111. *A Development in Olefin Synthesis: The Reaction of Some Allylic Mesitoates with Aliphatic Grignard Reagents.*

By G. M. C. Higgins, B. Saville, and (in part) M. B. Evans.

Since αβ-unsaturated (allylic) alcohols can often be obtained easily as virtually pure stereoisomers, a highly stereoselective synthesis of olefinic hydrocarbons might result if allylic hydroxyl groups could be replaced by alkyl groups without disturbing the geometry about the ethylenic linkage.

Conversion of the alcohol into the corresponding 2,4,6-trimethylbenzoic (mesitoic) ester followed by replacement of the mesitoate group by an alkyl group under attack by a Grignard reagent has now been investigated, particularly with regard to the formation of *trans*-olefins. Especially encouraging are some fairly selective syntheses of hitherto difficultly accessible *trans*-trialkylethylenes. Extensions have also been made to the production of open-chain *trans*-di-isoprenic homologues through reactions of geranyl mesitoate, but when the procedure was applied to neryl mesitoate a very complex mixture of olefins resulted. Although these observations indicate the method to be inappropriate for producing pure *cis*-1,5-trialkylethylenic dienes, they do lend weight to the concept that the allylic mesitoate reacts under the action of the Grignard reagent *via* the intermediacy of allylic carbonium ions.

It appears that the satisfactory retention of the original ethylenic geometry in most reactions studied must reflect a considerable barrier to a racemising rotation about the βγ-bonds of the allylic carbonium systems.

An approach to olefin synthesis which has received little attention is to recognise that αβ-unsaturated alcohols can often be obtained as practically pure stereoisomers *[1] so that if the alcoholic hydroxyl group could be replaced by an alkyl group without altering the geometry about the C=C link then olefinic hydrocarbons of known stereochemistry could be prepared. This would be particularly valuable in the case of trialkylethylenes for which only recently has a moderately stereoselective method [2] been devised.

Arnold and his collaborators [3,4] showed that when allyl 2,4,6-trimethylbenzoate (allyl mesitoate) was treated with ethereal phenylmagnesium bromide the main neutral product was allylbenzene. This indicates that the normal attack by a Grignard reagent at an ester carbonyl group can be prevented by steric hindrance, leaving attack at the electrophilic allyl centre as the only alternative:

$$\mathrm{PhMgBr} + \mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}OCOQ} \longrightarrow \mathrm{PhCH_2{\cdot}CH{:}CH_2} + \mathrm{BrMgOCOQ}$$

It would therefore appear that a useful general olefin synthesis might be developed along the lines:

$$\mathrm{All{\cdot}OH} \xrightarrow{1} \mathrm{All{\cdot}O{\cdot}COQ} \xrightarrow{2} \mathrm{All{\cdot}R}$$

Reagents: 1. Mesitoyl chloride in chloroform–pyridine.
2. RMgX in ether. All = an allylic group. Q = $2,4,6\text{-}\mathrm{Me_3C_6H_2}$.

However, it has been shown [4,5] for a limited number of esters that both the α- and the γ-carbon atom of the allylic group can be attacked by the phenyl group of phenylmagnesium bromide, suggesting the general form of the reaction to be,

$$\mathrm{R'CH{:}CH{\cdot}CHR''O{\cdot}COQ} + \mathrm{PhMgBr} \longrightarrow \begin{array}{l} \nearrow \mathrm{R'CH{:}CH{\cdot}CHR''Ph} + \mathrm{XMgO{\cdot}COQ} \\ \qquad\qquad \text{(I)} \\ \searrow \mathrm{R'CHPh{\cdot}CH{:}CHR''} + \mathrm{XMgO{\cdot}COQ} \\ \qquad\qquad \text{(II)} \end{array}$$

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* Because they are usually made by reducing unsaturated aldehydes or acids which themselves have resulted from eliminations in which tight steric control has operated to produce a high proportion of a preferred configuration at the double bond.

[1] Green and Hickinbottom, *J.*, 1957, 3262.

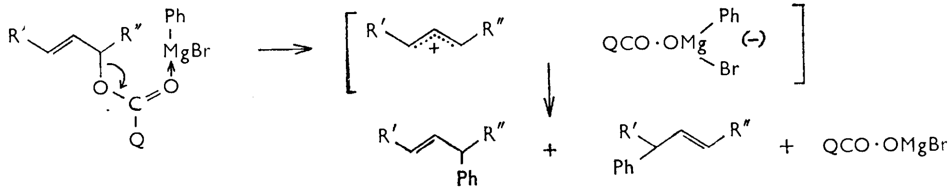
[2] Cornforth, Cornforth, and Mathew, *J.*, 1959, 112, 2539.

[3] Arnold and Liggett, *J. Amer. Chem. Soc.*, 1942, **64**, 2875; 1945, **67**, 337.

[4] Arnold and Searles, *J. Amer. Chem. Soc.*, 1949, **71**, 2021.

[5] Wilson, Roberts, and Young, *J. Amer. Chem. Soc.*, 1949, **71**, 2019.

where the normal (I) and the isoallylic * (II) isomer can both result; in cases studied the normal isomers predominated. Young *et al.*[5] also observed that t-butyl mesitoate readily gave t-butylbenzene on treatment with the reagent, lending strong support to the idea that the allylic esters probably react through the preliminary heterolysis of an ester–Grignard complex to a carbonium ion which then presents two centres to the nucleophilic phenyl groups in leading to the observed alkenylbenzenes.



With the exception of Corey's synthesis[6] of α-santalene, no work in developing these observations has been reported.

Our interest in Arnold's reaction rested on the hypothesis that even though intermediate carbonium ions seemed mechanistically implicated the stereochemistry of the allylic group might be well-retained in the olefinic product of attack at the allylic α-carbon atom. Such a conclusion would follow if the lowering of the C_β–C_γ bond-order in forming an allylic ion,

is insufficient to permit easy racemising rotation about C_β–C_γ before the ion unites with a nucleophile. Thus we set out to study the use of the reaction in general olefin synthesis and the feasibility of stereoselective formation of particular olefins, especially trialkylethylenes.

Suitable allylic alcohols were conveniently converted into corresponding mesitoates by allowing them to react with mesitoyl chloride in pyridine–chloroform, unchanged alcohols being removed from the crude esters, before distillation, by treatment with alumina. The reactivity, with an excess of ~3M-ethereal aliphatic Grignard reagent, of the esters varied with constitution but approximate conditions of reaction were of the order of several hours at reflux temperature.

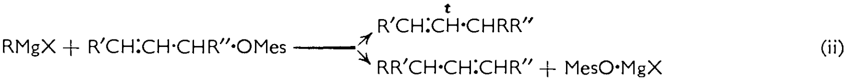
As examples of the formation of Δ^1-olefins, supplementing Arnold's earlier work, we prepared hept-1-ene [equation (i); R = Bu^n, R′ = H, X = Br] in 55% yield from allyl

$$RMgX + CH_2{:}CR'{\cdot}CH_2{\cdot}OMes \longrightarrow CH_2{:}CR'{\cdot}CH_2R + MesO{\cdot}MgX \qquad \text{(i)}$$

(Mes ≡ 2,4,6-trimethylbenzoyl)

mesitoate, and 2-methyloct-1-ene in 14% yield from 2-methylallyl mesitoate [(i); R = n-C_5H_{11}, R′ = Me, X = Cl]. In both cases, consistently with the expected chemistry, no alternative olefinic isomer was found.

With *trans*-dialkylethylenic allylic misitoates interest centred particularly in the degree of configurational retention exhibited by the resulting olefins. Thus, *trans*-but-2-enyl mesitoate and n-butylmagnesium bromide provided a 59% yield of olefin consisting of 10% of 3-methylhept-1-ene and 90% of *trans*-oct-2-ene, containing no trace of the *cis*-isomer. The Δ^1-isomer could be easily removed by careful distillation. These products conform with equation (ii) [R = Bu^n, X = Br, R′ = Me, R″ = H].



$$RMgX + R'CH{:}CH{\cdot}CHR''{\cdot}OMes \longrightarrow \begin{cases} R'CH{:}\overset{t}{C}H{\cdot}CHRR'' \\ RR'CH{\cdot}CH{:}CHR'' + MesO{\cdot}MgX \end{cases} \qquad \text{(ii)}$$

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* The term isoallylic is used here to denote an isomeric pair related as follows, with Y as a mobile group:

$$R^1R^2C{:}CR^3{\cdot}CR^4R^5Y \longleftrightarrow R^1R^2CY{\cdot}CR^3{:}CR^4R^5$$

[6] Corey, Chow, and Scherrer, *J. Amer. Chem. Soc.*, 1957, **79**, 5773.

If R′ and R″ are the same the allyl system would become symmetrically substituted so that the isoallylic and normal products become identical apart from the possibility of the former being in either *cis*- or *trans*-modification. To investigate this point we allowed *trans*-1-methylbut-2-enyl mesitoate (R′ = R = Me) to react with ethylmagnesium bromide (R = Et, X = Br); the olefin (42% yield) produced was shown by g.l.c. to be entirely one component. This is presumably *trans*-4-methylhex-2-ene, the lack of a *cis*-component illustrating that not only must the attack at the α-carbon of the allylic group proceed without disturbing the double-bond's configuration, but also that the allylic shift, occurring if the γ-carbon of the original allylic group is attacked by the nucleophilic ethyl group, takes place to give a *trans*-dialkylethylenic linkage.

Syntheses of Trialkylethylenes.—Two approaches have been used whereby an appropriate Grignard reagent is allowed to react with either a 2,3- or 3,3-disubstituted allyl mesitoate: *i.e.* (isoallylic isomers shown in parentheses)

$$\mathrm{RMgX + R'CH{:}CR''{\cdot}CH_2{\cdot}OMes \longrightarrow R'CH{:}CR''{\cdot}CH_2R\ (R'{\cdot}CHR{\cdot}CR''{:}CH_2)} \tag{iii}$$

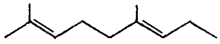
$$\mathrm{RMgX + R'R''C{:}CH{\cdot}CH_2{\cdot}OMes \longrightarrow R'R''C{:}CH{\cdot}CH_2R\ (RR'R''C{\cdot}CH{:}CH_2)} \tag{iv}$$

There would seem ample scope within these two modifications for the synthesis of a wide range of trialkylethylenic structures. Of particular interest to us were cases leading to possible *cis*- and *trans*-trialkylethylenes and the question of how well-retained the allylic configuration would be during the conversion of ester into olefin.

Indicative of reaction by path (iii), 96% pure *trans*-2-methylpent-2-enyl mesitoate [(iii); R′ = Et, R″ = Me] with methylmagnesium iodide (R = Me) gave, in 45% yield, an olefin containing 8·4% of the isoallylic isomer, 2,3-dimethylpent-1-ene, and 91·6% of the expected 3-methylhex-3-ene having a *cis* : *trans* ratio of 6 : 94. This is consistent with a high measure (*ca.* 97—98%) of retention of the original allylic configuration. The identity of the *cis–trans* pair was confirmed through use of the *cis–trans* interconversion catalyst dibenzoyl disulphide,[7] and we conclude further that the American Petroleum Institute's spectrum of *cis*-3-methylhex-3-ene should, in fact, refer to the *trans*-isomer.[8] Similar discrepancies have been noted by other workers.[2,9]

trans-3-Methylhex-2-ene accompanied by 2,3-dimethylpent-1-ene was also prepared in good yield from *trans*-2-methylbut-2-enyl mesitoate [(iii); R′ = R″ = Me] and ethylmagnesium bromide (R = Et).

We have also made a more extensive study of the reactions of methyl-, ethyl-, and isobutyl-magnesium halides with *trans*- and *cis*-3,7-dimethylocta-2,6-dienyl mesitoates (equation iv), this being undertaken in an effort to produce the olefins (III—VIII) containing *cis*- and *trans*-di-isoprenic open-chain systems.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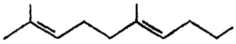
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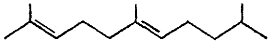
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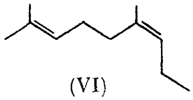
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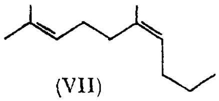
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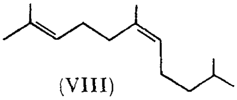
(VIII)

On account of the simpler chemistry it is easier first to consider results obtained by using 99% pure *trans*-ester, geranyl mesitoate. From this the crude olefins (III—V) were obtained in good yields, and contained as contaminants some 2—4% of the *cis*-counterparts (VI—VIII), respectively, together with 9—10% of the corresponding isoallylic isomers (IX—XI) as expected on the basis of opportunities for attack at the 1- and the 3-position of the geranyl carbonium ion by the alkyl groups.

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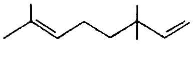
[7] Cunneen, Higgins, and Watson, *J. Polymer Sci.*, 1959, **40**, 1.

[8] A.P.I. Research Project No. 44, No. 1816, April 1956.

[9] Hively, *Analyt. Chem.*, 1963, **35**, 1921.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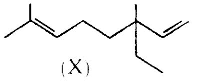
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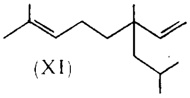
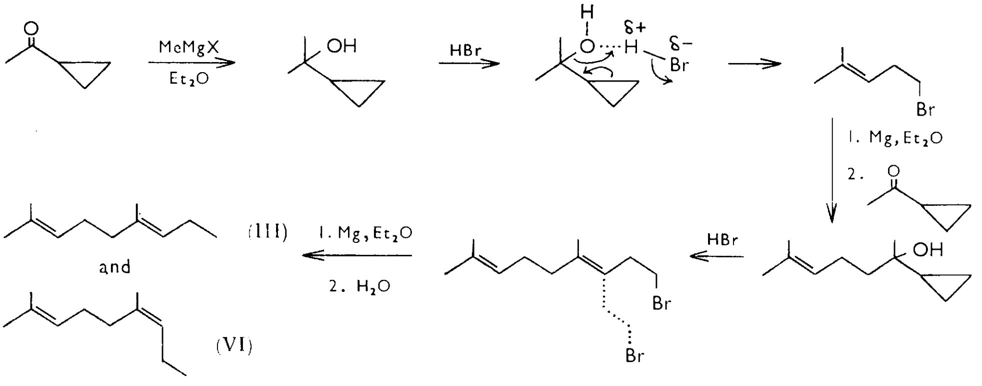

(XI)

These results appear to indicate a very satisfactory degree of retention of the *trans*-configuration in a system where a well-stabilised allylic carbonium ion might be an intermediate.

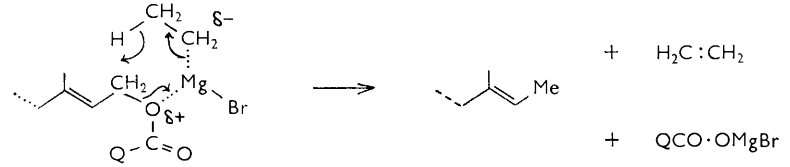
In this work, the identities of *trans*- (III), and *cis*-2,6-dimethylnona-2,6-dienes (VI) were established by an independent synthesis of a 1 : 2 *cis–trans*-mixture by Julia's procedure [10] followed by addition of water at the third Grignard stage:



This preparation gave a pair of dienes chromatographically (g.l.c.) identical with that from the reaction of geranyl mesitoate with methylmagnesium iodide. It was also possible to raise the proportion of the assigned *cis*-component (VI) by heating a substantially *trans*-preparation with a little dibenzoyl disulphide or thiolbenzoic acid, reagents known to cause only *cis–trans* isomerisation of olefins.[7]

The isolation of substantially pure trialkylethylenes (III and IV) from the crude olefinic products of the geranyl ester set the problem of how best to remove the corresponding isoallylic isomers (IX and X). Although this might be accomplished by careful fractionation we have found an attractive alternative in use of the selective reactivity of (IX) or (X) towards bis-(1,2-dimethylpropyl)borane (cf. Brown and Zweifel [11]), and have easily thus obtained olefins containing only 1—2% of isoallylic isomer in the desired dienes which then had *cis* : *trans* ratios of 3—4 : 97—96.

The olefinic products from reaction of geranyl mesitoate with ethylmagnesium bromide contained a small proportion (*ca.* 2% by weight of the total yield of C_{12} dienes) of mainly *trans*-2,6-dimethylocta-2,6-diene; this may have arisen through the ethyl group of the reagent functioning as a donor of hydride ion with simultaneous fragmentation to ethylene as suggested below:



Swain [12] has taken a similar view in explaining the reduction of di-isopropyl ketone by n-propylmagnesium bromide.

The corresponding reactions of aliphatic Grignard reagents with *cis*-3,7-dimethylocta-2,6-dienyl (neryl) mesitoate led to an extremely complex state of affairs. All three Grignard

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[10] Julia, Julia, and Guegan, *Compt. Rend.*, 1959, **248**, 149.

[11] Brown and Zweifel, *J. Amer. Chem. Soc.*, 1960, **82**, 3223; 1961, **83**, 1241.

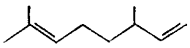
[12] Swain and Boyles, *J. Amer. Chem. Soc.*, 1951, **73**, 870.

reactions were accompanied by copious evolution of gas, presumably C_1—C_4 hydrocarbons, at temperatures below those of the refluxing mixtures. The customary isolation procedures then afforded mesitoic acid nearly quantitatively and olefinic fractions in substantial yields. The olefin mixture was very complex, but analyses were possible by use of advanced quantitative g.l.c. techniques, prediction of retention data, and infrared spectral data. The essential facts are presented in the following Table.[†]

TABLE 1.

Components of the olefinic product of reactions of *cis*-3,7-dimethylocta-2,6-dienyl mesitoate with aliphatic Grignard reagents (RMgX).

No.	Retention [*] index (*I*)	Wt. % of component in total olefinic product for			Structural assignment
		R = Me [†]	R = Et [†]	R = Bu^i [‡]	
1	925		0·5		Unidentified
2	961		0·4	0·2	(a)
3	1010	0·2	1·2	1·5	(b) (*cis*)
4	1020		0·4	0·7	(c) (*trans*)
5	1028	4·2			(d)
6	1035	1·5			Unidentified
7	1054	7·4	19·5	13·9	(e)
8	1067	26·3	25·8	25·0	(f)
9	1088	37·9			(g) (*cis*)
10	1099	11·7	1·8	5·2	(h) (*trans*)
11	1117	4·9			(i)
12	1130	4·6	4·3	7·0	(j)
13	1143		3·2		(k)
14	1150	1·3	4·4	0·2	Unidentified
15	1173		24·3	0·2	(l) (*cis*)
16	1189		6·3		(m) (*trans*)
17	1197		1·9		Unidentified
18	1236		6·3		(n)
19	1279			7·5	(o)
20	1293			1·4	Unidentified
21	1301			8·8	,,
22	1319			13·8	(p) (*cis*)
23	1328			3·0	Unidentified
24	1339			8·8	(q) (*trans*)
25	1371			2·8	(r)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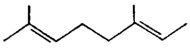
(b)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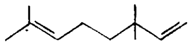
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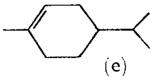
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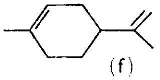
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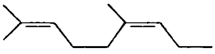
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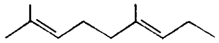
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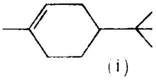
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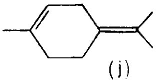
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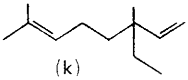
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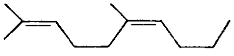
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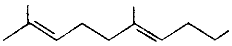
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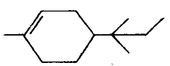
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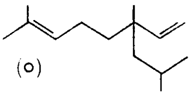
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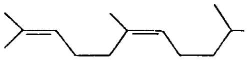
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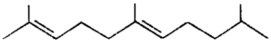
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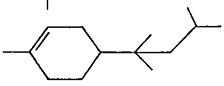
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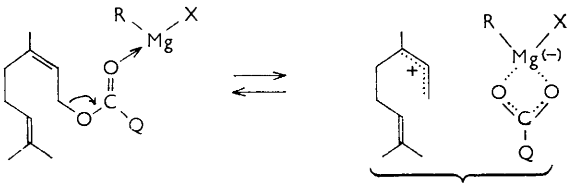
[*] Data for 20% silicone MS 550–Celite column at 100°; see ref. 13 for definition of *I*. [†] Data for reaction in diethyl ether. [‡] Data for reaction in 4 : 1 benzene-tetrahydrofuran (v/v).

[†] A more complete account of this work has been deposited with the library of the Natural Rubber Producers' Research Association, 48—56 Tewin Road, Welwyn Garden City. Interested readers may apply to the librarian for details.

[13] Kovats, *Helv. Chim. Acta*, 1958, **41**, 1915.

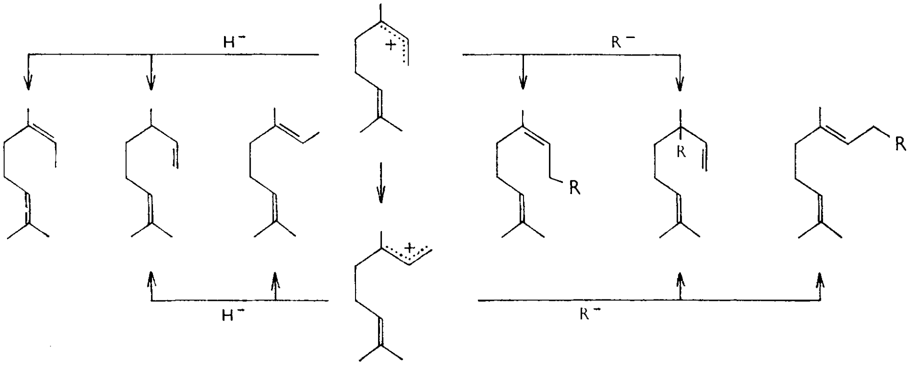
It is apparent from these results, which identify 97·2, 93·2, and 86·5% of the olefins from the reactions of neryl mesitoate with methyl-, ethyl-, and isobutyl-magnesium halides, respectively, that the open-chain dienes (VI—VIII) contribute only one-third, one-quarter, and one-seventh to the total respective olefinic fractions. Clearly, important competing processes have occurred notably to produce cyclic hydrocarbons of the *p*-menthane skeleton.

However, the overall picture can, we believe, be adequately explained in terms of several special opportunities available to an ion-pair (XII) formed by rate-determining heterolysis of a co-ordination compound of neryl mesitoate with the alkylmagnesium halide:



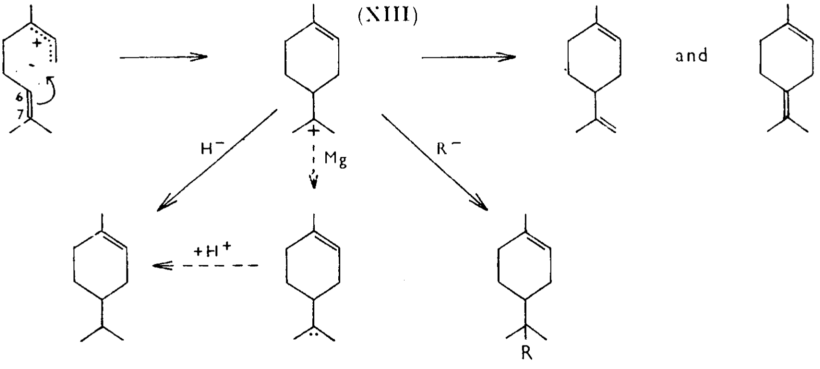
(XII)

Thus, the alkyl group of the complex anion being visualised both as source of R$^-$ and of H$^-$ (*via* fragmentation as suggested earlier in the *trans*-systems), and on the assumption that it is possible in part for the *cis–trans* interconversion barrier in the carbonium ion to be overcome, the following routes for the open-chain products become possible:



Significantly, there is no experimental evidence of loss of a proton from either *cis*- or *trans*-allylic carbonium ions leading to trienes. It is further noteworthy that for R = Et, R$^-$ attack affords 33·8% of the total olefins compared with H$^-$ attack which provides some 2·0%, *i.e.*, an Et$^-$/H$^-$ reactivity of *ca.* 17 obtains. In addition to these processes the original *cis*-allylic carbonium ion might rearrange by intramolecular nucleophilic attack at the primary position by the conformationally well-placed 6,7π-bond to the carbonium ion (XIII) as a new reactive entity which can afford cyclic hydrocarbons in fast consummation steps:

(XIII)

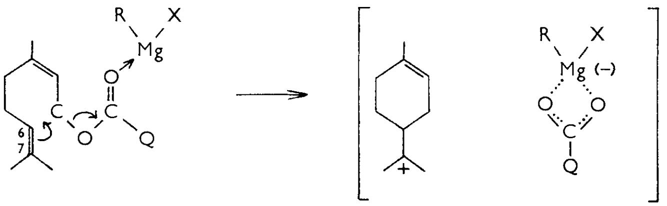


We also indicate by broken arrows a possible scheme whereby carvomenthene can be formed when methylmagnesium iodide is the reagent, since fragmentation of Me^- to H^- and methylene seems unlikely. The magnesium metal still present in the mixture is visualised as supplying an electron pair to the carbonium ion to provide a carbanion which gives carvomenthene by acquiring a proton when reaction is quenched by water during isolation.

The major decomposition route of (XIII), however, is one of proton removal—as shown by the high yields of limonene and α-terpinolene (*f* and *j* in Table 1)—a result in sharp contrast with the complete absence of deprotonation as a mode of reaction of the *allylic* ion precursor (XII). It is also seen that the ratio of Et^-/H^- acquisition by the tertiary carbonium centre is only 0·32 compared with the figure of 17 for the open-chain allylic carbonium ion. This difference seems explicable on steric considerations.

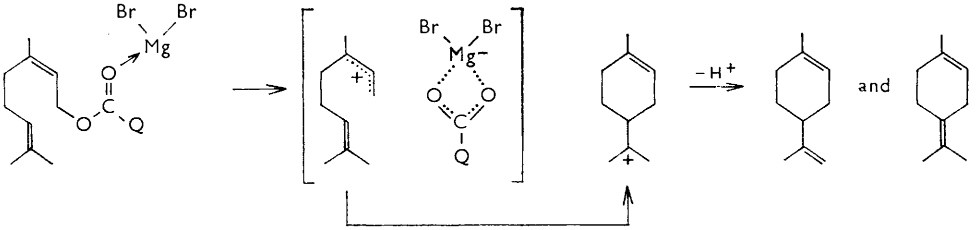
Although these results show that Arnold's reaction cannot usefully be applied to the production of specially constituted *cis*-dienes from neryl mesitoate, they do provide evidence that the reactions, even in ether, stem from virtual carbonium ion intermediates—or at least that the breaking of the allylic–oxygen bonds are considerably ahead of the formation of new bonds by nucleophilic attack. We now present further supporting experimental evidence.

First, to remove the argument that the ion (XIII) might be formed by a direct intramolecular S_N2-type process, such as



we have shown that the ratio of rates of decomposition of neryl and geranyl mesitoate in ethereal magnesium bromide at 25° is 1·3 : 1. Clearly, the 6,7π-bond of the neryl system is not strongly implicated kinetically, as it would be if intramolecular S_N2 were important.

Secondly, if the esters react *via* preliminary C $\curvearrowright$ O ionisation then the nucleophilic character of the Grignard reagent should be of little importance in providing the driving force. One is therefore led to believe that the electrophilic magnesium centre is all-important in co-ordinating to the ester's oxygen atoms to provide a heterolytically reactive complex. If this were so it was thought that magnesium bromide itself—presumably even better as an electrophile than an alkylmagnesium compound—should be able to cause decomposition of neryl ester:



Experiment showed this to be true, mesitoic acid, limonene, and α-terpinolene being isolated from the products.

Finally, it was shown that if, in the Grignard reactions, ether is replaced as solvent by tetrahydrofuran or 1,2-dimethoxyethane, thus co-ordinating to the magnesium centre more firmly, the rates of reactions were markedly lowered. This would be in harmony with the greater difficulty of forming in solution a reactive ester–Grignard reagent complex. However, the solvent change should (following Nyholm's principle [14]) lead to an increase in charge density and nucleophilicity of the alkyl portion of the reagent, and we thus expected an increase in the proportion of open-chain olefins in the products from neryl mesitoate. Although this was shown qualitatively to take place it still did not lead to a useful means of preparing the required *cis*-dienes.

Arnold's reaction therefore provides a useful approach to the synthesis of olefins where stereoselectivity is required, but that since reaction seems to proceed *via* carbonium intermediates one must consider in advance whether obvious rearrangements would be likely to detract from the usefulness of the method, in any particular case.

EXPERIMENTAL

All intermediates were checked by infrared spectroscopic (i.r.) and gas–liquid chromatographic (g.l.c.) techniques to be of high ($\nless$ 98%) purity, unless stated. Light petroleum was redistilled, b. p. 30—40°.

Allylic Alcohols.—Allyl and 2-methylallyl alcohols were fractionated from commercially available materials. Geraniol (99%; well-separated from isomeric nerol by g.l.c. on a 20% neopentyl glycol succinate *–Celite column at 100°) was supplied by Boake Roberts and Co., and was redistilled, b. p. 118°/15 mm. Nerol (*ca.* 98% purity; Boake Roberts) was redistilled, the centre-cut, of b. p. 79—80°/0·001 mm., being used. *trans*-Crotyl alcohol (but-2-en-1-ol) was made by reducing crotonaldehyde (51 g.) with lithium aluminium hydride (9·5 g.) in ether (275 ml.). Isolation by decomposing with ice–water and dilute acid, washing, drying, and distillation afforded the alcohol in a purity of 98·7%. *trans*-1-Methylbut-2-en-1-ol was made from the Grignard reagent [magnesium (14·6 g.) methyl iodide (78 g.), and ether 150 ml.)] and crotonaldehyde (28 g.) at −40°. Decomposition with ice-cold ammonium chloride (40 g.) in water (150 ml.) followed by the usual isolation procedure gave the required alcohol (29 g.), b. p. 36°/11 mm., n_D^{20} 1·4276 (Found: C, 69·7; H, 11·5. Calc. for $C_5H_{10}O$: C, 69·8; H, 11·6%). 2-Methylpent-2-en-1-ol (98% *trans*) was described recently,[15] and *trans*-2-methylbut-2-en-1-ol was prepared in these laboratories by Mr. R. A. Wilkes by reducing tiglaldehyde. Mesitoic acid and mesitoyl chloride were obtained as described in " Organic Syntheses," Coll. Vol. III, pp. 663 and 556 (Note 3), respectively.

Preparation of Allylic Mesitoates.—A typical procedure was as follows: to mesitoyl chloride (32·8 g., 0·18 mole) in ethanol-free chloroform (40 ml.) at 0° was added with stirring during 15 min. a solution of the allylic alcohol (0·20 mole; always in slight excess) in dry pyridine (21·8 g., 0·275 mole) and chloroform (45 ml.). After being kept for 1 hr. at 0° the mixture was set aside overnight at room temperature, and then washed with water (2 × 50 ml.), 5% aqueous hydrochloric acid (50 ml.), and 5% aqueous sodium hydroxide (50 ml.). The product was distilled to remove chloroform (steam-distillation was often convenient), the residue taken up in light petroleum (70 ml.) and passed down a high-capacity column of alumina (40 × 2 cm.) with more petroleum (final eluted volume, 500 ml.), and the solvent removed. This method gave alcohol-free esters, already quite pure, which in some cases could be distilled; overall yields were 90—95% based on the acid chloride. Table 2 summarises our results on these esters.

General Procedure for Olefin Syntheses.—Grignard reagents were prepared in the usual way, about 5% excess of magnesium being used, reaction being completed by boiling under reflux for 1 hr. and adjusting the volume of ether so as to achieve [RMgX] $\sim$ 3M. To the reagent at 20° was then added the requisite allylic mesitoate (*ca.* 0·5—0·75 mole per mole of available RMgX), and the mixture was boiled under reflux with stirring until 2 hr. after precipitation of magnesium salts.

For the geranyl and neryl esters the reaction mixtures boiled smoothly spontaneously for 30 min., and in large-scale preparations caution, in the form of *gradual* additions of ester during 2 hr., was exercised. Isolation of products consisted generally of (i) adding a little water to the well-cooled mixture, (ii) adding sufficient 10% aqueous acetic acid to produce two clear

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* Available from Applied Science Laboratories, Inc., 140 N. Barnard Street, State College, Pennsylvania, U.S.A.

[14] Nyholm, *Proc. Chem. Soc.*, 1961, 279.

[15] Evans, Higgins, Saville, and Watson, *J.*, 1962, 5045.

TABLE 2.

Allylic mesitoates.

Alkenyl group	B. p./mm.	Found (%)		Calc. (%)	
		C	H	C	H
Allyl	82—3°/0·002	76·2	7·7	76·5	7·8
2-Methylallyl	98—100°/0·002	76·9	7·9	77·1	8·2
trans-But-2-enyl	90°/0·001	77·3	8·2	77·1	8·2
trans-1-Methylbut-2-enyl	100°/0·001	77·5	8·8	77·6	8·6
trans-2-Methylpent-2-enyl	118—20°/0·001	77·5	8·8	77·6	8·6
trans-3,7-Dimethylocta-2,6-dienyl *	—	80·1	9·5	80·0	9·33
cis-3,7-Dimethylocta-2,6-dienyl †	—	79·8	9·2	80·0	9·33

* One component only by g.l.c. on 5% neopentyl glycol succinate–Celite at 183°. † 98% one component by g.l.c. on 5% neopentyl glycol succinate-Celite at 183°.

liquid layers, (iii) extraction of the ethereal phase with 5% sodium hydroxide to remove mesitoic acid (subsequently isolated quantitatively by acidifying the alkaline phase), and (iv) careful, efficient, distillation of the dried ethereal phase. At first the whole of the olefin was collected as one fraction for analysis by g.l.c. and i.r. spectroscopy; it was then fractionated as required. In this way the following olefins were obtained.

Hept-1-ene. Allyl mesitoate (0·233 mole) and n-butylmagnesium bromide (0·35 mole) heated for 9·5 hr. at reflux and kept overnight at room temperature, gave mesitoic acid, m. p. and mixed m. p. 152—154°, in 71% yield, and crude hept-1-ene (14·1 g.), b. p. 92—99°, containing 13% of n-octane and hept-1-ene (12·5 g.) in 55% yield. Redistillation gave pure hept-1-ene, b. p. 94°, identified by comparison with A.P.I. spectrum no. 723.

2-Methyloct-1-ene. 2-Methylallyl mesitoate (0·133 mole) and n-pentylmagnesium chloride (0·2 mole) gave, after 7 hr. at reflux, only 14% of mesitoic acid and an olefin, b. p. 86—103°/100 mm. (2·35 g., 14%). In spite of the wide boiling range, due to distillation from a mass of. unchanged ester, the olefin was shown to be one component only by g.l.c. on 20% squalane–celite at 65°. It showed only 1,1-dialkylethylenic unsaturation (bands at 1645 and 890 cm.$^{-1}$).

trans-*Oct-2-ene.* *trans*-But-2-enyl mesitoate (0·20 mole) and n-butylmagnesium bromide (0·32 mole) appeared to have reacted completely after 12 hr. at reflux, and there was obtained mesitoic acid (72%) and an olefin fraction, b. p. 119—123° (13·3 g., 59·5%). This contained (g.l.c. on 5% squalane–brickdust at 65°) two components. One (90% of total) corresponded to the *trans*-component from Phillips' *cis,trans*-oct-2-ene mixture. The smaller component was certainly the isoallylic isomer 3-methylhept-1-ene, as shown by correspondence of spectral absorption at 910 and 990 cm.$^{-1}$ (R·CH:CH_2) with the relative areas of the smaller component throughout several fractions of redistilled olefin. The material finally boiling at 124° was pure *trans*-oct-2-ene. G.l.c. confirmed the absence from all fractions of the *cis*-isomer which was known to be easily separable on our column from the *trans*-compound.

trans-*4-Methylhex-2-ene.* Reaction of *trans*-1-methylbut-2-enyl mesitoate (0·1 mole) with ethylmagnesium bromide (0·19 mole) seemed complete after 4 hr. at reflux, and there was obtained mesitoic acid (91%) and an olefin fraction (3·55 g., 42%), b. p. 86°, n_D^{20} 1·4013 (Found: C, 85·5; H, 14·2. Calc. for C_7H_{14}: C, 85·7; H, 14·3), which gave only one peak on g.l.c. (5% squalane–brickdust at 65°) and which matched the A.P.I. olefin spectroscopically. If a *cis*-isomer had been present it would have been separated on our column.

trans-*3-Methylhex-3-ene.* From 2-methylpent-2-enyl mesitoate (96% *trans*) (0·13 mole) and methylmagnesium iodide (0·2 mole) there was obtained, after 4·5 hr. at reflux and overnight at room temperature, mesitoic acid (81%) and an olefin fraction (5·9 g., 45%), b. p. 90—95°, n_D^{20} 1·4095 (Found: C, 85·3; H, 14·3. C_7H_{14} requires C, 85·7; H, 14·3%). This sample gave an i.r. spectrum identical, apart from increased absorption at 890 cm.$^{-1}$, with the A.P.I. spectrum assigned to *cis*-3-methylhex-3-ene.[8]* G.l.c. (5% squalane–brickdust at room temperature) showed 3 peaks of relative areas 8·4, 5·5, and 86·1, these being changed after the olefin had been heated with 3% dibenzoyl disulphide [7] for 48 hr. at 140°, *in vacuo*, to 8·9, 17·8, and 72·3. This procedure is known to effect only *cis–trans*-olefinic interconversions, and thus we assign

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* We have lately separated by preparative-scale g.l.c. a pure sample of the major component of this olefinic fraction. This gives a spectrum agreeing exactly with that of the A.P.I. *cis*-olefin. We believe therefore that the A.P.I. assignment [8] should refer to the *trans*-olefin.

the second and third eluted components to *cis*- and *trans*-3-methylhex-3-ene. When the olefin was carefully refractionated the material, b. p. 89—90°, was found to be enriched in the component corresponding to the first chromatographic peak, and moreover the relative area of this peak throughout chromatograms of several fractions paralleled i.r. absorption at 890 cm.$^{-1}$. The first component is therefore considered to be 2,3-dimethylpent-1-ene. It was also found as the isoallylic isomer accompanying 3-methylhex-2-ene in the products from a reaction of *trans*-2-methylbut-2-enyl mesitoate and ethylmagnesium bromide performed by Mr. R. A. Wilkes in these laboratories.

The best distilled sample of 3-methylhex-3-ene had b. p. 94—95°, and was 91·9% *trans*-, 5·2% *cis*-, with 2·9% of 2,3-dimethylpent-1-ene.

trans-2,6-*Dimethylnona*-2,6-*diene*. From geranyl mesitoate (0·1 mole) and methylmagnesium iodide (0·2 mole), after 30 min. at reflux and overnight at room temperature, there was obtained an olefin (8·75 g., 58%), b. p. 73—75°/16 mm. (Found: C, 86·2; H, 12·8. Calc. for $C_{11}H_{20}$: C, 86·85; H, 13·15%). G.l.c. (20% silicone MS550–Celite at 100°) showed three components (in elution order I, II, and III) having relative peak areas of 10, 2, and 88. Rational treatment of retention data and supporting i.r. evidence identified component I as 3,3,7-*trimethylocta*-1,6-*diene*. Components II and III are the *cis*- and *trans*-2,6-dimethylnona-2,6-dienes, as shown by the II : III ratio being increased substantially by heating the olefin with 3% dibenzoyl disulphide or thiolbenzoic acid,[7] and by comparison with an independently synthesised stereorandom mixture, as described under the next heading.

In order to remove the 3,3,7-trimethylocta-1,6-diene the crude olefin was distilled to give a fraction, containing 14% of the impurity, of which 6·4 g. was added at 0° to a preparation of " disiamylborane " [11] [from sodium borohydride (0·345 g.), dry diglyme (6 ml.), 2-methylbut-2-ene (2·55 ml.), and boron trifluoride etherate (1·51 ml.)] under dry nitrogen and left overnight. The mixture was treated with 3N-sodium hydroxide (3·63 ml.) and 30% aqueous hydrogen peroxide (3·63 ml.) and, after 30 min., with acetic acid (3 ml.) in water (50 ml.). Extraction with light petroleum gave a liquid which, when washed and dried, was passed with more petrol through a column of alumina (30 × 2 cm.), which retained alcohols. Distillation of the eluate then afforded an olefin (4·0 g., 62·5%), b. p. 72—73°/14 mm., n_D^{20} 1·4489 (Found: C, 86·75; H, 13·25%) which contained 1·8% of the Δ^1-isomer, 2·8% of *cis*- and 95·4% of *trans*-2,6-dimethylnona-2,6-diene.

2,6-*Dimethylnona*-2,6-*diene* (ca. 1 : 2 cis : trans). 1-Bromo-4,8-dimethylnona-3,7-diene was kindly synthesised by Professor Marc Julia (University of Paris).[10]

To magnesium (0·8 g.) was added ethyl bromide (1 ml.) and ether (4 ml.), then the bromodiene (4·6 g.) in ether (20 ml.) was added during 10 min. Reaction was completed by heating under reflux for 30 min., and the mixture was poured on to crushed ice (100 g.) and acetic acid (5 ml.). The ether layer, after being washed with water and 5% aqueous sodium hydroxide, was dried and distilled to give an olefin fraction (2·3 g.), b. p. 67·5—69·0°/12 mm., n_D^{20} 1·4521 (Found: C, 86·4; H, 12·8. Calc. for $C_{11}H_{20}$: C, 86·85; H, 13·15%), which in addition to a small impurity (by g.l.c.) originally present in the bromide had two components, relative proportions 32 : 68, respectively identified as components II and III of the preceding preparation. Hydrogenation of the olefin mixture over platinum–charcoal gave a single saturated hydrocarbon, presumably 2,6-dimethylnonane as expected from saturation of a *cis–trans*-olefin pair.

trans-2,6-*Dimethyldeca*-2,6-*diene*. This was prepared several times in yields of 63—80%, typically from ethylmagnesium bromide (0·55 mole) and geranyl mesitoate (0·367 mole) added carefully during 2 hr., and continuing the heating for a further hour. Of the olefin thus obtained *ca.* 5% boiled at 65—70°/12 mm., and the remainder mainly at 81—85°/12 mm., n_D^{20} 1·4517 (Found: C, 86·7; H, 13·2. Calc. for $C_{12}H_{22}$: C, 86·75; H, 13·25%). The small early fraction contained significant amounts of *trans*- and some *cis*-2,6-dimethylocta-2,6-dienes (*ca.* 2% of total olefin yield) by g.l.c. comparison with authentic samples. The main fraction was substantially a mixture of the expected 3-ethyl-3,7-dimethylocta-1,6-diene (9·0%), and the *cis*- (3·8%) and *trans*- (85·4%) 2,6-dimethyldeca-2,6-dienes, these assignments being reached in a manner similar to that employed for the dimethylnonadienes.

Redistillation and use of " disiamylborane " reduced the level of the isoallylic isomer to about 0·8% giving virtually pure 2,6-dimethyldeca-2,6-diene of *cis* : *trans* ratio 4 : 96. It had b. p. 83—84°/13 mm., n_D^{20} 1·4512 (Found: C, 86·8; H, 13·3%).

2,6,10-*Trimethylundeca*-2,6-*diene*. This was obtained in only moderate yield (30%) from geranyl mesitoate and isobutylmagnesium bromide after 3 hr. at reflux. The crude olefin, b. p. mainly 115—119°/13 mm. (Found: C, 87·1; H, 13·0. Calc. for $C_{13}H_{24}$: C, 86·7; H, 13·3%), was only 68% pure (*cis* : *trans* ratio 5 : 95) and contained the isoallylic isomer (6·7%), much unidentified material, limonene (6%), carvomenthene (3·6%), terpinolene (3·2%), and a little *cis*- and *trans*-2,6-dimethylocta-2,6-diene. The formation of the cyclic hydrocarbons is more typical of reactions of the neryl ester (see Table 1, main text). No attempt was made to isolate a substantially pure olefin.

Reaction of Neryl Mesitoate with Grignard Reagents.—The reagents were prepared at about the 3M concentration level, in ether for methylmagnesium iodide and ethylmagnesium bromide, and in 4 : 1 benzene–tetrahydrofuran for isobutylmagnesium bromide. To a given reagent was added the ester (0·67 mole per mole of available RMgX) during 2 hr. at 25—30°, and the mixture was then stirred under reflux for 1 hr. During all three reactions there was smooth evolution of gas.

Isolation of products, by the usual method, afforded in all cases 96 ± 1% yields of mesitoic acid and olefin fractions as follows: from MeMgI reaction, b. p. 68—71°/13 mm. (Found: C, 86·8; H, 12·85%), 63% yield based on $C_{11}H_{20}$ expected from a simple displacement reaction; from EtMgBr reaction, b. p. 65—85°/11 mm. (Found: C, 87·1; H, 12·8%), 67% yield; from Bu^iMgBr reaction, b. p. 65—110°/14 mm. (Found: C, 87·2; H, 12·8%), 62% yield. Analyses of these fractions were carried out by instrumental techniques (see footnote on p. 710).

Kinetics of Decomposition of Geranyl and Neryl Mesitoates in Ethereal Ethylmagnesium Bromide.—To previously prepared ethereal ethylmagnesium bromide (1·23M; 20 ml.) was added a solution of the ester (3 g.) and n-tetracosane as internal chromatographic standard (*ca.* 1·5 g., accurately weighed) in a total ethereal volume of 30 ml. at 25°. These quantities led to initial concentrations of Grignard reagent (0·5M) and of the ester (0·2M).

At times of up to 4 hr. portions (5 ml.) were removed, added to 6% aqueous acetic acid (5 ml.), and shaken; each organic layer was mixed with n-heptane (2 ml.) and shaken with 5% aqueous sodium hydroxide (10 ml.) before being analysed by g.l.c. (5% neopentyl glycol succinate-Celite at 183°) for ester concentrations. No attempt was made to fit these results to a particular kinetic expression bearing in mind a probable complex reaction order and inevitable solvent losses.

From the data the decomposition half-lives of geranyl and neryl mesitoates were 163 and 125 min., respectively.

Decomposition of Neryl Mesitoate in Ethereal Magnesium Bromide.—To magnesium (0·25 g.) under ether (5 ml.), with ice-cooling, was added dropwise bromine (0·50 ml.). A vigorous reaction took place leaving a little unchanged magnesium. A two-layer system resulted consistent with the reported [16] solubility characteristics of $MgBr_2(Et_2O)_2$. Neryl mesitoate (1·50 g. 0·005 mole) was added in ether (1 ml.) and the two layers became one. The mixture was heated for 45 min. during which time the two-layer system reappeared, clearly indicative of ester decomposition. After cooling the mixture and cautious addition of water, the organic phase gave, by the usual techniques, mesitoic acid (0·52 g., 63·5%) and a residue (0·94 g.) containing (quantitative g.l.c.) unchanged ester, limonene (35%), with some α-terpinolene and a little carvomenthene.

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[16] Seidell, " Solubilities of Inorganic and Metal Organic Compounds," 3rd edn, Vol. 1, Van Nostrand, New York, 1940, p. 937.