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Complexes of Terpenes with Transition Metals. Part III.† Dimerisation by means of Tetrakis(triphenylphosphine)palladium

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Tetrakis(triphenylphosphine)palladium is shown to dimerise nerolidyl acetate, and 1-vinylcyclohexyl acetate to linear dimers, and myrcene to a monocyclic dimeric product.

WE obtained evidence of dimerisation of ocimene and myrcene in their reaction with disodium tetrachloropalladate(II).¹ Olefin oligomerisation has, however, more generally been studied with zerovalent metal complexes. Tetrakis(triphenylphosphine)palladium² appeared to be a convenient reagent of this type since

it is readily soluble in organic solvents, and has one or more phosphine ligands which may readily be displaced.

† Part II, preceding paper.

¹ Part I, K. Dunne and F. J. McQuillin, J. Chem. Soc. (C), 1970, 2196. ² L. Malatesta and M. Angoletta, J. Chem. Soc., 1957, 1186.

As a suitable model for preliminary work, we chose 1-vinylcyclohexyl acetate (I), which by reaction with tetrakis(triphenylphosphine)palladium in chloroform at room temperature gave, in addition to unchanged vinylcyclohexyl acetate, a higher boiling product showing i.r. bands at 1735 and 1245 cm⁻¹, and giving in the mass spectrometer an ion at m/e 278 (C₁₈H₃₀O₂). The n.m.r. spectrum of this product showed only one olefinic proton signal as a multiplet at τ 4·9. Structure (II) represents a rational formulation for this product which also accounts for the mass spectral cracking pattern shown. The fragment ions (III) and (IV)



* = Metastable transition.

establish the main features of the structure, but other fragment ions may indicate the presence of isomers of (II).

The dimeric product, $C_{18}H_{30}O_2$, was accompanied by a palladium-complex, $R_F 0.05$ on silica gel in benzeneethyl acetate (5:1), which gave an analysis consistent with the formula Pd(Ph₃P)C₈H₁₃OCOCH₃. The n.m.r. spectrum showed a three-proton signal at τ 7.97, but the acetate residue gave rise to i.r. bands at 1575 and 1425 cm⁻¹, *i.e.* corresponding to the acetate ion.³ This product is accordingly represented as (V), formed by displacement of the acetate residue, and oxidation of



the metal: $Pd^0 \longrightarrow Pd^{II}$. The formation of the dimeric product (II) may therefore be rationalised as in

Scheme 1. The nature of the proton donor, HX, which must be invoked in this reaction scheme cannot be specified. Triphenylphosphine oxide, which was also isolated from the reaction mixture, may represent the



end product of an oxidation process capable of generating HX, or HX may represent acetic acid formed from (I) by elimination.

As a terpenoid analogue of (I) we examined nerolidyl acetate (VI) which with tetrakis(triphenylphosphine)-palladium gave three products separated on silica gel by t.l.c.



The first product, a liquid, b.p. ca. 110° at 2 mmHg, gave farnesane on hydrogenation, and showed n.m.r. bands at τ 4.87 (3H), 5.22 (2H), 8.3 and 8.38 (12H), and 7.95 (6H), corresponding to farnesene or isomers.

A second liquid product, b.p. ca. 230° at 0.5 mmHg, showed i.r. absorption at 1735 and 1240 cm⁻¹ and on hydrogenation gave a hydrocarbon $C_{30}H_{62}$, identified by an ion at m/e 422 in the mass spectrum. By analogy with (II) the hydrogenation product of this nerolidyl acetate dimer should resemble squalane. The n.m.r. spectra of the two were very similar, both had a ratio of methyl protons (τ 9.1, 9.12, and 9.19) to methylene and methine protons (τ 8.78) of 1:1.58 in each case. The mass spectra were also similar, showing ions at m/e 422, (M^+) and 407 (M-15), with the next most abundant ion at m/e 337 (C₂₄H₄₉), and thence a typical alkane cracking pattern. On these general grounds and by analogy with (II), the nerolidyl acetate dimer may be formulated as (VII), the acetoxy-group being lost through hydrogenolysis to give a perhydro-dimer, C₃₀H₆₂.



In addition to these products a palladium complex, Pd(Ph₃P)C₁₅H₂₅O COCH₃, corresponding with (VIII), *i.e.* an analogue of (V) was formed. The n.m.r. spectrum

^a Cf. S. D. Robinson and B. L. Shaw, J. Organometallic Chem., 1965, **3**, 367.

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showed signals at τ 7.98 (3H, AcO) and 4.86 (3H) and signals due to MeC= at τ 8.3 and 8.36 (12H).



Farnesyl acetate was found much less reactive than nerolidyl acetate towards tetrakis(triphenylphosphine)palladium, and the main product was farnesene, with no evidence of dimer formation. Geranyl acetate (IX) reacted similarly with elimination of acetic acid to give *cis*- and *trans*-ocimene (X) together with some limonene (XI). These processes may be rationalised as shown in Scheme 2.

The production of ocimenes and faresene in these reactions suggested that dienes could possibly be intermediates in dimerisation and that the reactions of suitable dienes towards tetrakis(triphenylphosphine)palladium should be examined. As an example we now report on the reaction of myrcene (XII) which after



24 h with tetrakis(triphenylphosphine)palladium in chloroform gave a fraction, b.p. 140° at 1 mmHg, as well as unchanged myrcene. The higher boiling fraction was hydrogenated to a product which in the mass spectrometer gave an ion at m/e 280 ($C_{20}H_{40}$) *i.e.* corresponding to a dimer containing one carbocyclic ring. The n.m.r. spectrum of the parent dimer showed a somewhat broad two-proton signal at τ 5·2, and a three-proton multiplet at τ 4·9. However, the characteristic quartet signal at τ 3·67 due to the >CH=CH₂ group of myrcene was absent. This absence of the vinyl group was taken to indicate coupling through the vinyl group, which is, however, expected.

Cyclodimerisation of butadiene and similar 1,3-dienes

⁴ G. Wilke, Angew. Chem., Internat. Edn., 1963, 2, 105; C. W. Bird, 'Transition Metal Intermediates in Organic Synthesis,' Logos Press, London, 1967, p. 35 et seq. catalysed by nickel(0) and other low valent transitionmetal complexes leads generally to a cyclo-octadiene ⁴ or vinylcyclohexene derivative.⁵ On this basis myrcene may give isomeric di-isohexenylcyclo-octadienes, isohexenyl-(6-methylheptenyl)cyclohexenes, or vinyl-diisohexenylcyclohexenes.

A di-isohexenylcyclo-octadiene structure is not consistent with the signal at $\tau 5.2$ in the n.m.r. spectrum of the dimer, and in the mass spectrometer the perhydrogenated dimer showed, *inter alia*, the fragmentation $280^+ \rightarrow 167^+ + C_8H_{17}$, *i.e.* with loss of an iso-octyl residue. This fragmentation together with a further transition $167^+ \rightarrow 85^+ + C_6H_{10}$ is in better agreement with a structure of the type (XIII) or (XIV), the C_6H_{10} fragment representing a cyclohexene or bicyclohexene residue from cleavage at (a) and (b).



The mass spectrum of the perhydro-dimer, however, also contained ions, of rather smaller intensity, indicating transitions: $280^+ \rightarrow 251^+ + C_2H_5$, $280^+ \rightarrow 195^+ + C_6H_{13}$, and $195^+ \rightarrow 111^+ + C_6H_{12}$, indicating the presence of structures of the type (XV) or (XVI). Thus dimerisation appears to proceed by two paths (Scheme 3), leading to products, (XVII) and (XVIII), which together account well for the mass spectral data.



This conclusion is in accordance with the observed cyclo-additions of isoprene catalysed by various transition-metal nitrosyl carbonyls.⁵

⁵ J. P. Candlin and W. P. Janes, J. Chem. Soc. (C), 1968, 1856.

J. Chem. Soc. (C), 1970

EXPERIMENTAL

1-Vinylcyclohexyl acetate ⁶ was prepared by half hydrogenation of 1-ethynylcyclohexyl acetate over 2% palladised strontium carbonate in ethanol; b.p. 65° at 1 mmHg; ν_{max} 1735, 1235, 1640, 990, and 913 cm⁻¹; τ 3.8 (1H, q, *J* 17.6 and 9.9 Hz), 4.84 (1H, q, *J* 17.6 and 1.3 Hz), 4.86 (1H, q, *J* 9.6 and 1.3 H), 8.01 (3H, s, AcO), 8.61 (4H), and 8.5 (8H).

Tetrakis(triphenylphosphine)palladium was prepared by stirring triphenylphosphine and freshly precipitated, washed palladium oxide in ethanol for 6 h. The crude product was obtained, m.p. 100° , by recrystallisation from chloroform-ethanol (lit.,² $100-105^{\circ}$).

Dimerisation of 1-Vinylcyclohexyl Acetate.—1-Vinylcyclohexyl acetate (9 mmol) and tetrakis(triphenylphosphine)palladium (2 mmol) in chloroform (25 ml) were set aside for 36 h. After removal of chloroform in vacuo the unco-ordinated material was extracted into light petroleum and distilled. The petroleum-insoluble residue was purified by t.l.c. on silica gel in benzene-ethyl acetate (5:1) to give a colourless product, $R_{\rm F}$ 0.95, shown to contain triphenylphosphine, triphenylphosphine oxide, and a yellow complex, $R_{\rm F}$ 0.05.

The petroleum extract gave a liquid containing unchanged vinylcyclohexyl acetate, b.p. 100—110° at 15 mmHg, and a fraction, b.p. 140—150° at 1.5 mmHg; ν_{max} 1735, 1245, and 1675 cm⁻¹; *m/e* 278, 208, 167, 166, 154, 141, 123, 109, 99, and 81; τ 4.9 (1H, m), 7.78—7.9 (16H), and 8.36 (13H). This product is formulated as 1-(4-cyclohexylidenebutyl)-cyclohexyl acetate (II).

The structure of the yellow complex, $R_{\rm F}$ 0.05; $\nu_{\rm max.}$ 1575, 1400, 1485, 1440, 1100, 750, and 730 cm⁻¹; $\tau 2.3$ — 2.5 (15H), 8.0 (6H), 8.0—8.4 (4H), and 8.55 (5H) {Found: C, 62.2; H, 5.3. [PdP(C₆H₅)₃C₈H₁₃OCOCH₃] requires C, 62.8; H, 5.7%}, bis-(μ -acetoxy)-bis-[(2-cyclohexylidene-ethyl)triphenylphosphine)palladium] (V), is discussed in the text.

Nerolidyl Acetate with Tetrakis(triphenylphosphine)palladium.—Nerolidyl acetate (4 mmol) and tetrakis(triphenylphosphine)palladium (6 mmol) were kept in chloroform (20 ml) for 24 h. T.l.c. on silica gel in benzeneethyl acetate (5:3) gave two liquid products, $R_{\rm F}$ 0.9 and 0.5, and a yellow complex, $R_{\rm F}$ 0.2.

The liquid product, $R_{\rm F}$ 0.9, yielded unchanged nerolidyl acetate, b.p. 110° at 2 mmHg, and gave also a fraction, b.p. *ca.* 230 at 0.5 mmHg, which was hydrogenated over platinum in ethanol to give a product, τ 8.8 (38H), and 9.1 and 9.15 (24H, d, J 5 Hz); *m/e* 422, 337, 267, 239, 225 . . . 127, 113, 99, 85, 71, and 57.

Squalane, b.p. 230° at 0.5 mmHg, was prepared for comparison by hydrogenation of squalene; τ 8.77 (38H), and 9.07 and 9.12 (24H, d, J 5 Hz); the mass spectrum showed all the aforementioned ions.

The yellow complex, $R_{\rm F}$ 0·2; $\nu_{\rm max}$ 1567, 1402, 1486, 1440, 1100, 757, and 726 cm⁻¹; τ 2·3—2·5 (15H), 4·86 (2H, m), 7·94br (8H), 7·98 (3H, s), 8·3 and 8·36 (12H); m/e 206, 179, 177, 161, 151, 137, 121, 109, 95, 93, 81, 69, 55, and 43 [Found: C, 66·5; H, 7·1. PdP(C₆H₅)₃·C₁₅H₂₅-OCOCH₃ requires C, 66·3; H, 6·8%], was assumed to be bis-(μ -acetoxy)-bis[farnesyl(triphenylphosphine)palladium].

Dimerisation of Myrcene.—Freshly distilled myrcene (4 mmol) and tetrakis(triphenylphosphine)palladium (1 mmol) were kept in chloroform (20 ml) for 24 h. After removal of chloroform in vacuo the residue was extracted with light petroleum. The extract gave on distillation unchanged myrcene, b.p. 75° at 15 mmHg (g.l.c. analysis), and a fraction, b.p. 140° at 1.5 mmHg; τ 4.9 (3H, m), 5.2br (2H, s), 7.9—8.0 (14H), and 8.23 and 8.35 (15H). Hydrogenation over platinum in ether gave a product with m/e 280, 251, 195, 167, 125, 113, 111, 97, 85, 83, 71, 69, 57, 43, and 41, discussed in the text.

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⁶ N. A. Milas and C. P. Preising, J. Amer. Chem. Soc., 1957, 79, 6294.