3g.) was triturated with sodium hydroxide (20c.c. of 5.N.) and the resulting pasty solid was washed, dried in vacuo and extracted with ether. The ether extracts were concentrated and mixed with light petroleum; the precipitated carbocycl (1.3g.), m.p. 78-90°C, had $[\alpha]_D^5$ $+25.5^0$ (1, 2; c, 1.0) in carbon disulphide.

Action of Dilute Aqueous Sodium Hydroxide on (α) di-α-Naphthylamidocarbonyl Hydrogen Phthalate. A solution of the ester (10g.) in cold dilute sodium hydroxide (81c.c. of 0.3M) turned turbid within 30 minutes, and after 48 hours, had deposited a thick bulky mass of fine crystals. This was filtered off, thoroughly washed with cold water, and dried in vacuo (7.8g., calc. 8.0g.) On re-crystallisation from benzene-cyclo hexane, di-α-naphthylamidocarbonyl phthalate separated in clusters of small nodules, m.p. 187-128°C (decomp.)

(Found: C, 79.7; H, 5.2; 2.772g. for complete hydrogen hydrolysis required 8.50c.c. of N. NaOH, whence equivalent wt. = 326; C$_{44}$H$_{34}$O$_6$ requires C, 80.2; H, 5.2%; equivalent wt., 329).

The aqueous filtrate and washings gave no precipitate with dilute acid - showing that the hydrogen phthalate had been completely decomposed - and on concentration yielded phthalic acid (1.85g., calc. 2.0g.)
(B) (-)-α-Naphthylisocarboxyl Hydrogen Salicylate.

A solution of the (-)-ester (3g.), $[\alpha]_{5893} ^0 = -38^\circ$, (1,2; c,1) in carbon disulphide, in cold sodium hydroxide (10c.c. of 0.3N), after 33 hours, deposited the neutral ester as a mass of fine crystals, which was filtered off, washed with cold water, and dried in vacuo (1.8g.), m.p. 103-103 $^0$; $[\alpha]_{5893} ^0 = 24.6^\circ$ (1,2; c,1) in carbon disulphide. To a solution of this material (0.8g.) in cold absolute alcohol (120c.c.) was added sodium hydroxide (0.5c.c. of 50%), and the whole rapidly heated on the steam-bath for several minutes. The separated sodium phthalate dissolved on addition of an excess of water, and from the resulting clear solution the crystalline carbinol was rapidly deposited, m.p. 73-73 $^0$; $[\alpha]_{5893} ^0 = -28.2^\circ$ (1,2; c, 1.5) in carbon disulphide.

(c) (-)-α-Naphthylisocarboxyl Hydrogen Succinate.

A solution of the (-)-ester (7.3g.); $[\alpha]_{5893} ^0 = 50.2$ after two days, deposited the neutral ester as a bulky precipitate (5.7g., calc. 6.1g.) m.p. 57-58 $^0$, $[\alpha]_{5893} ^0 = -28.0^\circ$ (1,2; c,1) in benzene. To a solution of this material (4g.) in cold absolute alcohol (200c.c.) was added sodium hydroxide (10c.c. of 50%), and the whole rapidly heated on the steam-bath for several minutes. The bulky precipitate of sodium succinate, which separated, dissolved on the addition of an excess of water to the alcoholic solution, and on standing the clear solution the crystalline carbinol was rapidly deposited (3g., m.p. 70-73 $^0$); $[\alpha]_{5893} ^0 = 28.6^\circ$ (1,2; c, 1.5) in carbon disulphide.
This partially active carbinal, on recrystallisation from ether-light petroleum deposited, in the first crop, cotton-wool-like clusters of needles, consisting of almost optically pure (-)-$\alpha$-naphthylcarbinol, (m.p. 112-113°C), $[\alpha]$$_{5893}$ -58.0$^\circ$ (1,2; c, 1.5) in carbon disulphide. The ether-light petroleum mother-liquor on standing, then deposited a second crop of polystatic crystals, m.p. 57$^\circ$, which was optically inactive. The amounts of the optically active and inactive forms recovered were approximately equal (about 1.5g.).

The half recrystallised neutral ester (3g.) for complete hydrolysis required 5.7cc. of 6 N NaOH, hence equivalent wt. 235.5; C$_{46}$H$_{34}$O$_6$ requires equivalent wt. 304.4.

Dismutation of (a) dl-$\alpha$-Naphthylcarboxylic Acid

Phthalate into dl-dl-$\alpha$-Naphthylcarboxylic Phthalate and Phthalic acid in Chloroform Solution. A clear solution of the dil-acid ester (3.25g.) in dry chloroform (30c.c.) was heated under gentle reflux; within 10 mins., phthalic acid began to separate. After the heating had been continued several hours, the acid was filtered off, washed with chloroform, and dried (16c., calc. 1.7g.)

The combined chloroform filtrate and washings were evaporated, and the residual gum on triturating with light petroleum rapidly set to a solid mass. This was pulverised to a fine powder, and on re-crystallisation from benzene - cyclo-hexane, the neutral ester was obtained in clusters of small nodules, (3.45g., calc. 3.3g.), m.p. 127-128$^\circ$ (Second.)
(b) \((-\)-\(\alpha\)-Naphthalane\(\alpha\)carbinyloxy Hydroygen Pthalate into di-di-\(\alpha\)-Naphthalane\(\alpha\)carbinyloxy Pthalate and Pthalic Acid in Chloroform solution."

A solution of the \((-\)- acid ester (4.2g.) in dry chloroform (20c.c.) was kept at room temperature for 2 days. The separated pthalic acid (0.95g., calc. 0.95g.) was filtered off, and from the filtrate there was recovered - in the manner described in the previous experiment - the neutral ester (3.1g., calc. 3.3g., m.p. 123-125\(^\circ\) decompl.), which was optically inactive (1,2; c. 1.5) in carbon disulphide and chloroform.

(c) \(\alpha\)-Naphthalane\(\alpha\)carbinyloxy Hydroygen Succinate into di-di-\(\alpha\)-Naphthalane\(\alpha\)carbinyloxy Succinate and Succinic Acid in Chloroform Solution. A clear solution of the di-acid ester (7.3g.) in dry chloroform (40c.c.) was kept at room temperature for 30 days, and then evaporated to dryness. The partially crystalline residue, on trituration with dilute sodium hydroxide (70c.c. of 0.3M) left an insoluble oily residue (2.4g.) which was mainly the neutral ester.

(Found: by titraton hydrolysis with N, NaOH soln., equiv. wt.: 298.5; calc. 304.4) The alkaline extracts slowly deposited a further amount of the neutral ester (4.0g.) in a finely divided state. This acid ester had suffered only partial dismutation when dissolved in chloroform.

\(\alpha\)\(\alpha\)-Tolyl-\(\alpha\)-Naphthalane\(\alpha\)vinylmethy Sulphone (a) from di-\(\alpha\)-Naphthalane\(\alpha\)carbinyloxy Hydroygen Pthalate. The ester (4.1g.) was dissolved in sodium hydroxide (30c.c. of 0.3M) and the solution immediately filtered through glass-wool into a solution of sodium \(\alpha\)-tolylene-sulphinate (2.2g.) in water (50c.c.). A turbidity began
to appear within 30 mins., and after 2 days the sulphone, which had
separated as a bulky white crystalline mass, was filtered off,
 washed with water, and dried in vacuo. (3.0g., calc. 4.0g.).
Recrystallisation from alcohol yielded clusters of prisms, m.p. 141°
(Found, S, 8.1; C_{25}H_{22}O_{3}S requires 8.8.0).

From the aqueous filtrate, by concentration and acidification,
phthalamic acid was obtained (1.5g., calc. 1.7g.).

(b) From (-)-α-Naphthylisocarbonyl Hydrogen phthalate. The (-)
ester (4.1g.) was dissolved in sodium hydroxide (34c.c. of 0.3N) and
the solution immediately filtered through glass-wool into a solution
of sodium p-toluenesulphonate (2.25g.) in water (50c.c.). After two
days the sulphone was filtered off, washed with water, and dried
(3.8g., calc. 4.0g.). Recrystallisation from alcohol gave prisms
(m.p. 141°), which were optically inactive in chloroform solution
(1,2; c, 2.5).

(c) From (α)-α-Naphthylisocarbonyl Hydrogen Succinate. The α-
ester (3.6g.) was rapidly dissolved in sodium hydroxide (34c.c. of
0.3N) and the solution filtered through glass-wool into a solution
of sodium p-toluenesulphonate (2.25g.) in water (50c.c.). A
turbidity began to appear within 20 mins. After two days the fine
crystalline precipitate (3.8g., calc. 4.0g.) was filtered off,
washed, dried, and recrystallised from alcohol. Prisms, m.p. 141°,
optically inactive in chloroform solution (1,2; c, 2.5).
α-Naphthylisopropyl Ethyl Ether (a) From α-α-Naphthylisopropyl Hydrogen Phthalate. A solution of the ester (4.1g.) in absolute alcohol (20c.c.) was heated under reflux for 6 hours and then set aside for several hours. The ether (2.1g.), which separated in rhombic crystals, was filtered off, and the filtrate evaporated to dryness. The crystalline residue so obtained was separated by extraction with light petroleum into phthalic acid (1.6g., calc. 1.7g.) and a further amount (0.75g.) of the ether (calc. 2.9g.). Recrystallisation from alcohol yielded flat rhombs, m.p. 61.5°. (Found, C, 82.4; H, 7.0; C₂₀H₂₀O₂ requires C, 82.2, H, 7.0%).

(b) From (-)-ester-Naphthylisopropyl Hydrogen Phthalate. A solution of the (-)-ester (2.0g.), [α]₅₈₉₃⁻32.2 (1.2; c,1) in benzene—in absolute alcohol (15c.c.) was left in an open vessel for 10 days. The crystalline residue was separated by extraction with light petroleum into phthalic acid and the ether, m.p. 61-61.5°, which was optically inactive in light petroleum and alcohol (1,2; c,1).

(c) From α-α-Naphthylisopropyl Hydrogen Phthalate. A solution of the α(3.3g.) in absolute alcohol (25c.c.) was heated under reflux for 8 hours. From the evaporated solution there was obtained, by extraction with light petroleum, phthalic acid (0.6g.) and the ether (2.75g.), m.p. 61-61.5°.

(d) From (-)-α-Naphthylisopropyl Hydrogen Phthalate. The partially active ester (3.7g.), [α]₅₈₉₃⁻24.5° (c,1; 1,2) in carbon disulphide, was dissolved in absolute alcohol (25c.c.) and heated
under reflux for 8 hours. Evaporation of the solvent left a crystalline residue which was separated, by extraction with light petroleum, into phthalic acid and the ether, m.p. 61°-61.5°, which was optically inactive in light petroleum and alcohol.(1,2; c,1).

(e) From dl-α-Naphthylanisylcarbethoxy Hydrogen Succinate. The ester (3.6g.) was dissolved in absolute alcohol (25c.c.) and the solution heated under reflux for 3 hours. Evaporation of the solvent left a residue which was separated, by extraction with light petroleum, into succinic acid and the ether (1.4g.) m.p. 61-61.5°.

(f) From (+)-α-Naphthylanisylcarbethoxy Hydrogen Succinate. A solution of the (+)-ester (3.6g.) in absolute alcohol (25c.c.) was heated under reflux for 3 hours. Evaporation of the solvent left a crystalline residue which was separated by extraction with light petroleum into succinic acid and the ether (1.6g.), m.p. 61-61.5°. The ether was optically inactive in light petroleum and alcohol.(1,2; c,1).

(g) From dl-α-Naphthylanisyl Chloride. A solution of α-naphthylanisyl chloride (2.5g.) in absolute alcohol (25c.c.) on keeping at room temperature deposited the ether in flat rhombic f.l. (2.8g.), m.p. 61-61.5°.
\( \text{\textalpha-Naphthylanisylmethyl Methyl Ether:} \) The dl-\( \text{\textalpha-Naphthylanisyl-} \)methyl methyl ether was readily obtained when (i) the (-)-hydrogen phthalate, (ii) the (-)-hydrogen succinate, (iii) the (-)-neutral phthalate, and (iv) the (-)-neutral succinate were heated with methyl alcohol. The ether separates from methyl alcohol in rhombs, m.p. 50° (Found, C, 81.6; H, 6.5; C\(_{19}\)H\(_{18}\)O\(_2\) requires C, 82.0; H, 6.5%).

\( \text{dl-di-\textalpha-Naphthylanisyl methyl Ether.} \) The dl-carbinol (4g.) was heated at 200° for 30 mins, moisture being evolved. Extraction of the cooled mass with ether left an insoluble portion (1.2g.), m.p. 152-154°. Three recrystallisations from ether containing a small proportion of benzene deposited the di-ether in clusters of prisms, m.p. 150-151°. (Found: C, 84.9; H, 5.8; C\(_{36}\)H\(_{30}\)O\(_3\) requires C, 84.7; H, 5.9%). From the ethereal extracts, unchanged carbinol (2.8g.), m.p. 87°, was recovered.

From the (-)-carbinol (2g.), after heating at 200° for 30 mins. and working up in the manner described above, there was obtained the optically inactive di-ether (0.8g.) m.p. 150-151°, and the optically inactive carbinol (1.1g.) m.p. 87°.

\( \text{dl-\textalpha-Naphthylanisylmethyl Chloride.} \) (1) from dl-\( \text{\textalpha-Naphthyl-} \)anisyl Carbinol. The dl-carbinol, when treated with an excess of concentrated hydrochloric acid, was changed into a heavy oil. This was separated, washed with concentrated hydrochloric acid, and dried over lime. It was soluble in warm light petroleum, from which it separated as a transparent oil.
Then 2.01 g. of this material was dissolved in alcohol (p.p.c.) and warmed for several minutes with an excess of NaOH, it neutralised 10.5 c.c. of the alkali; hence equiv. wt. 277.1 (calc. 282.3).

(11) From (+)-α-Naphthyliseryl carbinal. A few grains of the (+)-carbinal, when treated with concentrated hydrochloric acid and worked up in the manner described above, yielded a chloride which was optically inactive (1,2; c, 2.2) in ether.

#### TABLE I.

<table>
<thead>
<tr>
<th>Solvent</th>
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<th>[α]_6438</th>
<th>[α]_5893</th>
<th>[α]_5780</th>
<th>[α]_5461</th>
<th>[α]_4800</th>
<th>[α]_4358</th>
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#### TABLE II.

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Specific rotatory powers of (-)-α-Naphthyliseryl carbinal hydrogen thiolate in various solvents. (1,2; c, 1.00).
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<th>c. t.</th>
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TABLE IV.

Recrystallization of (-)-L-Naphthylaminocarbonyl Hydrogen Sulfonate in Various Solvents at Room Temperature.

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<th>Solvent, (g/1000 c.c.)</th>
<th>CHCl</th>
<th>CHNO₂</th>
<th>CH₂OH</th>
<th>CH₃CHO</th>
<th>CH₃COOH</th>
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<td>2.00</td>
<td>2.20</td>
<td>2.80</td>
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<table>
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<th>TIME (mins)</th>
<th>[α]₁₅₄₃ (°)</th>
<th>TIME (mins)</th>
<th>[α]₁₅₄₃ (°)</th>
<th>TIME (mins)</th>
<th>[α]₁₅₄₃ (°)</th>
<th>TIME (mins)</th>
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<th>TIME (mins)</th>
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<td>-20.9</td>
<td>0</td>
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<tr>
<td>40</td>
<td>22.4</td>
<td>45</td>
<td>16.3</td>
<td>24</td>
<td>11.8</td>
<td>24</td>
<td>12.1</td>
<td>90</td>
<td>6.3</td>
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<tr>
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**dl-p-Methyl-p'-methoxybenzhydrol.** A Grignard reagent was prepared by adding a solution of p-bromotoluene (171g.) in ether (300c.c.) to magnesium (24g.) covered with a layer of ether (100c.c.). The reaction started readily on adding a few crystals of iodine. The halide was added over a period of about 4 hours, and then the reaction flask was gently heated for a further half-hour to complete the reaction. To this reagent, cooled in a freezing mixture, was added during 4 hours, a solution of anisaldehyde (122g., 0.9 mol.) in ether (200c.c.). The resulting complex was hydrolysed with ice and ammonium chloride, and then separated ether layer was hydrolysed with ice and ammonium chloride, and the separated ether layer was washed, dried with anhydrous potassium carbonate, concentrated to small bulk, and mixed with light petroleum. The p-methyl p'-methoxybenzhydrol (170g., 83% yield) was recrystallised from ethyl light petroleum. It can be recrystallised, if necessary, from ether-light petroleum. (Found C, 73.8; H, 7.0; C<sub>H</sub>O requires C, 73.9; H, 7.0%)

**dl-p-Methyl p'-methoxybenzhydrol Hydrogen Phthalate.** Finely powdered phthalic anhydride (15g.) was added to a solution of p-methyl p'-methoxybenzhydrol (23g.) in benzene (20c.c.) and pyridine (10c.c.), and brought into solution by stirring and gently warming. After standing at room temperature for three days, the solution was mixed with an equal volume of acetone and washed with dilute hydrochloric acid until free from pyridine, whereupon the ester rapidly crystallised from the benzene solution. It was removed by filtration, dried, and recrystallised from benzene-light
petroleum. Clusters of needles, m.p. 127-128°. Yield, 34-35 g. = 90-95% of the theoretical. Found by rapid titration with 0.1N NaOH, M = 377.5; C\textsubscript{23}H\textsubscript{20}O\textsubscript{5} requires M, 376.

When molecular proportions of \( \text{\textit{n}-methyl \textit{n}'-methoxybenzhydrol} \), \( \text{\textit{phthalic anhydride}} \), and \( \text{\textit{pyridine}} \) were heated together on the steam bath, and the homogeneous reacting product decomposed with dilute hydrochloric acid, and worked up in the usual way, it was found that extensive decomposition had occurred, and only a 30% yield of the hydrogen phthalate was obtained.

\( \text{\textit{dl\text{-}p\text{-Methyl \textit{n}'-methoxybenzhydrol Hydrogen Succinate}}.} \) Finely divided succinic anhydride (10g.) was added to a solution of \( \text{\textit{\textit{n}-methyl \textit{n}'-methoxybenzhydrol}} \) (23g.) in benzene (12c.c.) and pyridine (20c.c.), and brought into solution by very gentle warming. After standing at room temperature for three days, the solution was mixed with an equal volume of acetone and washed with dilute hydrochloric acid until free from pyridine. In cooling, in an ice bath, the resulting benzene solution, the hydrogen succinate rapidly separated in a mass of spherical clusters of needles. This was filtered off and after drying was recrystallised from ether-light petroleum.

Needles, m.p. 59-60°, yield 30g. = 90% of theory. (Rapid titration with 0.1N NaOH gives M, 306; C\textsubscript{12}H\textsubscript{20}O\textsubscript{5} requires M, 307).

\( \text{\textit{Attempted Resolution of dl\text{-}p\text{-Methyl \textit{n}'-methoxybenzhydrol Hydrogen Succinate}}.} \) To a solution of the dl-ester (15g.) in acetone (30c.c.) was added cinchonidine (15g.) and a clear solution obtained by gentle warming. After keeping in the ice-box overnight, the fine crystalline material (10g.) was filtered off and recrystallised four times from
acetone. Fine irregular crystals (12g., m.p. 140-141°). This salt, mixed with twice its weight of acetone, was decomposed with cold dilute hydrochloric acid, and the precipitated oil, on cooling, set to a hard mass, which was found to be optically inactive in chloroform, carbon disulfide, and ether (l.c.; c, 1.0). The hydrogen succinate, obtained by decomposition of the cinchonidine salt in the more soluble acetone fractions, was also found to be optically inactive.

The ester failed to give crystalline salts with quinidine and brucine.

**Partial Resolution of dl-p-Methyl p'-Nitrophenylhydroyl Hydrogen Phthalate.** To a solution of the dl-ester (19g.) in acetone (40c.c.) was added quinidine (18g.), and a clear solution obtained by gentle warming. The crystalline material (21g.) which separated overnight was removed by filtration, and thrice recrystallised from the minimum amount of acetone. Decomposition of a portion of the quinidine salt, at this stage, yielded a hydrogen phthalate of low rotatory power, $[\alpha]_{D}^{293} = -3.2^\circ$ (1.0; c, 1.5) in acetone. Further recrystallisations of the quinidine salt, improved the rotatory power only slightly; $[\alpha]_{D}^{293} = -11.7^\circ$ (1.0; c, 1.5) in acetone. Recrystallisation of this partially active hydrogen phthalate at room temperature in various solvents are recorded below:
Further attempts to resolve the hydrogen phthalate by the fractional crystallisation of the quinidine salt showed that the separation was irregular and on the whole unsatisfactory.

### Action of Dilute Aqueous Sodium Hydroxide on (a) dl-p-Methyl p'-Methoxybenzhydryl Hydrogen Phthalate

A solution of the ester (7.2 g) in cold dilute sodium hydroxide (70 c.c. of 0.3N) rapidly turned turbid (10 mins.) and after some 30 mins. the separation of the di-phthalate appeared to be complete. It was filtered off, washed thoroughly with water, and dried. After two recrystallisations from ether-light petroleum, it was obtained in clusters of needles (5.1 g) m.p. 116-117° (Found, C 81.8; H 5.8; C_{20}H_{34}O requires C 82.1; H 5.8%).

From the aqueous filtrate, after acidification and concentration phthalic acid was recovered (1.2 g., calc. 1.5 g.).

### Action of Dilute Aqueous Sodium Hydroxide on (b) dl-p-Methyl p'-Methoxybenzhydryl Hydrogen Succinate

The ester (3.1 g.) was triturated with cold dilute sodium hydroxide (30 c.c. of

<table>
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<tr>
<th>Solvent</th>
<th>Ethyl alcohol</th>
<th>Acetone</th>
<th>Nitromethane</th>
<th>Chloroform</th>
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0.3N), a turbidity appears almost immediately. As the ester dissolved, a mass of fine needles began simultaneously to separate. When the separation was complete, the crystalline material was filtered off, washed with water, and dried in vacuo (3.5 g). Recrystallization from ether-light petroleum yielded needles (3.1 g), m.p. 61° alone or mixed with an authentic specimen of p-methyl p'-methoxybenzhydrol.

Interaction of sodium-\(\alpha\)-toluene sulphonate and \(\alpha\)-\(\alpha\)-methoxybenzhydryl Hydrogen Phthalate. The ester (3.8 g) was dissolved in cold dilute sodium hydroxide (34 c.c. of 0.3N) and rapidly filtered into a solution of sodium \(\alpha\)-toluene sulphonate (2.3 g) in water (50 c.c.) The solution soon went turbid, and began to deposit a fine crystalline material. After 30 min. the separation appeared to be complete, and it was then filtered off and dried (3.8 g, 82). Recrystallization from alcohol yielded prisms, m.p. 93-94° (Found, S 8.8; \(C_9\)H \(O_3\) requires S 8.8). The sulphonate can be recovered unchanged from hot concentrated hydrochloric acid and from glacial acetic acid.

dl-\(\alpha\)-\(\alpha\)-Methyl p'-methoxybenzhydryl Ether. \(\alpha\)-Methyl-p'-methoxybenzhydrol (4g) was heated with a piece of porous pot in an oil bath at 140° C, when a vigorous reaction set in, and bubbles of moisture were evolved. After 10 min. the reaction subsided, and practically ceased after heating for a further 10 min.

The resulting oil was dissolved in the minimum amount of ether, and methyl alcohol was added. On standing over night large well formed clusters of prismatic rods separated (3g, m.p. 101-103°).
Rectification from ether-methyl alcohol raised the m.p. to 103–
104° (Found, C, 82.4; H, 6.8; C\textsubscript{30}H\textsubscript{30}O requires C, 82.1; H, 6.9%).

dl-p-Methyl-p'-methoxybenzhydryl Chloride. p-Methyl-p'-methoxy
benzhydryl (4g.), on trituration with concentrated hydrochloric
acid (25c.c.) changed into a pasty solid, which was dried over lime.
After extraction with light petroleum the chloride was deposited as
a colourless oil on cooling.

When 2.5g. of the chloride was dissolved in alcohol and heated
with an excess of NaOH, it neutralised 10c.c. of the alkali, whence
equiv. wt. = 250 (Calc. 246.3).

Interaction of Sodium p-toluenesulphonate and dl-p-Methyl-p'
Methoxybenzhydryl Chloride. A solution of the chloride (2.5g.) in
acetone (20c.c.) was added to a solution of sodium p-toluenesulphonate
(2.2g) in warm water (10c.c.) and to the whole was added sufficient
acetone to render the whole homogeneous. Sodium chloride was
rapidly deposited, and after 4 hours was filtered off. Addition of
water to the clear filtrate resulted in the separation of prisms
(3.3g.) which after recrystallisation from ethyl-alcohol had m.p.
93-94°, alone or mixed with an authentic specimen of p-tolyl-p-
methyl-p'-methoxybenzhydryl sulphone.

p-Bromocumene. Bromine (107g.) was very slowly added to a well
cooled solution of iodine (10g.) in cumene (80g.), copious
fumes of hydrogen bromide being evolved. After the reaction
was complete, the liquid was washed with dilute alkali until
colourless, and then distilled in a current of steam. It was
dried with calcium chloride, and finally distilled under diminished pressure. Colourless liquid, b.p. 115-117°/20m.m. (116g. = 83% yield). The method is described by Oscar Jacobsen (Ber., 12, 430.)

p-Isopropyl p'-methoxybenzhydryl. A Grignard reagent was prepared by the slow addition of a solution of p-bromocumene (100g.) in ether (250c.c.) to magnesium (12g.) covered with a layer of ether. A few crystals of iodine and gentle warming were required to start the reaction. The addition of the halide took about 4 hours. To the reagent, cooled in a freezing mixture, was added with stirring during 4 hours, a solution of anisaldehyde (61g. = 0.45 mols.) in ether (150c.c.) The resulting complex was decomposed with ice, washed, dried with anhydrous potassium carbonate, concentrated to small bulk and mixed with light petroleum. The p-isopropyl-p'-methoxybenzhydryl (63g. = 55% yield) separated in masses of needles, m.p. 63-64°. It can if necessary, be recrystallised from ether-light petroleum.

p-Isopropyl-p'-methoxybenzhydryl Hydrogen Phthalate. Finely divided phthalic anhydride (15g.) was added to a solution of p-isopropyl-p'-methoxybenzhydryl (26g.) in benzene (200c.c.) and pyridine (100c.c.) and brought into solution by gentle warming. After standing at room temperature for 2-3 days, the solution was mixed with an equal volume of acetone, and thoroughly washed with dilute acid until free from pyridine. The resulting solution of the hydrogen phthalate in benzene was surrounded by a freezing mixture whereupon a mass of needles separated. They were removed by filtration and dried (38g. = 92% yield) Recrystallisation from benzene-light petroleum yielded needles, m.p. 110-111°. (Found by rapid
titration with 0.1N NaOH, $M=398$; $C_{27}H_{24}O_5$ requires $N$, 404).

Action of Dilute Aqueous Sodium Hydroxide on $p$-Isopropyl-$p'$-methoxybenzhydrol Hydrogen Phthalate. The ester (3.1g.) was dissolved in cold dilute sodium hydroxide (68c.c. of 0.3N). A turbidity appeared within 15 minutes, and the neutral ester began to separate in a finely divided state. After 3 hours the separation appeared to be complete. It was filtered off and dried (5.8g., calc. 6.2g.) The material so obtained could not be induced to crystallise. It was readily soluble in warm benzene, from which on addition of light petroleum, it separated as an oil. Then 3g. of the material were hydrolysed with alcoholic potash, 1.9g. of $p$-isopropyl-$p'$-methoxybenzhydrol were obtained (calc. 2.2g.)


The ester (4g.) was dissolved in cold dilute sodium hydroxide (34c.c. of 0.3N) and rapidly filtered into a solution of sodium p-toluene sulphinate (2.2g.) in water (50c.c.) After 2 hours the separation of the sulphone appeared to be complete. It was filtered off and dried. (3.5g., calc. 3.9g.) Three recrystallisations from ethyl alcohol yielded prisms, m.p. 123-124° (Found, S 8.9, $C_{24}H_{20}O_S$ requires S 8.15)

The sulphone can be recovered unchanged from hot glacial acetic acid.

$1$-$p$-Isopropyl-$p'$-methoxybenzhydrol Ether. $p$-Isopropyl-$p'$-methoxybenzhydrol (4g.) was heated with a piece of porous pot in an oil-bath. At 135-140°C a fairly vigorous reaction set in and bubbles of moisture were evolved.
After the evolution had ceased (25 minutes) the resulting oil was cooled, dissolved in ether, filtered, and mixed with methylalcohol. On standing the d1-ether separated in prism (3.2g.) Three recrystallisations from ether-methylalcohol gave the pure material, m.p. 101-102° (Bou d, C, 82.9, H, 7.7, C\(_{34}\)H\(_{30}\)O\(_{3}\) requires C, 82.6, H, 7.7%).

**3-Methoxybenzaldehyde.** This compound is conveniently prepared by the methylation of salicylaldehyde with dimethylsulphate.

(Ber. 1904, 37,2, 2347) Salicylaldehyde (24g.) is treated with dimethyl sulphate (50g.) and boiling dilute sodium hydroxide (200c.c. of 8%), the reaction mixture being shaken. 3-Methoxybenzaldehyde, which separates as an oil on cooling the mixture, is taken up in ether, carefully washed with dilute sodium hydroxide, and dried with calcium chloride. The solvent is then removed by distillation. The residue is finally dried in vacuo, where upon it crystallises in prisms, m.p. 38°. (17g. = 65% yield).

**α-Naphthyl-o-methoxyphenyl Carbinol.** A Grignard reagent was prepared by adding, during 2½ hours - 3 hours, α-bromonaphthalene (207g.) dissolved in ether (400c.c.) to magnesium (24g.) covered with ether (100c.c.) To initiate the reaction, about 1g. of iodine was used, after which the reaction was maintained at a fairly brisk rate. After the addition of the halide, the reaction mixture was heated for a further 30 minutes. The Grignard reagent which separated as a heavy oil, was brought into solution by the addition of dry benzene (535c.c.) (If this step is avoided, the reagent crystallises in a hard mass during the subsequent cooling). To this solution,
cooled in a freezing mixture, was added during 4 hours a solution of O-methoxybenzaldehyde (120g. = 0.9mols.) in ether (200c.c.). The complex separated as a white solid, and was hydrolysed by the addition of cold saturated ammonium chloride solution (about 140c.c.). The end of the 90 hydrolysis was indicated by the sudden appearance of clearing of the solution in the reaction flask. The separated ether-benzene layer was dried with anhydrous potassium carbonate, concentrated to small bulk and mixed with light petroleum. 

3-Naphthyl O-methoxyphenyl carbinitol, 138g. = 88% yield, separated in prisms. It was recrystallised from ether-light petroleum. Prisms, m.p. 107-103° (Found, C, 82.1; H, 5.9; C_{19}H_{16}O_2 requires C, 81.8; H, 6.1%).

3-Naphthyl O-methoxyphenylcarbinyl Hydrogen Phthalate:

Finely divided phthalic anhydride (15g.) was added to a solution of 3-naphthyl O-methoxyphenyl carbinitol (26.5g.) in benzene (30c.c.) and pyridine (10c.c.) and brought into solution by stirring and gentle warming. After standing at room temperature for 3 days, the solution was diluted with an equal volume of acetone and washed with dilute aq tartaric acid till free from pyridine. From the benzene solution, the acid ester rapidly separated as a crystalline solid, m.p. 171°. It was recrystallised from benzene. Prisms, m.p. 174-175° (38g., yield 91%). Found by rapid titration with 0.1N NaOH, N, 413.5; C_{26}H_{20}O_5 requires N, 412).
pyridine (10 c.c.), and brought into solution by stirring and warming. The solution was kept at room temperature for 3 days, then diluted with an equal volume of acetone, and washed with dilute acid until free from pyridine. The acid ester rapidly recrystallised cut from the benzene solution in a finely divided condition, and was recrystallised from benzene-light petroleum. Clusters of prisms, m.p. 128-127°C (34 g.) 90% yield. Found: by rapid titration with 0.1N NaOH, H, 336; C, H, O requires H, 364.

Interaction of Sodium p-toluene sulphinic acid and L-Na-ethyl-o-methoxyphenylcarbonyl Hydrogen Phthalate in Aqueous Solution.

The ester (4.1 g.) was dissolved in cold sodium hydroxide (34 c.c. of 0.3N) and rapidly filtered through glass wool into a solution of sodium p-toluene sulphinic acid (2.2 g.) in water (50 c.c.) After 4 days the separation of the sulphone appeared to be complete. It was filtered off, washed, and dried in vacuo (3.8 g., calc. 4 g.) Recrystallisation from ethyl alcohol gave large irregular crystals m.p. 187-189°C (Found: S, 7.7%, C, H, O, requires S, 8.0%).

Interaction of Sodium p-toluene Sulphinic acid and L-Na-ethyl-o-methoxyphenylcarbonyl Hydrogen Succinate in Aqueous Solution.

The ester (3.8 g.) was dissolved in cold sodium hydroxide (34 c.c.) of 0.3N) and rapidly filtered through glass wool into a solution of sodium-p-toluene sulphinic acid (2.2 g.) in water (50 c.c.) After 5 days the bulky crystalline material was filtered off, washed with cold water, dried in vacuo, and recrystallised from ethyl alcohol. The sulphone was obtained in large, irregular crystals, m.p. 186-189°C (3.8 g.).
Action of Dilute Aqueous Sodium Hydroxide on (a) $\alpha$-Naphthyl-o-methoxyphenylcarbiny1 Hydrogen Phthalate. The ester (10g.) was dissolved in cold sodium hydroxide (21c.c. of 0.3N) and from the clear filtered solution, after 7 days, the bulky crystalline material was filtered off, washed with water, and dried in vacuo. The resulting material was extracted with ether, and the insoluble residue (5.8g.) m.p. 210-215° was thrice recrystallised from benzene-light petroleum from which it was obtained in needles, m.p. 222-223°, alone or mixed with $\alpha$-Naphthyl-o-methoxyphenyl phthalate prepared by heating $\alpha$-naphthyl-o-methoxyphenyl carbinal and phthalic acid. (Found C, 80.2; H, 5.21; $C_{24}H_{34}O_6$ requires C, 80.2; H, 5.2%) From the ethereal extract, $\alpha$-Naphthyl-o-methoxy phenyl carbinal (2g.) was obtained.

(b) $\alpha$-Naphthyl-o-methoxyphenylcarbiny1 Hydrogen Succinate. The ester (7.3g.) was dissolved in cold sodium hydroxide (67c.c. of 0.3N). The clear filtered solution, after 7 days, deposited a crystalline material which was filtered off, washed with water, dried and recrystallised from ether-light petroleum, (4.5g.), m.p. 102-103° alone or mixed with an authentic specimen of $\alpha$-Naphthyl-o-methoxyphenyl carbinal.

Action of Concentrated Hydrochloric Acid on $\alpha$-Naphthyl-o-methoxyphenyl Carbinal. The carbinal (4g.) was triturated with cold concentrated hydrochloric acid (25c.c.) whereupon it changed into a paste which rapidly set to a mass of fine crystals. These were filtered off, washed with concentrated hydrochloric acid, and dried over lime. From light petroleum the chloride was deposited in prisms (4g.)
3.5g. of this material, dissolved in alcohol, neutralised 18.5c.c. of
N.NaOH, whence equiv. wt. = 280.6 (C\textsubscript{18}H\textsubscript{15}O Cl requires equiv. wt.
282.8).

**Action of Concentrated Hydrochloric Acid on \( \alpha \)-naphthyl-o-methoxy-
phenylcarbonyl Phthalate.** The ester (2.5g.) was heated several
hours with an excess of concentrated hydrochloric acid. The residue
(2.5g. calc. 2.8g.) after drying over lime and recrystallisation from
light petrol um had m.p. 142° alone or mixed with an authentic specimen
of \( \alpha \)-naphthyl-o-methoxyphenylmethyl chloride.

From the hydrochloric acid solution there was obtained, by
concentration and evaporation to dryness, phthalic acid 0.6g.,
(calc. 0.8g.).

**Interaction of \( \alpha \)-Naphthyl-o-Methoxyphenylmethyl Chloride and Sodium
p-toluene Sulphinate in Aqueous Acetone.** A solution of the
chloride (2.5g.) in acetone (20c.c.) was added to a solution of
sodium p-toluene sulphinate (2.2g.) in warm water (10c.c.) and to the
mixture was added sufficient acetone to render the whole homogeneous.
Sodium chloride was rapidly deposited, and after 2 days, was filtered
off. Addition of water to the clear filtrate resulted in the
separation of prisms (3.8g.), which on recrystallisation from ethyl
alcohol had m.p. 141°, alone or mixed with an authentic specimen of
p-tolyl-\( \alpha \)-naphthyl-o-methoxyphenylmethyl sulphone.

**\( \alpha \)-naphthyl-o-methoxych enyl methyl Ether.** The esterinoi (4g.)
was heated with a piece of porous pot at 195° when a considerable
evolution of moisture occurred. After 4 minutes the reaction began
to subside with the separation from the melt of an excess of fine crystals. The heating was continued for a further 10 minutes, after which time the reaction had ceased and a residue of hard crystals remained. This was pulverised, extracted with ether, and the residue (3.8 g.) recrystallised from benzene (prisms, m.p. 255-258 °C) and finally from methylene chloride-light petroleum (prisms, 3 g., m.p. 261-262 °C). (Found, C, 84.3; H, 5.6; C₃₆H₇₀ requires C, 84.7; H, 5.9%).