Stereoselectivity in the Carbonyl Insertion Reaction between Tetracarbonyldichlorodirhodium and Substituted Cyclopropanes

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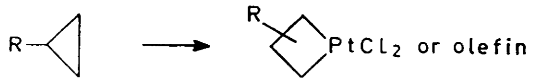
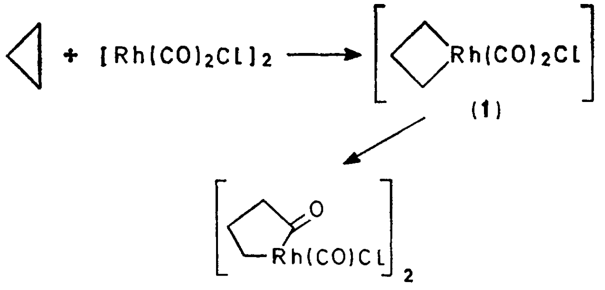
The insertion reaction between tetracarbonyldichlorodirhodium and phenylcyclopropane, benzylcyclopropane, and bicyclo[4,1,0]heptane has been examined, and the structures of the rhodacyclopentanones deduced by sodium borohydride reduction. Evidence is found for some cyclopropane ⟶ olefin isomerisation during the insertion reaction.

THE reaction between $PtCl_2$ and various cyclopropanes exemplified in the preceding paper indicates the polarisability of a cyclopropane carbon–carbon bond towards an electrophilic transition metal derivative. In the case of $PtCl_2$ this may result in metal insertion, or in hydrogen transfer to yield an olefin depending on the substitution of the cyclopropane:



In the formation of the insertion product the $PtCl_2$ residue acts not only as the polarising electrophile, but also as the nucleophile in simultaneously forming a second carbon–platinum bond. In the related reaction [1] of cyclopropane with $[Rh(CO)_2Cl]_2$ a (propane-1,3-diyl)-rhodium derivative (1) is not isolated, but some such



(1)

(2)

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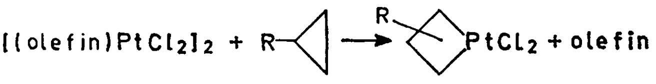
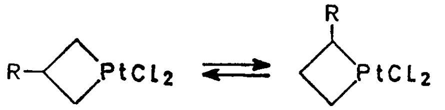
[1] D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 845.

intermediate undergoes carbonyl insertion to yield a rhodacyclopentanone (**2**).

In the formation of the (propane-1,3-diyl)$PtCl_2$ complexes discussed in the preceding paper there appears to be a general preference for fission of the less substituted carbon–carbon bond. This is consistent with formation of the more stable platinum carbon bonds, *i.e.* by bonding to the less substituted carbon atoms. However, the displacement process



has been shown, in particular examples, to be reversible. It is therefore *a priori* possible to envisage equilibration * between isomeric (propane-1,3-diyl)$PtCl_2$ derivatives:



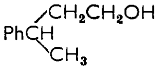
For this reason the isolated dichloro(propane-1,3-diyl)-platinum complex may represent the outcome of thermodynamic rather than kinetic reaction control.

It appeared to us that the corresponding reaction with $[Rh(CO)_2Cl]_2$ leading to a rhodacyclopentanone may be less easily reversible. We have therefore examined the behaviour of some substituted cyclopropanes towards $[Rh(CO)_2Cl]_2$ to determine how far the course of reaction parallels that which is observed with $PtCl_2$, and also how far insertion may be accompanied by isomerisation to olefins.

Phenylcyclopropane warmed[1] with tetracarbonyldichlorodirhodium precipitated a derivative, $[(PhC_3H_5CO)Rh(CO)Cl]_2$, m.p. 177° (dec.), showing ν_{CO} bands at 1640 and 1600, and a terminal CO band at 2080 cm^{-1}. The mass spectrum showed an ion *m*/*e* 118 = $PhC_3H_5^+$, and no ion corresponding to $[PhC_3H_5CO]^+$, but the substance was too insoluble for n.m.r. examination.

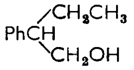
This 1-chloro-1-carbonylphenylrhodacyclopentanone with triphenylphosphine in chloroform gave a derivative $(PhC_3H_5CO)RhCl(PPh_3)_2$, m.p. 184° (dec.), ν_{CO} 1640 cm^{-1}, which in the mass spectrometer showed a low intensity peak *m*/*e* 146 = $[PhC_3H_5CO]^+$ as well as a principal ion at *m*/*e* 118. This product gave an n.m.r. spectrum showing aromatic protons (35 H) at τ 2·1—2·7, and multiplet signals at 6·66 (1H), 8·12 (2H) and 8·9 (2H) with evident splitting of the τ 6·66 signal due to ^{103}Rh–H coupling (*J ca.* 1·5 Hz).

The structures of these products were derived by sodium borohydride reduction. Both 1-chloro-1-carbonylrhodacyclopentanone and its triphenylphosphine derivative gave the same product, *m*/*e* 150 = $C_{10}H_{14}O$, which appeared homogeneous to g.l.c. Of the possible alternatives (**3**), (**4**), (**5**) the n.m.r. spectrum: τ 2·9 (5H), 6·49 (2H, t, 6 Hz), 7·42 (2H, t, 6 Hz), 7·77 (1H, s), 8·44 (4H, m) indicated structure (**5**). The absence of CH_3– doublet or triplet signals excludes (**3**) and (**4**) which could not lead to the τ 7·42 $PhCH_2$– triplet signal. The mass spectral breakdown



$PhCH(CH_2CH_2OH)(CH_3)$

(**3**)



$PhCH(CH_2CH_3)(CH_2OH)$

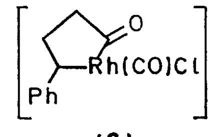
(**4**)

$Ph(CH_2)_3CH_2OH$

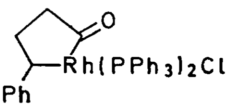
(**5**)

m/*e* 150 ⟶ 104 (150 − H_2O − C_2H_4), 150 ⟶ 117 ⟶ 115, 150 ⟶ 91 and 77 is consistent with (**5**).

We therefore infer for the parent materials structures (**6**) and (**7**), and we note that (**7**) is consistent with the



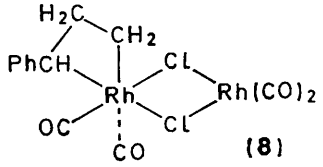
(**6**)



(**7**)

observed ^{103}Rh–H coupling for the low-field benzylic proton signal at τ 6·66.

It appears therefore that, as in the oxidation of phenylcyclopropane[2] with $Hg(OAc)_2$, $Tl(OAc)_3$, or $Pb(OAc)_4$, 1,2-bond fission is kinetically preferred, and the major product of the reaction of phenylcyclopropane with $PtCl_2$ is therefore probably the thermodynamic product. However, we also note that the alcohol from reduction has structure (**5**) rather than (**4**). In an intermediate such as (**8**) both sites (PhCH and CH_2) are accessible to



(**8**)

carbonyl insertion. The choice in favour of (**6**) is likely to be determined by the formation of the stronger carbon–carbonyl bond.

Benzylcyclopropane behaved similarly in giving products $[(PhCH_2C_3H_5CO)Rh(CO)Cl]_2$, m.p. 125°, ν_{CO} 1735, 1715, and 2060 cm^{-1}, and $(PhCH_2C_3H_5CO)Rh[PPh_3)_2Cl$, dec. 205°, ν_{CO} 1630 cm^{-1}, which were characterised by a mass ion *m*/*e* 132 = $[PhCH_2C_3H_5]^+$. The 1-chloro-1-carbonylbenzylrhodacyclopentanone was sufficiently soluble ($CDCl_3$) to give an n.m.r. spectrum: 2·77 (5H), 6·5—6·9 (m, 2H), 7·25 (m, 4H), and 8·2—8·6 (m, 1H), but the signals were not well resolved, and for the triphenylphosphine derivative also, only the benzyl proton signal at τ 8·29 (d, *J* 9 Hz) could be assigned with certainty.

Sodium borohydride reduction of both these products gave the same alcohol, homogeneous to g.c., *m*/*e* 164 = $C_{11}H_{16}O$, ν_{CO} 3400 cm^{-1}, n.m.r.: τ 2·82 (5H, m), 6·35 (2H, t, 7 Hz), 7·45 (2H, m), 8·3—8·8 (3H, m), 9·12 (3H, d, 7 Hz), *m*/*e*: 164 ⟶ 146 (−H_2O) ⟶ 131 (−Me) ⟶

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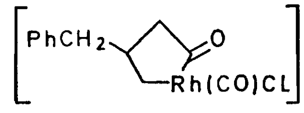
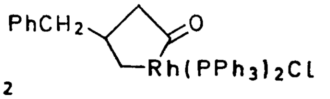
* The displacement: $C_3H_6PtCl_2$ + Ph– ⟶ (PhC_3H_5)-$PtCl_2$ has been demonstrated.

[2] R. J. Oulette and D. L. Shaw, *J. Amer. Chem. Soc.*, 1964, **86**, 165; R. J. Oulette, R. D. Robins, and A. South, *ibid.*, 1968, **90**, 1619; R. J. Oulette and A. South, *ibid.*, p. 7064; R. J. Oulette, D. Miller, A. South, and R. D. Robins, *ibid.*, 1969, **91**, 971; V. I. Sokalov, N. B. Rodina, and O. A. Reutov, *J. Organometallic Chem.*, 1969, **17**, 477.

91 ($-C_3H_4$) and 77. These data are consistent only with a structure: $PhCH_2CH(Me)CH_2CH_2OH$ (**9**), and hence (**12**) and (**13**) for the parent complexes. However, a metastable ion transition: $146^+ \longrightarrow 104^+$, is more easily rationalised in terms of a structure: $Ph(CH_2)_4CH_2OH$, (**10**), *viz.* $146 = [PhCH(CH_2)_3CH_2]^+ \longrightarrow PhCH{=}CH_2^+ = 104 + C_3H_6$. A second transition: $146 \longrightarrow 117$ is also most naturally derived from a structure $PhCH_2CH(Et)CH_2OH$, (**11**), *viz*: $164 \xrightarrow{-H_2O} 146 \xrightarrow{-Et} 117$. Thus although the n.m.r. data indicate the major component to be (**9**), some of the isomers (**10**) and (**11**) may also be present. However, (**12**) and (**13**) clearly represent the structures of the major products.



(**12**)



(**13**)

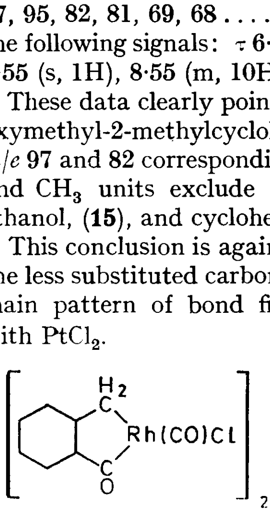
It appears, however, that benzylcyclopropane behaves similarly towards $PtCl_2$ and $[Rh(CO)_2Cl]_2$ in undergoing preferential insertion into the less substituted carbon–carbon bonds.

Towards $PtCl_2$, bicyclo[4,1,0]heptane reacts with isomerisation. With $[Rh(CO)_2Cl]_2$, however, bicycloheptane gave a product $[(C_7H_{12}CO)Rh(CO)Cl]_2$, dec. 140°, ν_{CO} 1735, 1755, and 2050 cm^{-1}. The n.m.r. spectrum showed a broad 2H-signal at τ 6·6 with the remaining protons (10H) as broad signals between τ 7·6 and 8·8. The mass spectrum contained an ion *m*/*e* $96 = C_7H_{12}^+$. The derived triphenylphosphine derivative $(C_7H_{12}CO)Rh(PPh_3)_2Cl$, dec. 185°, ν_{CO} 1605 cm^{-1}, gave an additional low intensity ion *m*/*e* $124 = [C_7H_{12}CO]^+$, and n.m.r. signals: τ 2·2 and 2·6 (Ar–H), 7·8—8·3 (2—3H), and 8·7—9·4 (9—10H) as broad bands.

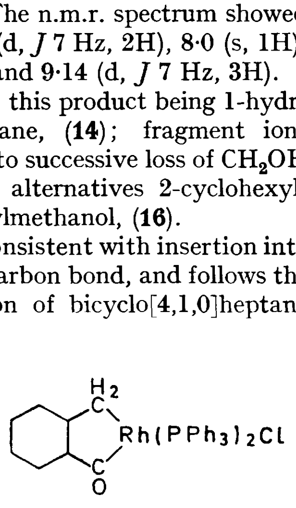
Reduction of either complex with sodium borohydride in ethanol gave a product, ν_{CO} 3400 cm^{-1}, showing in the mass spectrum no molecular ion (*m*/*e* 128), but ions *m*/*e* $110 = C_8H_{14}^+ = C_8H_{16}O - H_2O$, and *m*/*e* 97, 95, 82, 81, 69, 68 .... The n.m.r. spectrum showed the following signals: τ 6·46 (d, *J* 7 Hz, 2H), 8·0 (s, 1H), 8·55 (s, 1H), 8·55 (m, 10H), and 9·14 (d, *J* 7 Hz, 3H).

These data clearly point to this product being 1-hydroxymethyl-2-methylcyclohexane, (**14**); fragment ions *m*/*e* 97 and 82 corresponding to successive loss of CH_2OH and CH_3 units exclude the alternatives 2-cyclohexylethanol, (**15**), and cycloheptylmethanol, (**16**).

This conclusion is again consistent with insertion into the less substituted carbon–carbon bond, and follows the main pattern of bond fission of bicyclo[4,1,0]heptane with $PtCl_2$.



(**17**)



(**18**)

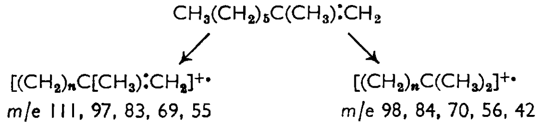
Whereas phenylcyclopropane and benzylcyclopropane are stable to isomerisation by reaction with $[(C_2H_4)PtCl_2]_2$ formation of the carbonylchlororhodium derivatives (**6**) and (**12**) was found to be accompanied by a slow isomerisation of the unreacted cyclopropane.

Phenylcyclopropane kept with $[Rh(CO)_2Cl]_2$ at 60° for some days was found to contain $PhCH{=}CHCH_3$ (CH_3-doublet τ 8·14) and $PhC(CH_3){=}CH_2$ (CH_3-singlet τ 7·87) in a ratio of 4 : 1 (g.l.c.), together with unchanged phenylcyclopropane. Allyl benzene ($-CH_2$-doublet τ 6·65) was absent.

Benzylcyclopropane was similarly isomerised to give what appeared (g.l.c.) to be a single olefin, $\nu(C{=}CH_2)$ 895 cm^{-1}, showing n.m.r. signals: τ 2·8 (5H), 5·24 (m, 2H), 6·71 (s, 2H), 8·35 (s, 3H). These data are consistent with the olefin being 2-benzylprop-1-ene (**19**) which is also consistent with the observed mass spectral cracking pattern, *viz*: *m*/*e* $132 \xrightarrow{-CH_3}$ *m*/*e* $117 \xrightarrow{-2H}$ *m*/*e* 115; *m*/*e* $132 \longrightarrow$ *m*/*e* 91 and 41 ($C_3H_5^+$), and also *m*/*e* 77.

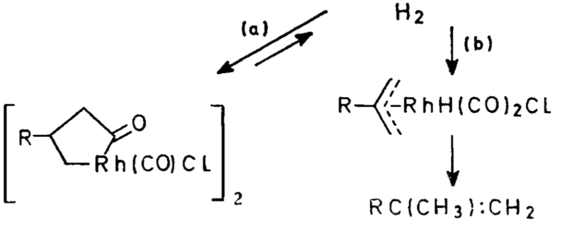
Bicyclo[4,1,0]heptane was isomerised rather slowly to give a product showing the n.m.r. spectrum of methylenecyclohexane ($=CH_2$ at τ 5·44).

n-Hexylcyclopropane on the other hand gave no rhodacyclopentanone derivative, but was isomerised to a mixture of olefins (3 : 1 by g.l.c.). The principal olefinic proton signal in the n.m.r. spectrum of this material was found at τ 5·33 (s, 2H), in agreement with an i.r. band at 895 cm^{-1}, together with a singlet CH_3 signal at τ 8·32. This product is therefore regarded as 2-methyloct-1-ene, *i.e.* corresponding with fission along the less substituted carbon–carbon bond. The mass spectrum contained ions *m*/*e* 126 ($=C_9H_{18}$), 111, 97, 83, 69, 55, as well as ions *m*/*e* 98, 84, 70, 56, and 42, which are rationalised:



The minor component in the olefinic mixture showed an n.m.r. signal at τ 4·65 (m) very similar to that shown by an authentic sample of *trans*-non-2-ene.

An overall mechanism for insertion and isomerisation may therefore be outlined:



An alternative to (b) dependent on carbon–carbon hydride shift is inconsistent with the observations of

Katz and Cerefice[3] on the rearrangement of 3,3-dideuterio-*exo*-tricyclo[3,2,1,$0^{2,4}$]oct-6-ene by means of $(Ph_3P)_3RhCl$. However, step (a) is represented as being intrinsically reversible, since 1-chloro-1-carbonylphenylrhodacyclopentanone, (**6**), when refluxed with excess of triphenylphosphine in chloroform gave $(Ph_3P)_2Rh(CO)Cl$, and propenylbenzene. This reaction presumably represents a thermal decomposition of (**7**). The mechanism is not clear, but it is interesting that propenylbenzene rather than phenylcyclopropane is isolated.

ν_{CO} cm^{-1} (KBr disc)

	Rh(CO)Cl complex		$Rh(Cl)(PPh_3)_2$ derivative
(**6**)	1600, 1640, 2080	(**7**)	1640
(**12**)	1715, 1735, 2060	(**13**)	1630
(**17**)	1735, 1755, 2050	(**18**)	1605
*	1730, 1745, 2041	*	1670

* Corresponding products from cyclopropane (ref. 1).

The Table collects ν_{OO} values for the various rhodacyclopentanones. Complex (**6**) 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 (**7**).

EXPERIMENTAL

Reaction of Various Cyclopropanes with Tetracarbonyldi-μ-chloro-dirhodium.—(i) (a) Phenyl cyclopropane (1 ml) and tetracarbonyldichlorodirhodium (0·11 g) were kept at 60° in a sealed tube for 48 h. A white precipitate formed and precipitation was completed by addition of hexane. The product 1-chloro-1-carbonyl(5-phenylrhodacyclopentan-2-one), (**6**) (0·13 g, 75%) obtained after washing with ether decomposed at 177° without melting. Found: C, 42·2; H, 3·2. $C_{11}H_{10}ClO_2Rh$ requires C, 42·5; H, 3·1%. I.r.: 705, 765 (ArH), ν_{CO} 1600, 1640, and 2080 cm^{-1}.

(b) 1-Chloro-1-carbonyl-(5-phenylrhodacyclopentan-2-one) (0·25 g) and triphenylphosphine (0·5 g) were stirred in chloroform (20 ml) for 1 h, the solution was then filtered and evaporated. The residue, recrystallised from methylene chloride–hexane formed pale yellow crystals, dec. 184°, of 1-chloro-1,1-bis(triphenylphosphine-5-phenylrhodacyclopentan-2-one), (**7**). Found: C, 67·5; H, 4·9; Cl, 4·5. $C_{46}H_{40}ClOP_2Rh$ requires C, 68·1; H, 4·9; Cl, 4·4%. N.m.r.: τ 2·1—2·7 (35 H), 6·66 (m, 1H), 8·12 (m, 2H), and 8·9 (m, 2H).

(c) 1-Chloro-1-carbonyl-5-phenylrhodacyclopentan-2-one (0·085 g) with triphenylphosphine (0·29 g) in chloroform (5 ml) heated under reflux for 20 min gave a yellow solution. Evaporation gave a residue from which hexane extracted material which g.l.c. analysis (apiezon column) indicated contained only propenylbenzene. The residue, recrystallised from ethanol, formed a yellow crystalline solid (0·15 g), ν_{CO} 1960 cm^{-1}, identified as carbonylchlorobis(triphenylphosphine)rhodium by comparison with an authentic sample.

(ii) Benzylcyclopropane (1·4 g) with tetracarbonyldichlorodirhodium (0·1 g) was maintained at 55° for 60 h in a sealed tube. A white complex which began to separate was precipitated by addition of hexane. This material, washed with ether gave a product (0·09 g), 1-chloro-1-carbonyl-4-benzylrhodacyclopentan-2-one, (**12**), dec. 125°. Found: C, 44·7; H, 3·7; Cl 10·7. $C_{12}H_{12}ClO_2Rh$ requires C, 44·2; H, 3·7; Cl, 10·9%. N.m.r.: τ 2·77 (m, 5H), 6·5—6·9 (m, 2H), 7·25 (m, 4H), and 8·2—8·6 (m, 1H).

This material (0·18 g) was kept with triphenylphosphine (0·32 g) in chloroform (5 ml) for 2 min, the solvent removed, and the residue recrystallised from chloroform–hexane to give 1-chloro-1,1-bis(triphenylphosphine)-4-benzylrhodacyclopentan-2-one), (**13**), as pale yellow crystals, dec. 205°. Found: C, 67·9; H, 5·0; Cl, 4·3. $C_{47}H_{42}ClOP_2Rh$ requires C, 68·8; H, 5·1; Cl, 4·3%.

(iii) Bicyclo[4,1,0]heptane (0·5 g) and tetracarbonyldichlorodirhodium (0·07 g) was maintained at 60° for 48 h, and then evaporated *in vacuo*. The complex was recrystallised from hexane by cooling to give 8-chloro-8-carbonylbicyclo[4,3,0]-8-rhodanonan-7-one, (**17**) (0·095 g), dec. 140°. Found: C, 37·4; H, 4·1. $C_9H_{12}ClO_2Rh$ requires C, 36·7%; H, 4·1%. N.m.r.: τ 6·6 (2H), 7·6—8·8 (10H).

This material (0·095 g) with triphenylphosphine (0·22 g) in chloroform (10 ml) was kept for 1 min, reduced to half volume, and diluted with hexane. 8-Chloro-8,8-bis(triphenylphosphine)-8-rhodabicyclo[4,3,0]nonan-7-one (**18**) formed yellow crystals, dec. 185°. Found: C, 67·1; H, 5·3; Cl, 4·5. $C_{44}H_{48}ClOP_2Rh$ requires C, 67·2; H, 5·3; Cl, 4·5%. N.m.r. τ 2·2 and 2·6 (30 H), 7·8—8·3 (2—3H), 8·7—9·4 (9—10H).

Sodium Borohydride Reduction.—(i) 1-Chloro-1-carbonyl-5-phenylrhodacyclopentan-2-one (0·25 g) in pyridine (3 ml) was treated with sodium borohydride (0·8 g) added with stirring during 2 h. After a further 1 h the product was isolated by dilution with water, ether extraction, washing, *etc*. The product (**5**) (0·065 g, 60%) appeared to be a single substance to g.l.c. on a polyethylene glycol succinate column, ν_{OO} 3400 cm^{-1}, n.m.r. (CCl_4): τ 2·9 (m, 5H), 6·49 (t, *J* 6 Hz, 2H), 7·42 (t, *J* 6 Hz, 2H), 7·7 (s, 1H), and 8·44 (m, 4H).

The corresponding 1-chloro-1,1-bis(triphenylphosphine)-5-phenylrhodacyclopentan-2-one) treated similarly gave a product which was extracted into hexane to remove triphenylphosphine and shown by n.m.r. to be identical with the product above.

(ii) The rhodacyclopentanone derivatives from benzylcyclopropane were treated similarly except that the bis(triphenylphosphine) complex was sufficiently soluble for use of ethanol as solvent, and the reduction product was purified by t.l.c. on silica gel in benzene. The product (**9**) (40%), R_f 0·25, appeared homogeneous to g.l.c., and showed ν_{OH} 3400 cm^{-1}, and τ 2·82 (m, 5H), 6·35 (t, *J* 7 Hz, 2H), 7·45 (m, 2H), 8·3—8·8 (m, 3H), and 9·12 (d, *J* 7 Hz, 3H).

(iii) The rhodacyclopentanone derivatives from bicyclo-[4,1,0]heptane treated as in (ii) gave a product (**14**), without t.l.c. purification (85%), ν_{CO} 3410 cm^{-1}, and n.m.r. bands ($CDCl_3$): 6·46 (d, *J* 7 Hz, 2H), 8·0 (s, 1H), 8·55 (m, 10H), and 9·14 (d, *J* 7 Hz, 3H).

Isomerisation by Means of $[Rh(CO)_2Cl]_2$.—(i) (a) Phenylcyclopropane (0·5 ml) kept with tetracarbonyldichlorodirhodium (0·05 g) at 60° for 10 days gave a recovered product containing 50% phenylcyclopropane, 40% propenylbenzene, and 10% 2-methylstyrene by integration of n.m.r. signals at τ 8·9—9·4 (PhC_3H_5), 8·14 (d, $PhCH{:}CHCH_3$), and 7·87 [s, $PhC(CH_3){:}CH_2$].

(b) Phenylcyclopropane (0·5 ml with 1-chloro-1-carbonyl-5-phenylrhodacyclopentan-2-one (0·04 g) was maintained at 60° for several weeks. The recovered organic material was then found to contain propenylbenzene (30%) and α-methylstyrene (8%) by n.m.r. analysis.

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[3] T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, 1971, **93**, 1049.

(ii) Benzylcyclopropane after repeated reaction with tetracarbonyldichlorodirhodium was found to have been wholly converted into 2-methyl-3-phenylprop-1-ene (*m/e* 132), ν($C=CH_2$) 895 and 1650 cm^{-1}, n.m.r. bands: τ 2·8 (m, 5H), 5·24 (2H), 6·71 (s, 2H), and 8·35 (s, 3H).

(iii) Bicyclo[4,1,0]heptane treated as in (i) was found to contain methylenecyclohexane by n.m.r. comparison with an authentic sample.

Reaction of n-Hexylcyclopropane with $[Rh(CO)_2Cl]_2$.—n-Hexylcyclopropane (0·5 g) with tetracarbonyldichlorodirhodium (0·05 g) at 60° for 3 days gave no rhodacyclopentanone product. On cooling (−78°) only $[Rh(CO)_2Cl]_2$ was recovered. The organic material was distilled and characterised by (a) g.l.c. (Apiezon column) which indicated two components (75 : 25), (b) n.m.r. which showed bands at τ 5·33 (s, $C=CH_2$) and 4·65 (m), ratio 3 : 1. Additional bands appeared at τ 8·0 (2H), 8·32 (s, 3H), 8·7 (8H), and 9·7 (t, *J* 5 Hz, 3H), and i.r. bands at 3090, 1653, and 895 cm^{-1} (ν$C=CH_2$). The τ 4·65 multiplet corresponds with a signal shown by *trans*-non-2-ene, but there was no similarity with the spectrum of non-1-ene.

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