

Pyrolysis of Di-t-butyl-diphenylcyclobutadienepalladium Chloride

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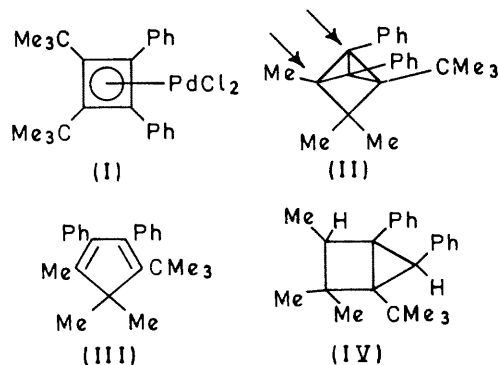
Summary Pyrolysis of di-t-butyl-diphenylcyclobutadienepalladium chloride gives the homo-tetrahdrane compound (II).

We recently described the synthesis of 1,2-di-t-butyl-3,4-diphenylcyclobutadienepalladium chloride (I)¹. Roumanian workers² have, independently, prepared the same complex. We now report that the cyclobutadiene ligand isomerizes to a homo-tetrahdrane 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 C₂₄H₂₈, an isomer of di-t-butyl-diphenylcyclobutadiene. The n.m.r. spectrum showed peaks due to three nonequivalent methyl groups at τ 7.93 (s, 3H), 8.86 (s, 9H), and 8.92 (s, 6H) besides an aromatic proton peak at τ 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 dienes³ eliminates the structure (III). Moreover, the u.v. maximum at 272 nm ($\log \epsilon$ 3.65) supports the structure (II), since Woodward and Dalrymple⁴ 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) (C₂₄H₃₀, 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 τ 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).



Thus, the compound (II) has the homo-tetrahdrane 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-tetrahdrane§ 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. Roumaine 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.