

Reactions of Cyclopropanes with Dicarbonylchlororhodium: Carbonyl Insertion and Isomerisation

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Summary With $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, substituted cyclopropanes undergo stereoselective ring-fission with the formation of carbonyl inserted and/or olefinic products.

TRANSITION-METAL-CATALYSED isomerisation reactions of strained cycloalkanes are of some current interest. Examples of isomerisation catalysed by suitable Rh^{I} complexes¹ or Ag^+ salts² are numerous. However, carbonyl insertion by means of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, exemplified for cyclopropane,³ quadricyclene,⁴ and cubanes,⁵ may represent a related process. We have therefore examined this reaction for various cyclopropanes to establish the preferred mode of ring-fission, and the extent of any concomitant isomerisation.

Dicarbonylchlororhodium was kept with excess of the cyclopropane in a sealed tube at 50–60° for some days.³ Phenylcyclopropane gave a derivative in 75% yield, shown to be (1), which precipitated, and benzylcyclopropane, similarly, gave a product (70%), (2), which although more soluble also crystallised from the reaction mixture. The product, (5), from bicyclo[4.1.0]heptane was isolated (yield 90%) only after removal of the excess of bicycloheptane *in*

vacuo, and whilst n-hexylcyclopropane appeared to react, no rhodium derivative could be isolated, and on cooling to –78° only $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ precipitated, and was identified.

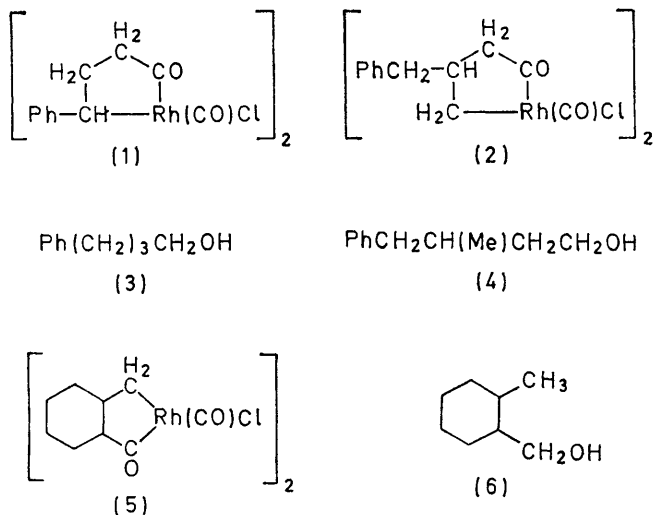
I.r. data (ν_{CO}) for (1), (2), and (5) and their triphenylphosphine derivatives: $(\text{RCO})\text{RhCl}(\text{PPh}_3)_2$, $\text{R} = \text{PhC}_3\text{H}_5$ (7), $\text{R} = \text{PhCH}_2\text{C}_3\text{H}_5$ (8), and $\text{R} = \text{C}_7\text{H}_{12}$ (9) are given in the Table together with ν_{CO} values for the already known corresponding derivatives obtained from cyclopropane.³

Structures (1), (2), and (5) depend on analysis, mass spectra, which gave only the hydrocarbon ions, *m/e* 118, 132, and 96, respectively, and on sodium borohydride reduction from which the organic moiety could be isolated as an alcohol.

In this way (phenylketotrimethylene)carbonylchlororhodium, (1) gave an alcohol, $\text{C}_{10}\text{H}_{14}\text{O}$ (*m/e* 150), homogeneous to g.l.c., and with an n.m.r. spectrum: τ 2.9 (5H), 6.49 (2H, t, *J* 6.5 Hz), 7.42 (2H, t, *J* 6.5 Hz), 7.77 (1H, s), and 8.44 (4H, m). These data, and in particular the absence of signals attributable to a CH_3 or CH_3CH_2 group, identify this product as 4-phenylbutan-1-ol (3), and the parent complex as (1).

The benzylcyclopropane complex similarly gave an

alcohol, m/e 164 = $C_{11}H_{16}O$, with an n.m.r. spectrum: τ 2.82 (5H), 6.35 (2H, t, J 6 Hz), 7.45 (2H, m), 8.3–8.8 (3H, m) and 9.12 (3H, d, J 7 Hz). Of the possible alternatives, these data identify this alcohol as (4), and the parent complex as (2). Thus phenyl- and benzyl-cyclopropane differ in reacting at the more and the less substituted edge of the cyclopropane ring, respectively.



The bicyclo[4,1,0]heptane complex on borohydride reduction gave an alcohol, which the n.m.r. spectrum: τ 6.46 (2H, d, J 7 Hz), 8.0 (1H, s), 8.55 (10H, m.) and 9.14 (3H, d, J 7 Hz), identified as (6), and hence the rhodium carbonyl complex as (5). The alcohol (6) failed to give the molecular ion, but an ion $M - 18$ (110) was observed together with strong fragment ions: m/e 97 ($M - CH_2OH$), 82 ($M - CH_2OH - CH_3$), and 55 = CH_3 -allyl⁺.

These examples indicate significant selectivity in the direction of ring fission.

TABLE
 ν_{CO} cm^{-1} (KBr disc)

Rh(CO)Cl Complex	Rh(Cl)(PPh ₃) ₂ Derivative
(1) 1600, 1640, 2080	(7) 1640
(2) 1715, 1735, 2060	(8) 1630
(5) 1735, 1755, 2050	(9) 1605
^a 1730, 1745, 2041	^a 1670

^a From ref. 3 for the corresponding products obtained from cyclopropane.

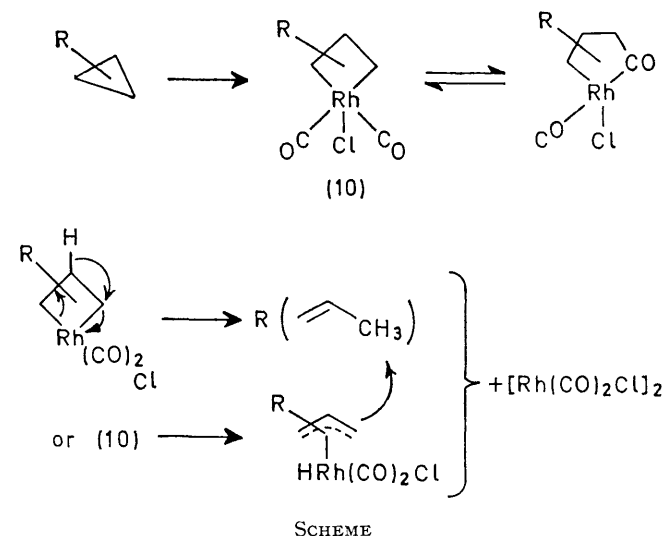
The product (1) shows an anomalously low ν_{CO} for the inserted carbonyl group, although ν_{CO} for the terminal

carbonyl is normal, and the anomaly disappears in the triphenylphosphine derivative (7). The structure (1) provides no evident explanation; $>CO-Rh$ bonding in the crystals may be responsible.

After treatment with $[Rh(CO)_2Cl]_2$ the recovered excess of cyclopropane was generally found to contain olefinic products. Phenylcyclopropane gave propenylbenzene and a little α -methylstyrene. Benzylcyclopropane gave 2-methyl-3-phenylprop-1-ene, m/e 132, characterised by n.m.r. Bicyclo[4,1,0]heptane was also found to be isomerised, although more slowly, to give methylenecyclohexane. n-Hexylcyclopropane, which gave no complex, was found on recovery to contain $CH_3 \cdot [CH_2]_5 \cdot C(CH_3)=CH_2$, and $C_6H_{13} \cdot CH=CH \cdot CH_3$, identified by n.m.r. comparison, in a ratio of *ca.* 3:1. Thus in insertion and isomerisation the modes of ring-fission correspond.

The complex (1) treated with an excess of triphenylphosphine in hot chloroform gave propenylbenzene and $RhCO(PPh_3)_2Cl$, and phenylcyclopropane kept with the pre-formed complex (1) for 14 days at 60° gave some propenylbenzene.

These observations suggest a common reaction pathway in which an intermediate (10) may be trapped by carbonyl insertion, or isomerised by hydrogen transfer.



Borohydride reduction of the triphenylphosphine derivatives (7), (8), and (9) gave the same alcohol products as reduction of (1), (2), and (5), respectively, *i.e.* we found no evidence of insertion of a second carbonyl group as envisaged by Halpern.⁴

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