Phosphate Esters. Part II.[1] The Formation of Monoterpene Hydrocarbons from Geranyl and Neryl Diphenyl Phosphates

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The spontaneous decomposition of geranyl and neryl diphenyl phosphates in an inert solvent is shown to give a complex mixture of acyclic and cyclic terpene hydrocarbons. The constituents of the mixture have been identified, and possible mechanisms for their formation are discussed.

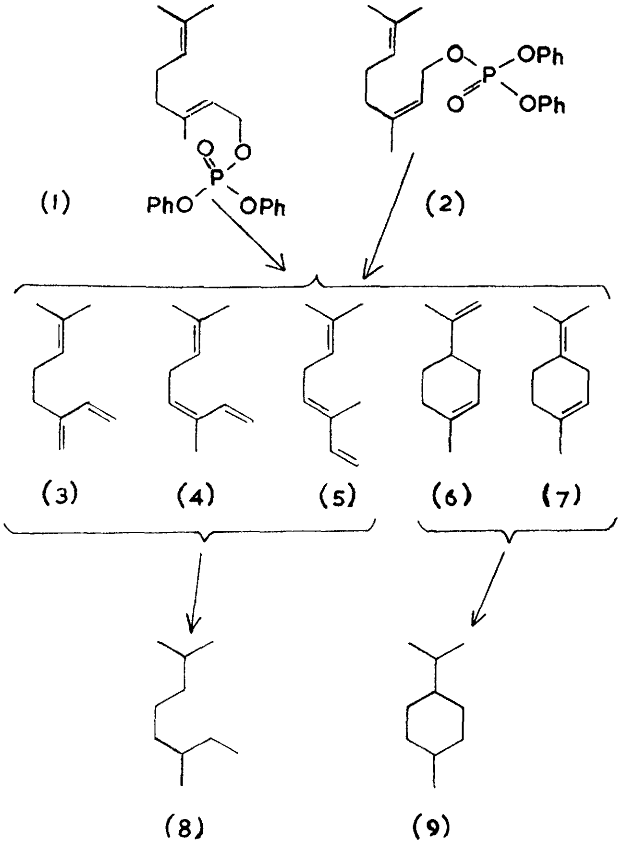
Terpene hydrocarbons are also formed when the two diphenyl phosphate esters are reduced with sodium borohydride. Reaction between allylic diphenyl phosphates and aryl Grignard reagents gives allylbenzenes in high yield.

A COMMON biosynthetic reaction in the terpene field involves attack by a nucleophilic reagent on an electron-deficient carbon atom such as that present in an allyl pyrophosphate ester. It has been suggested[2] that the chief function of the magnesium ion, which is almost invariably associated with such enzymatic reactions involving pyrophosphate, is to 'neutralise' the negative charges which would exist on the pyrophosphate at biological pH values and thus give this group some of the character of a fully esterified phosphate.

In Part I[1] we described the reaction between phenols (the nucleophilic reagents) and a series of allyl diphenyl phosphates. These reactions gave phenolic isoprenoids analogous to those which occur naturally, and established that such fully esterified phosphate esters can simulate the role played by pyrophosphate esters in biological systems. We now report further studies of the chemistry of terpene diphenyl phosphates, including their reaction with various nucleophilic species.

Atherton[3] has reported that geranyl diphenyl phosphate (1), when stored at room temperature for several days, eliminates diphenyl hydrogen phosphate to give monoterpene hydrocarbons, although these were not identified further. We have re-investigated this reaction. Geranyl diphenyl phosphate (1), prepared from pure geraniol as in our earlier work,[1] was set aside in ether at 37° for several days. Diphenyl hydrogen phosphate was formed together with a mixture of five hydrocarbons which appeared to be monoterpenes (g.l.c.). Catalytic hydrogenation of this mixture gave 2,6-dimethyloctane (8) and 1-isopropyl-4-methylcyclohexane (9), identified by direct comparison with authentic material prepared by hydrogenation of myrcene (3) and limonene (6) respectively. This establishes that each of the five components of the original mixture has one of two basic carbon skeletons, one being acyclic and the other monocyclic.

The five compounds were eventually identified as the acyclic trienes myrcene (3), *cis*-β-ocimene (4), and *trans*-β-ocimene (5), and the monocyclic dienes limonene (6) and terpinolene (7) by their characteristic g.l.c. retention indices. These were calculated according to the formula of Kovats *et al.*,[4] and agree well with literature values.[4-6] The mass spectra of the individual hydrocarbons, obtained from a combined gas chromatograph–mass spectrometer unit were also identical with the published spectra[7-9] of these monoterpenes. The composition of the mixture is shown in the Table; the total yield of monoterpene hydrocarbons was 53%.



Similar treatment of neryl diphenyl phosphate (2),

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[1] Part I, J. A. Miller and H. C. S. Wood, *J. Chem. Soc.* (*C*), 1968, 1837.

[2] E. M. Kosower, 'Molecular Biochemistry,' McGraw-Hill, New York, 1962, p. 259 *et seq.*

[3] F. R. Atherton, personal communication, also referred to by A. R. Todd, *Proc. Nat. Acad. Sci. U.S.A.*, 1959, **45**, 1389.

[4] G. Ohloff, J. Seibl, and E. sz. Kovats, *Annalen*, 1964, **675**, 83.

[5] E. sz. Kovats, *Z. analyt. Chem.*, 1961, **181**, 351.

[6] F. Cramer and W. Rittersdorf, *Tetrahedron*, 1967, **23**, 3015.

[7] R. Ryhage and E. von Sydow, *Acta. Chem. Scand.*, 1963, **17**, 2025.

[8] A. F. Thomas and B. Willholm, *Helv. Chim. Acta*, 1964, **47**, 475.

[9] H. C. Hill, R. I. Reed, and M. T. Robert-Lopes, *J. Chem. Soc.* (*C*), 1968, 93.

which has the *cis* configuration about the allylic double bond, gave the same five monoterpenes, although the percentage of cyclic hydrocarbons was considerably higher (Table).

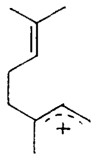
Cramer and Rittersdorf,[6] in a study of the acid hydrolysis of the phosphate and pyrophosphate esters of geraniol and nerol, obtained a small percentage (1·7—4·9%) of terpene hydrocarbons in the hydrolysis products. Their analysis of this hydrocarbon fraction shows an overall similarity to our results in the nature and relative amounts of the terpene hydrocarbons (Table).

Composition of the hydrocarbon mixture formed from terpene phosphates

Terpene phosphate	Total yield of hydrocarbons (%)	Composition (%)				
		Myrcene	*cis*-β-Ocimene	*trans*-β-Ocimene	Limonene	Terpinolene
Geranyl diphenyl phosphate (1) ...	53	23	14	30	23·5	9·5
Neryl dipenyl phosphate (2)	60	8·5	2·5	13	57	19
Geranyl pyrophosphate *	1·7	18	29	44	4	5
Neryl pyrophosphate *	3·0	3	1	3	44	46

* From ref. 6.

The formation of the acyclic trienes (3—5) could involve either ionization of the diphenyl phosphate ester (1 or 2) to give an intermediate allylic cation (10 or 11) followed by elimination of the appropriate proton, or a concerted displacement reaction [*e.g.* (12)]. The high yield of cyclic hydrocarbons from neryl diphenyl phosphate (2) is not unexpected, since the 6,7-double bond is configurationally well placed to participate in the reaction. Indeed, the ready cyclisation of nerol to give α-terpineol in dilute sulphuric acid was the original basis for assignment[10] of the *cis*-configuration to this compound. The reaction would thus involve either the *cis*-allylic carbonium ion (11), or an anchimerically assisted nucleophilic attack [(2) ⟶ (13)] by the 6,7-double bond on the electron-deficient carbon atom bearing the diphenyl phosphate residue. Rittersdorf and Cramer[11] made a similar suggestion to explain the solvolysis of neryl phosphate.



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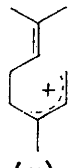

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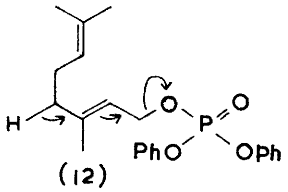

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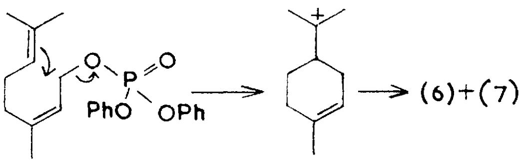
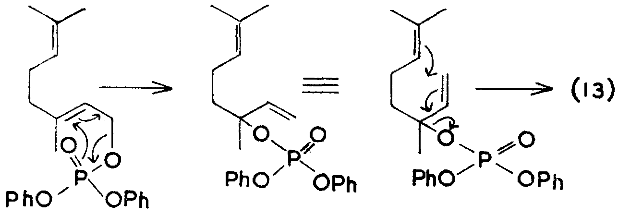


(2) (13)

The formation of *ca.* 34% of cyclic hydrocarbons from geranyl diphenyl phosphate (1), which has the *trans*-configuration about the allylic double bond, requires further explanation. The cyclic hydrocarbons are not formed by an acid-catalysed cyclisation of one of the acyclic trienes since we have shown that myrcene (3), for example, is not isomerised by diphenyl hydrogen phosphate under the conditions of the decomposition reaction.

Winstein[12] has argued that allylic carbonium ions preserve their configuration, and thus, despite the fact that in our experiments the solvent and leaving group are different, we prefer not to suggest interconversion of the carbonium ions (10) and (11). A process of internal return leading to linaloyl diphenyl phosphate, (1 ⟶ 14), is therefore likely in the formation of cyclic hydrocarbons from geranyl diphenyl phosphate. We have not detected any of the linaloyl ester in our experiments, but the results of Rittersdorf and Cramer[11] with linaloyl phosphate suggest that it would cyclise with great ease (14) ⟶ (13).

Participation by the $P=O$ group in a reaction of this type has not apparently been suggested previously, and our proposal must therefore be tentative at this time. Recent papers,[13] however, have demonstrated the nucleophilicity of the $P=O$ group towards potentially electrophilic carbon atoms, and we are studying the reaction further.



(1) (14)

Reduction with Sodium Borohydride.—Studies with other nucleophilic reagents support the arguments outlined above. Thus geranyl diphenyl phosphate on treatment with sodium borohydride in aqueous 2,2′-dimethoxydiethyl ether gave, as the major product, *trans*-2,6-dimethylocta-2,6-diene (15) (80%), whereas neryl diphenyl phosphate under the same conditions gave the *cis*-isomer (16). The i.r. spectra of the dienes

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[10] O. Zeitschel, *Ber.*, 1906, **39**, 1780.

[11] W. Rittersdorf and F. Cramer, *Tetrahedron*, 1968, **24**, 43.

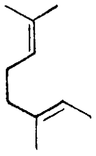
[12] S. Winstein, *Bull. Soc. chim. France*, 1951, **18**, C43; W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, 1960, **82**, 1376.

[13] J. I. G. Cadogan, R. K. Mackie, and J. A. Maynard, *J. Chem. Soc.* (*C*), 1967, 1356; B. A. Arbuzov and D. K. Jarmuhametova, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. khim. Nauk*, 1958, 1061 (*Chem. Abs.*, 1959, **53**, 3046); M. Green and R. F. Hudson, *J. Chem. Soc.*, 1963, 1004.

(15) and (16) were virtually identical with that of 2,6-dimethylocta-2,6-diene (mixed isomers ?) discussed by Sheppard and Sutherland,[14] and each of the compounds, on catalytic hydrogenation, gave 2,6-dimethyloctane (8). Assignment of the *trans*- and *cis*-configurations respectively to the dienes (15) and (16) is based on the known configuration of the starting material, and on the fact [4,15] that the retention index for a *trans*-isomer is invariably higher than that for the *cis*.

Three minor products (5% of hydrocarbon product) were also present in the reaction mixture from each of the borohydride reductions (g.l.c.), but not in sufficient quantity to permit isolation of pure material. However, they have been tentatively identified as 3,7-dimethylocta-1,6-diene (17), 4-isopropyl-1-methylcyclohexene (18), and limonene (6). The last two were compared (g.l.c.) directly with authentic materials; a sample of 4-isopropyl-1-methylcyclohexene (18) was prepared by partial hydrogenation [16] of limonene. Identification of the diene (17) is less certain, although catalytic hydrogenation gave 2,6-dimethyloctane (8), and the retention index is in the expected range.

Formation of the acyclic dienes (15) and (16) is compatible with nucleophilic attack by hydride ion at C-1 of the appropriate phosphate ester (1) and (2) or of the derived allylic carbonium ions (10 and 11), and the diene (17) by similar attack at the other end of the allylic system. The cyclohexene derivative (18) presumably arises by the action of hydride ion on the cyclic carbonium ion (13) formed as discussed above.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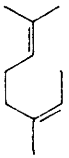
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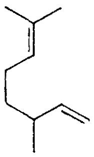
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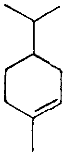
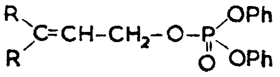

(18)

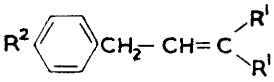
Reaction with Grignard Reagents.—Arnold and his colleagues [17] have studied the reaction between phenylmagnesium bromide and allyl 2,4,6-trimethylbenzoates. In these hindered esters, normal addition by the Grignard reagent at the carbonyl group is inhibited. Attack takes place at the electrophilic methylene group in the allyl residue to give allyl benzenes. Similar experiments with aliphatic Grignard reagents and more complex allyl trimethylbenzoates have been reported [18] by Higgins, Saville, and Evans.

We have now studied the analogous reaction between Grignard reagents and allyl diphenyl phosphates. Allyl diphenyl phosphate (19) and phenylmagnesium bromide gave allylbenzene (21) in good yield, and *p*-methoxyphenylmagnesium bromide similarly gave 1-allyl-4-methoxybenzene (22). 3,3-Dimethylallyl diphenyl phosphate (20) and phenylmagnesium bromide formed 3-methyl-1-phenylbut-2-ene (23) in somewhat lower yield, probably owing to the instability [1] of this phosphate ester.

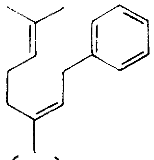


$R_2C{=}CH{-}CH_2{-}O{-}P({=}O)(OPh)_2$

(19) R = H
(20) R = Me



(21) $R^1 = R^2 = H$
(22) $R^1 = H, R^2 = OMe$
(23) $R^1 = Me, R^2 = H$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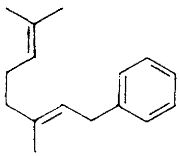
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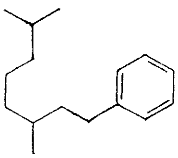
(26)

Geranyl diphenyl phosphate (1) and phenylmagnesium bromide gave a mixture of two isomeric dienes with similar g.l.c. retention times. Catalytic hydrogenation of the mixture gave 3,7-dimethyl-1-phenyloctane (26). We therefore conclude that these compounds are *cis*- and *trans*-3,7-dimethyl-1-phenylocta-2,6-diene, (24) and (25), and these structures are confirmed by spectroscopic evidence.

We suggest that the hydrocarbons formed in the above reactions result from attack by the strongly nucleophilic Grignard reagent at the electron-deficient methylene group in the allyl residue. The reactions are thus similar to those described for allyl trimethylbenzoates. The *cis*-diene (24), formed from geranyl diphenyl phosphate, presumably arises through the intervention of linaloyl diphenyl phosphate (14) as discussed earlier in this paper.

EXPERIMENTAL

I.r. spectra were obtained for liquid films with a Grubb–Parsons DP 1/54 spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer R10 spectrometer (40 MHz), with tetramethylsilane as internal standard. Analytical g.l.c. was carried out with a Perkin-Elmer F11 instrument and either column (A) (10% polyethylene glycol 20M on siliconised Celite, 80—120 mesh) or column (B) (20% Apiezon L on siliconised Celite, 80—120 mesh). Preparative g.l.c. was carried out with a Griffin and George Mark IIB instrument. Combined gas chromatography–mass spectrometry was carried out at Glasgow University on an LKB 9000 Combined GCMS unit, operating at 70 ev, by use of column (B).

Geranyl and Neryl Diphenyl Phosphates.—Geraniol and nerol were donated by Bush Boake Allen, London, and their purity was checked by g.l.c. on column (A). The esters were prepared as in our earlier work.[1]

Decomposition of Geranyl Diphenyl Phosphate in Ether.—A solution of geranyl diphenyl phosphate (29 g.) in anhydrous ether (150 ml.) was kept at 37° in a stoppered flask

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[14] N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 1947, 1540.

[15] A. Wehri and E. Kovats, *Helv. Chim. Acta*, 1959, **42**, 2709.

[16] W. F. Newhall, *J. Org. Chem.*, 1958, **23**, 1274.

[17] R. T. Arnold and R. W. Liggett, *J. Amer. Chem. Soc.*, 1945, **67**, 337; R. T. Arnold and S. Searles, *ibid.*, 1949, **71**, 2021; K. W. Wilson, J. D. Roberts, and W. G. Young, *ibid.*, 1949, **71**, 2019.

[18] G. M. C. Higgins, B. Saville, and M. B. Evans, *J. Chem. Soc.*, 1965, 702.

for 7 days. The ethereal solution was extracted with dilute sodium hydrogen carbonate (75 ml.), washed with water (75 ml.), and dried ($MgSO_4$). The filtered extract was evaporated *in vacuo* to leave a dark brown oil which was chromatographed on alumina (500 g.). Light petroleum eluted an almost colourless oil (5·4 g., 54%), shown by g.l.c. [column (B)] to consist of five monoterpene hydrocarbons, $\nu_{\text{max.}}$ 3102, 1817, 987, 915 ($-CH{=}CH_2$), 2988, 2945, (CH_3, CH_2), 1670, 1637, 828 ($>C{=}CH$), and 1600 (conj. C=C) cm.$^{-1}$.

The mass spectra of the five compounds, obtained from a gas chromatograph–mass spectrometer unit, showed that each hydrocarbon had *M* 136 ($C_{10}H_{16}$). The individual spectra, moreover, were identical with the published spectra [7-9] of the hydrocarbons listed below. Retention indices, which were calculated according to the formula of Kovats *et al.*,[4] were determined [column (B) at 150°] as follows: myrcene 984 (lit.,[4] 982), *cis*-β-ocimene 1037 (lit.,[4] 1032), *trans*-β-ocimene 1050 (lit.,[4] 1046), limonene 1067 (lit.,[5] 1067), terpinolene 1125 (lit.,[5] 1119).

The composition of the mixture is given in the Table.

Hydrogenation of the Hydrocarbon Mixture.—A sample (0·4 g.) of the hydrocarbon mixture from the above experiment was dissolved in glacial acetic acid (50 ml.) and hydrogenated over platinum oxide (20 mg.). When hydrogen uptake was complete, solid sodium hydrogen carbonate and water (50 ml.) were added to the filtered solution, which was then extracted with light petroleum (2 × 50 ml.). The extract was dried ($MgSO_4$) and the solvent was evaporated off *in vacuo* to leave a colourless oil (0·38 g., 96%), which gave a negative test with tetranitromethane and showed no i.r. C=C stretching frequencies.

G.l.c. [column (B)] showed the presence of two components with retention times identical with those of authentic specimens of 2,6-dimethyloctane and 1-isopropyl-4-methylcyclohexane. The mass spectrum of the two-component mixture showed two molecular ions, *m*/*e* 142 ($C_{10}H_{22}$) and 140 ($C_{10}H_{20}$).

2,6-Dimethyloctane was obtained (98%) by hydrogenation of myrcene in methanol over platinum oxide [19] and 1-isopropyl-4-methylcyclohexane was obtained similarly from limonene.[20]

Decomposition of Neryl Diphenyl Phosphate in Ether.—Neryl diphenyl phosphate decomposed in ether as described for the geranyl ester. The same five monoterpene hydrocarbons were obtained and characterised as before. The composition of the mixture is shown in the Table.

Stability of Myrcene towards Acid.—Myrcene (0·265 g.) and diphenyl hydrogen phosphate (0·2 g.) were dissolved in dry ether (50 ml.) and kept at 37° for 7 days. After extraction with dilute sodium hydrogen carbonate (10 ml.), the ethereal solution was dried ($MgSO_4$) and the ether evaporated off. G.l.c. [column (B)] showed that the myrcene was unchanged.

Reduction of Geranyl Diphenyl Phosphate with Sodium Borohydride.—Geranyl diphenyl phosphate (9·65 g.) was added slowly to a hot solution of sodium borohydride (7·05 g.) in water–2,2′-dimethoxy diethyl ether (7 : 13; 50 ml.) containing sodium hydroxide (2 g.). The mixture was stirred on a steam-bath for 1 hr., cooled, and extracted with n-pentane (50 ml.). The extract was evaporated to dryness *in vacuo*, water (75 ml.) was added, and the solution was again extracted with n-pentane (50 ml.). This last extract was dried and evaporated to dryness to leave a colourless oil (2·8 g., 82%). G.l.c. showed that this contained one major (>95%) and three minor components. Distillation gave the major component pure, *trans*-2,6-dimethylocta-2,6-diene, b.p. 34—36°/10 mm. τ ($CDCl_3$) 4·6—5·2 (2H, m, olefinic), 7·95 (4H, methylenes) and 8·4 (12H, 4Me), i.r. spectrum was virtually identical with that [14] of 2,6-dimethylocta-2,6-diene, retention index [column (B) at 150°] 989.

The three minor components were identified tentatively on the basis of their retention indices (given in parentheses) as 3,7-dimethylocta-1,6-diene (940), limonene (1067), and 4-isopropyl-1-methylcyclohexene (1074). Identification of the last two was confirmed by direct comparison with authentic materials; 4-isopropyl-1-methyl-cyclohexene was prepared by partial hydrogenation [16] of limonene.

Reduction of Neryl Diphenyl Phosphate with Sodium Borohydride.—Reduction of neryl diphenyl phosphate as described above gave as the major product *cis*-2,6-dimethyl-octa-2,6-diene (retention index 979) with spectral characteristics virtually identical with those of the *trans*-isomer. The three minor products (<5%) of the reaction were the same as those obtained from the geranyl ester.

Hydrogenation of the Hydrocarbon Mixture from the Above Borohydride Reductions.—A sample (0·4 g.) of the hydrocarbon mixture from either of the above borohydride reductions was hydrogenated in methanol over palladised charcoal (40 mg.). When hydrogen uptake was complete, the solution was filtered, water (100 ml.) was added, and the solution was extracted with light petroleum (50 ml.). The extract was dried and evaporated to leave a colourless oil (0·38 g.) which g.l.c. showed to consist of a mixture of 2,6-dimethyloctane and 4-isopropyl-1-methylcyclohexene, identified by direct comparison with authentic materials.[16,19]

Reaction between Allyl Diphenyl Phosphate and Phenylmagnesium Bromide.—Allyl diphenyl phosphate [1] (5·8 g.) was added dropwise to an ethereal solution of phenylmagnesium bromide [from magnesium (0·96 g.) and bromobenzene (5·1 g.)]. The mixture was heated under reflux for 9 hr., dilute acetic acid (10%; 50 ml.) was added, and the ethereal layer was separated. The extract was washed with dilute sodium hydroxide (50 ml.) and water (50 ml.), dried ($MgSO_4$), filtered, and evaporated to give allylbenzene (2·69 g., 80%) as a colourless oil, b.p. 82—84°/12 mm. $\nu_{\text{max.}}$ 1850, 1639, 996, 912 ($CH_2{=}CH-$), and 760 and 700 (monosubst. benzene) cm.$^{-1}$, τ ($CDCl_3$) 2·8 (5H, aryl), 3·5—4·9 (1H, $-CH_2-CH{=}CH_2$), 4·9—5·3 (2H, $-CH{=}CH_2$), and 6·65 (2H, d, *J* 7 c./sec., $-CH_2-CH{=}$), identical with an authentic specimen.

Reaction between Allyl Diphenyl Phosphate and p-*Methoxyphenylmagnesium Bromide*.—Allyl diphenyl phosphate (5·8 g.) was treated, as above, with *p*-methoxyphenylmagnesium bromide [from magnesium (0·96 g.) and *p*-methoxybromobenzene (6·08 g.)]. Work-up as before gave 1-allyl-4-methoxybenzene (2·7 g., 90%), b.p. 90—92°/10 mm. (lit.,[21] 95—96°/12 mm.), $\nu_{\text{max.}}$ 2985, 1850, 996, 912 ($CH_2{=}CH-$), 2825 (OMe), 1244 (Ar–O–C), and 826 (*p*-disubst. benzene) cm.$^{-1}$, τ ($CDCl_3$) 2·76—3·4 (4H, aryl), 3·67—4·5 (1H, $-CH_2-CH{=}CH_2$), 4·7—5·3 (2H, $-CH{=}CH_2$), 6·25 (3H, OMe), and 6·7 (2H, d, *J* 7 c./sec., $-CH_2-CH$).

Reaction between 3,3-*Dimethylallyl Diphenyl Phosphate and Phenylmagnesium Bromide*.—3,3-Dimethylallyl diphenyl phosphate [1] (12·74 g.) was added slowly to an

[19] J. Pliva and F. Sorm, *Coll. Czech. Chem. Comm.*, 1949, **14**, 276.

[20] H. A. Smith, J. F. Fuzek, and H. T. Meriwether, *J. Amer. Chem. Soc.*, 1949, **71**, 3765.

[21] M. Daufresne, *Bull. Soc. chim. France*, 1908, **3** [4], 333; *Ann. Chim.* (*France*), 1908, **13** [8], 405.

ethereal solution of phenylmagnesium bromide [from magnesium (1·92 g.) and bromobenzene (10·21 g.)]. The mixture was heated for 9 hr. and worked up as before to give 3-methyl-1-phenylbut-2-ene (3·6 g., 67%), b.p. 82—84°/9 mm. (lit.,[22] 86—90°/16 mm.) (Found: C, 90·2; H, 9·3. Calc. for $C_{11}H_{14}$: C, 90·5; H, 9·5%), $\nu_{max.}$ 2976, 2907 (CH_3, CH_2), 1443, 1395, 1379 (*gem*-dimethyl), 1672, 855 ($>$C=CH–), 738, and 696 (monosubst. benzene) cm.$^{-1}$ τ ($CDCl_3$) 2·8 (5H, aryl), 4·65 (1H, methine), 6·68 (2H, d, *J* 7 c./sec., methylene), and 8·37 (6H, 2Me).

Reaction between Geranyl Diphenyl Phosphate and Phenylmagnesium Bromide.—Geranyl diphenyl phosphate (19·3 g.) in anhydrous ether (50 ml.) was added during 10 min. to an ethereal solution of phenylmagnesium bromide [from magnesium (2·4 g.) and bromobenzene (12·6 g.)]. The mixture was heated under reflux for 9 hr. and worked up as above to give a colourless oil. This oil was chromatographed on alumina (200 g.); light petroleum eluted an oil (0·64 g., 10%) shown by g.l.c. to be a mixture of five monoterpene hydrocarbons (see above). Continued elution with light petroleum gave a second colourless oil (7·3 g., 69%), b.p. 92—94°/2 mm. G.l.c. showed the presence of two compounds identified as *cis*- and *trans*-3,7-*dimethyl*-1-*phenylocta*-2,6-*diene* (25 : 75) (Found for the mixture: C, 89·75; H, 10·1. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%), $\nu_{max.}$ 2967, 2899 (CH_3, CH_2), 1672, 831 ($>$C=CH), 739, and 697 (monosubst. benzene) cm.$^{-1}$, τ ($CDCl_3$) 2·8 (5H, aryl), 4·75 (2H, olefinic), 6·68 (2H, d, *J* 7 c./sec., ArCH_2–CH=), 7·88 (4H, methylenes), and 8·3 (9H, 3Me).

Bateman, Cuneen, and Lyons [23] describe a synthesis of 3,7-dimethyl-1-phenylocta-2,6-diene but conclude that the product is mixed with *ca.* 25% of the isomeric 1,6-diene.

Neryl diphenyl phosphate reacted similarly with phenylmagnesium bromide to give monoterpene hydrocarbons (25%) and a mixture of *cis*- and *trans*-3,7-di-methyl-1-phenylocta-2,6-diene (55%) (7 : 3).

Hydrogenation of Mixed cis- *and* trans-3,7-*Dimethyl*-1-*phenylocta*-2,6-*diene.*—The mixture of isomers (1·02 g.) from the above experiment in methanol (50 ml.) was reduced over palladised charcoal (20 mg.). When the uptake of hydrogen was complete, the solution was filtered, water (100 ml.) was added, and the solution was extracted with light petroleum (2 × 50 ml.). The extract was dried ($MgSO_4$) and the solvent evaporated off to leave 3,7-dimethyl-1-phenyloctane (1·03 g., 98%) as a colourless oil, b.p. 84—87°/2 mm. (lit.,[24] 140°/8·5 mm.) (Found: C, 87·5; H, 12·5. Calc. for $C_{16}H_{26}$: C, 87·2; H, 12·8%), $\nu_{max.}$ 2967, 2899, 2860 (CH_3, CH_2), 1479, 1382, 1366 (*gem*-dimethyl), 739, and 697 (monosubst. benzene) cm.$^{-1}$, τ ($CDCl_3$) 2·8 (5H, aryl), 7·47 (2H, t, *J* 8 c./sec., ArCH_2–CH_2), and 8·2—9·3 (19H, methyls and methylenes).

We thank Dr. F. R. Atherton, Roche Products Ltd., for comments in the early stages of this work, Dr. J. Watson of Glasgow University for the combined gas chromatography–mass spectrometry studies, and the S.R.C. for Research Studentships (to R. C. H. and J. A. M.).

[8/1343 *Received, September* 16*th*, 1968]

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[22] D. Seyferth and J. Fogel, *J. Organometallic Chem.*, 1966, **6**, 205.

[23] L. Bateman, J. I. Cunneen, and J. A. Lyons, *J. Chem. Soc.*, 1951, 2290.

[24] A. Klages and R. Sautter, *Ber.*, 1906, **39**, 1938.