# Pyrolysis of Di-t-butyldiphenylcyclobutadienepalladium Chloride

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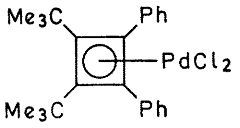
*Summary* Pyrolysis of di-t-butyldiphenylcyclobutadienepalladium chloride gives the homo-tetrahedrane compound (II).

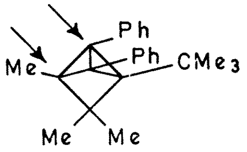
WE recently described the synthesis of 1,2-di-t-butyl-3,4-diphenylcyclobutadienepalladium chloride (I)[1] Roumanian workers[2] have, independently, prepared the same complex. We now report that the cyclobutadiene ligand isomerizes to a homo-tetrahedrane skeleton on pyrolysis of the complex.

When the complex (I) was heated at 240—250° under reduced pressure (1 mm Hg), it gave colourless crystals of (II) 22·6%, m.p. 152·5—153·5° (MeOH), and yellow oil. The elemental analysis and molecular-weight determination showed (II) to be $C_{24}H_{28}$, an isomer of di-t-butyldiphenylcyclobutadiene. The n.m.r. spectrum showed peaks due to three nonequivalent methyl groups at $\tau$ 7·93 (s, 3H), 8·86 (s, 9H), and 8·92 (s, 6H) besides an aromatic proton peak at $\tau$ 3·07 (s, 10H), suggesting two possible structures (II) and (III). However, the fact that there is no i.r. absorption† in the region expected for conjugated dienes[3] eliminates the structure (III). Moreover, the u.v. maximum at 272 nm (log $\epsilon$ 3·65) supports the structure (II), since Woodward and Dalrymple[4] have recently pointed out that the u.v. spectra of 1,2-diphenylbicyclobutanes show maxima at around 270 nm (log $\epsilon$ *ca.* 4).

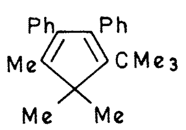
Catalytic hydrogenation of (II) with Pd-sponge gave the bicyclic compound (IV) ($C_{24}H_{30}$, *ca.* 30%) formed by the attack of hydrogen from the direction illustrated by the arrows in the diagram, besides two other unidentified materials. The structure was deduced from spectroscopic data.‡ In particular, the n.m.r. spectrum confirmed the structure and showed resonances at $\tau$ 2·88 (s, 5H, Ph), 2·92 (s, 5H, Ph), 6·63 (s, 1H, benzylic H), 7·54 (q, *J* 7 Hz, 1H, tertiary H), 8·71 (s, 3H, Me), 8·91 (d, 3H, Me), 8·90 (s, 9H, t-butyl H), and 9·45 (s, 3H, Me).



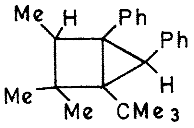
(I)



(II)



(III)



(IV)

Thus, the compound (II) has the homo-tetrahedrane skeleton (tricyclo[1,1,1,$0^{4,5}$]pentane system), which may be derived from the rearrangement of the t-butyl substituted cyclobutadiene ligand. This is the first example of the synthesis of the homo-tetrahedrane§ *via* a cyclobutadiene–metal complex. The bulky t-butyl groups may play an important role in the isomerization.

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† The i.r. spectrum of the yellow oil described above showed a strong band at 1632 $cm^{-1}$, suggesting that it contains the compound (III).

‡ The u.v. spectrum of the compound exhibited only end-absorption (shoulder at 220 nm; log $\epsilon$ 4·00), and no i.r. peaks due to olefinic stretching were observed. These facts are consistent with the structure (IV).

§ Such tricyclo[1,1,1,$0^{4,5}$] pentane systems have previously been prepared by the intramolecular addition of carbene. S. Masamune, (a) *J. Amer. Chem. Soc.*, 1964, **86**, 735; (b) *Tetrahedron Letters*, 1965, 945; (c) W. von E. Doering and M. Pomerantz, *ibid.*, 1964, 961.

[1] T. Hosokawa and I. Moritani, *Tetrahedron Letters*, 1969, 3021.
[2] M. Avram, I. G. Dinulescu, Gh. D. Mateescu, E. Avram, and C. D. Nenitzescu, *Rev. Roumanine Chim.*, 1969, **14**, 1181.
[3] I. A. D'yakonov, V. V. Razin, and M. I. Komendantov, *Tetrahedron Letters*, 1966, 1127, 1135.
[4] R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, 1969, **91**, 4612.