cis-Divinylcyclopropane and the Hexafluoroacetylacetonatorhodium(I) Complexes of *cis*- and *trans*-Divinylcyclopropane [1]

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The synthesis of *cis*-divinylcyclopropane has been achieved by Wittig reaction of *cis*-2-vinylcyclopropanecarbaldehyde with methylenetriphenylphosphorane at 5°. The product is stable at low temperatures, and rearranges quantitatively to cyclohepta-1,4-diene with a half-life of 11 min at 288.5 K. An approximate set of reaction rate measurements in $CFCl_3$ shows that $\Delta G^\ddagger$ = 86 kJ mol^{-1}. *cis*-Divinylcyclopropane reacts with bisethylenehexafluoroacetylacetonatorhodium(I) in isopentane to give a 1 : 1 complex with displacement of ethylene which is thermally stable for moderate periods at 65°, rearranging slowly to the hexafluoroacetylacetonatorhodium(I) complex of cyclohepta-1,4-diene. Spectroscopic evidence suggests that this former species has an intact cyclopropane ring. In contrast, *trans*-divinylcyclopropane reacts with bisethylenehexafluoroacetylacetonatorhodium(I) giving a 1 : 1 complex in which the cyclopropane ring has opened to form a bis-π-allylrhodium complex.

IN previous papers [1,2] we have examined the chemistry of hexa-1,5-dienerhodium complexes, and found simple examples to be unreactive towards Cope rearrangement and other C(3)–C(4) cleavage-initiated reactions. The corresponding complexes (1) of the strained hydrocarbon 6-vinylbicyclo[3.1.0]hex-2-ene are much more stable than the parent hydrocarbon, but rearrange above 80°. Here the major product is the corresponding complex (2) of bicyclo[3.3.0]octa-2,6-diene derived by 1,3-sigmatropic shift. It was therefore of interest to determine the stability of complexes derived from simple divinylcyclopropanes.

Synthesis of cis-*Divinylcyclopropane* (3).—Earlier work by Doering and Roth [3] and by Vogel and his co-workers [4] had established that *cis*-divinylcyclopropane was too unstable to be isolated by conventional techniques. Particularly as a result of Doering and Roth's attempt to prepare (3) by copper(I) chloride catalysed cyclopropanation of hexa-1,3,5-triene (carried out at −45° as well as at 0°) there had arisen the general conviction that '*cis*-divinylcyclopropane rearranges so fast that it cannot be isolated even at −40°'.[5] In fact, no attempt was made to isolate (3) at this temperature, the major piece of evidence being that in the low temperature cyclopropanation bicyclo[5,1,0]oct-3-ene was isolated in comparable quantity to cyclohepta-1,4-diene. By itself, of course, this result tells us nothing about the thermal stability of *cis*-divinylcyclopropane, since other interpretations [*e.g.* that Cope rearrangement of (3) is catalysed by Cu^I, or that excess of the methylenecopper cyclopropanating agent survives such that rearrangement and subsequent cyclopropanation to (4) occurs during work-up] are equally valid in the absence of corroborative evidence. Subsequent to this pioneering work, a number of *cis*-divinylcyclopropanes have been isolated.[6] Where the double bonds are terminal, or form part of a *cis*-fused ring with no stereoelectronic barrier to rearrangement, then activation barriers $\Delta G^\ddagger$ fall within the range 85—110 kJ mol^{-1}. Thus a barrier of *ca.* 70 kJ mol^{-1}, required for instability at −40°, seemed to be unreasonably low. Simple derivatives of *cis*-divinylcyclopropane have been prepared and in *e.g.* (5) where the transition state for Cope rearrangement experiences substantial steric destabilisation, the barrier is sufficient for ready isolation at room temperature.[7] These factors encouraged us to attempt a different approach to the synthesis of *cis*-divinylcyclopropane.

In Wittig reactions of aldehydes in dimethyl sulphoxide, formation and breakdown of betaine intermediates is rapid below room temperature and epimerisation is not a serious competing side-reaction. We therefore prepared *cis*-2-vinylcyclopropanecarbaldehyde (6) [8] using CrO_3–pyridine or CrO_3–2,5-dimethylpyrazole [9] to oxidise the corresponding alcohol. This was rapidly treated with methylenetriphenylphosphorane in dimethyl sulphoxide at 5°, under which conditions the reagent existed as a semi-solid slurry. After shaking for 30 s, the mixture was rapidly cooled to −80°, and extracted with isopentane. The resulting solution was transferred by pre-cooled syringe to a fractionating apparatus and isopentane removed at −65° and 2 mmHg. The residue was distilled at −40° and 0.01 mmHg and in initial experiments, diluted with $CFCl_3$ transferred by syringe to n.m.r. tubes held at −80°.

The n.m.r. spectrum of the solution (Figure 1) was consistent with that anticipated for *cis*-divinylcyclopropane whose cyclopropyl protons exhibited chemical shifts and coupling constants similar to related molecules.[10] At −20° little change was observed on repeated scanning, although warming the probe to around

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[1] J. M. Brown, B. T. Golding, and J. J. Stofko, jun., *J.C.S. Chem. Comm.*, 1973, 319; N. W. Alcock, J. M. Brown, J. A. Conneely, and J. J. Stofko, jun., *ibid.*, 1975, 234.

[2] V. Aris, J. M. Brown, J. A. Conneely, B. T. Golding, and D. H. Williamson, *J.C.S. Perkin II*, 1975, 4; V. Aris, J. M. Brown, and B. T. Golding, *ibid.*, 1974, 700.

[3] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 715.

[4] E. Vogel, K. H. Ott, and K. Gajek, *Annalen*, 1961, **644**, 172.

[5] *E.g.* H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103.

[6] J. M. Brown, *Chem. Comm.*, 1965, 226; K. Hojo, R. T. Seidner, and S. Masamune, *J. Amer. Chem. Soc.*, 1970, **92**, 6641; T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, p. 6643; M. S. Baird and C. B. Reese, *Chem. Comm.*, 1970, 1519.

[7] *Inter alia* J. A. Pettus, jun. and R. E. Moore, *J. Amer. Chem. Soc.*, 1971, **93**, 3087; T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, 1972, **37**, 466; L. Jaenicke, T. Akintobi, and F. J. Marner, *Annalen*, 1973, **767**, 1252; W. Pickenhagen, F. Naf. G. Ohloff, P. Muller, and J. C. Perlberger, *Helv. Chim. Acta*, 1973, **56**, 1868; J. E. Baldwin and C. Ullenius, *J. Amer. Chem. Soc.*, 1974, **96**, 1542.

[8] S. J. Rhoads and R. D. Cockroft, *J. Amer. Chem. Soc.*, 1969, **91**, 2815.

[9] E. J. Corey and G. W. J. Fleet, *Tetrahedron Letters*, 1973, 4499.

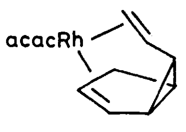
[10] G. Schrumpf, *Tetrahedron Letters*, 1970, 2571.

0° led to appreciable formation of cyclohepta-1,4-diene revealed by the appearance of methylene multiplets at δ 2.3 and 3.0. This rearrangement was followed semi-quantitatively at various temperatures between 11 and 35° monitoring the decay in vinyl resonance at δ 5.2 or alternatively the growth in absorbance at δ 3.0 due to the methylene resonance of cycloheptadiene. Results thus obtained are shown in the Table. Since our work was completed, an alternative and simple synthesis of *cis*-divinylcyclopropane (in approximately equal admixture with the *trans*-isomer) has been achieved by low-temperature photolysis of 3,5-divinylpyrazoline[11] (7). Dr. Schneider intends to carry out a more thorough examination of the kinetics of rearrangement of (3) over a wide range of temperatures.

Thermolysis of (3) in $CFCl_3$, monitored by n.m.r. Reaction rates were determined by monitoring the decay of the vinyl peak of (3) at δ 5.2 and/or the increase in methylene absorbance of cyclohepta-1,4-diene at δ 2.3

T/°C	11.3	15.5	20.4	35.0
$10^4 k_{obs}/s^{-1}$	4.49	10.8	15.4	77

$\Delta G^{\ddagger} = 86$ kJ. mol^{-1}



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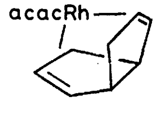

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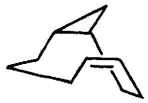

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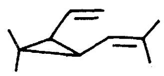

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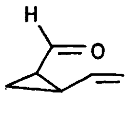

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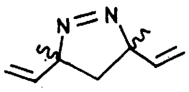

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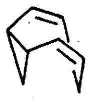
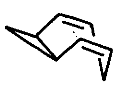


(8a)



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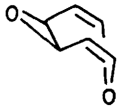

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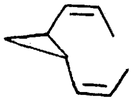

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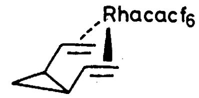

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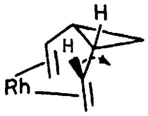
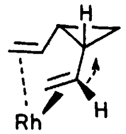
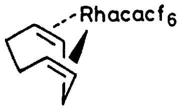


(13a)



(13b)



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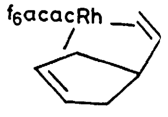

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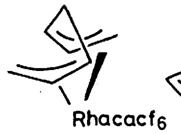
(16)



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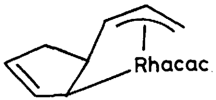
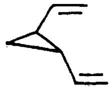


(18) (*n*-mer)



(19)

It is notable that the activation free energy of rearrangement accords well with other (non-degenerate) *cis*-divinylcyclopropane thermolyses recorded in the literature. In the case of (8b), part of the activation barrier derives from a pre-equilibrium between the transoid-conformation and the corresponding cisoid-conformation (8a) required for rearrangement. Dominance of the former at equilibrium is inferred from the high value of $J_{1,1'}$ (8.5 Hz), from the transoid structure of vinylcyclopropane, and the proximity strain involving *syn*-3- and *cis*-2-H in (8a). A similar situation arises in the degenerate rearrangement of bicyclo[5.1.0]-octa-2,4-diene,[12] and here Doering and Roth estimate an energy difference of *ca.* 3 kcal mol^{-1} between cisoid- and transoid-isomers. A detailed investigation of mechanism by n.m.r. total line-shape analysis permitted them to conclude that the *trans* $\rightleftharpoons$ *cis* interconversion was a rapid pre-equilibrium prior to rate-limiting Cope rearrangement.

Now that the rate of rearrangement of *cis*-divinylcyclopropane is defined, two factors are worth comment. One is the pattern of $-N^{13} > CH_2 \gg O^{13}$ for ease of reaction of (3) and its ring-substituted analogues. This is similar to the situation in corresponding bicyclo[6.1.0]nona-2,6-diene derivatives.[14] 4,8-Dioxabicyclo[5.1.0]octa-2,5-diene (9) likewise shows no sign by n.m.r. of degenerate rearrangement,[15] the barrier being at least 40 kJ mol^{-1} higher than in the parent (8). These results point to a substantial (and not yet properly

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[11] M. Schneider, *Angew. Chem. Internat. Edn.*, 1975, **14**, 707; M. Schnieder and J. Rebell, *J.C.S. Chem. Comm.*, 1975, 283.

[12] H. Gunther and J. Ulmen, *Chem. Ber.*, 1975, **108**, 3132; H. Gunther, J. B. Pawliczek, J. Ulmen, and W. Grimme *ibid.*, p. 3141; R. Bicker, H. Kessler, and W. Ott, *ibid.*, p. 3151; R. Bicker, H. Kessler, A. Stiegel and W. D. Stohner, *ibid.*, p. 2708.

[13] J. C. Pommelet and J. Chuche, *Tetrahedron Letters*, 1974, 3897; J. C. Pommelet, N. Manisse, and J. Chuche, *ibid.*, 1972, 3929, and references therein.

[14] W. Grimme and K. Seel, *Angew. Chem. Internat., Edn.*, 1973, **12**, 507.

[15] H. Klein and W. Grimme, *Angew. Chem. Internat. Edn.*, 1974, **13**, 672; W. H. Rastetter, *J. Amer. Chem. Soc.*, 1975, **97**, 210; (*cf.* H. Klein, W. Kussawa, and W. Grimme, *Angew. Chem. Internat. Edn.*, 1973, **12**, 507).

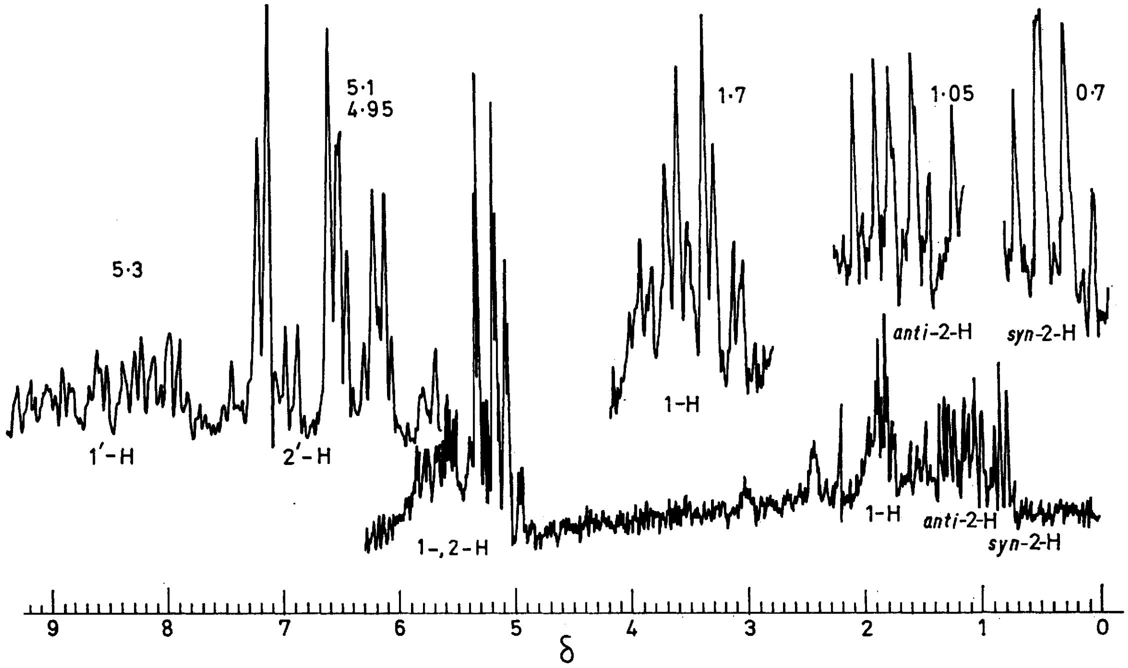

FIGURE 1 N.m.r. spectrum of *cis*-divinylcyclopropane (3) in $CDCl_3$ at —20°. δ Values are recorded relative to internal lock C_6H_6 at δ 7.27

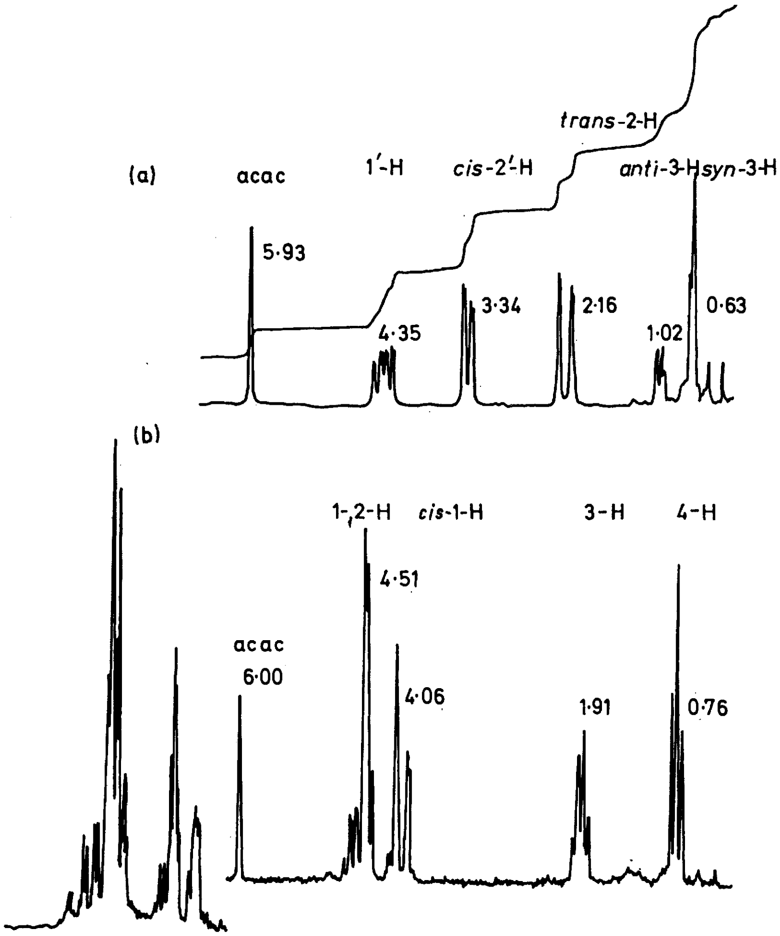

FIGURE 2 N.m.r. spectra of (a) *cis*- and (b) *trans*-divinylcyclopropanehexafluroacetylacetonatorhodium(I) in benzene solution

understood) ground-state stabilisation in divinyloxirans. Accordingly, the equilibrium constant for cycloheptatriene $\rightleftharpoons$ norcaradiene tautomerism is very large [16] whilst that for benzene ozide $\rightleftharpoons$ oxepin [17] is finely balanced. This is in spite of the fact that the strain energy in cyclopropanes and oxirans is very similar.[18] Secondly, the extreme importance of steric interactions in determining the course of boat-constrained Cope rearrangements may be assessed.[7,19] A *cis*-methyl group on the double bond destabilises the transition state by at least 20 kJ mol^{-1} and thus the compound with two *cis*-methyl groups (10) rearranges to the *trans*-isomer (11) faster than to 6,7-dimethylcyclohepta-1,4-diene. The activation energy for this latter process is 130 kJ mol^{-1} at 438 K. A similar situation arises in the *cis*-divinylcyclobutane $\longrightarrow$ cyclo-octa-1,5-diene rearrangement,[20] which is slowed down drastically by *cis*-methyl substitution on one or both double bonds.

Hexafluoroacetylacetonatorhodium(I) (Rhacacf$_6$) *Complexes*.—(i) cis-*Divinylcyclopropane*. Direct reaction between (3) and bisethylenehexafluoroacetylacetonatorhodium (12) in isopentane at −80° gave a 1 : 1 adduct isolated as well defined yellow needles. Structure (13) follows from the ^1H and ^{13}C n.m.r. spectra (Figure 2). In the latter, the ring carbon atoms are at high field, typical of substituted cyclopropanes, and no rhodium–carbon coupling is observed. The implication of an intact, non-interacting cyclopropane ring is supported by a very small coupling constant between 1- and 1′-H. In a complex of transoid stereochemistry with partial rehybridisation at C(1′), the dihedral angle between 1- and 1′-H will be decreased relative to the parent hydrocarbon with consequent reduction in coupling constant $J_{1,1'}$. Conversely, a complex of cisoid conformation having partial rehybridisation at C(1′) might be expected to have a large value of $J_{1,1'}$ since the dihedral angle is now close to 0° [compare (13a and b)].

The new complex (13) is quite stable at room temperature in solution, although changes in the n.m.r. spectrum become apparent on standing at 65°. Reaction was monitored at regular intervals by n.m.r. which demonstrated the formation of a single new compound (14) without intervention of observable intermediates. Several features of the new spectrum bore a strong resemblance to the known cycloheptatrieneacetylacetonatorhodium(I),[21] and addition of [$^2H_6$]dimethyl sulphoxide to the solution obtained after 20 h at 65° demonstrated that cyclohepta-1,4-diene was the only hydrocarbon ligand. It is unlikely, however, that rearrangement of (13) to (14) occurs within the co-ordination sphere. After addition of 20 mole % of bis ethylenehexafluoroacetylacetonatorhodium(I) to a solution of (13) in [$^2H_6$]benzene, and heating to 65° for 20 h, n.m.r. examination revealed very little rearrangement. This implies that (14) is formed *via* dissociation–decomposition of the starting material, and rearrangement of transient *cis*-divinylcyclopropane, which is effectively trapped by (12) with displacement of ethylene. No evidence was obtained in any thermolysis experiment for the formation of (15), the product of a 1,3 sigmatropic shift in (13) which might have been expected by precedent.[2] Its formation might be unfavourable on account of the high degree of angle strain required to align the pendant vinyl group such that good ligand–metal overlap ensues in a bidentate square-planar complex. In contrast, the distortion inherent in bicyclo[3.3.0]octa-2,6-diene leads to favourable binding, and the rearrangements leading to (2) occur readily.[2] The inertness of (13) may be related to co-ordination geometry, since (1) which rearranges more readily, is necessarily cisoid. Preparation of the isomeric (16) would provide revealing insights into the relationship between structure and reactivity in organorhodium–diene complexes.

(ii) trans-*Divinylcyclopropane*. The hydrocarbon was readily prepared from *trans*-2-vinylcyclopropanemethanol as above, and reacted with (12) in isopentane at 0° by displacement of ethylene. Both ^1H (Figure 2) and ^{13}C n.m.r. spectra of the resulting complex (17) were rather similar to that of the parent hydrocarbon, the only evidence for ring opening being the rhodium–carbon coupling which requires *s*-character in that metal–carbon interaction, and thus a contribution from σ-bonding. The *X*-ray structure confirms that ring opening has occurred, and demonstrates the solid-state conformation to be (17). Full structural details are discussed elsewhere.[22] For the present we note that (17) belongs to the growing family of linked bis-π-allyls [23,24] many of which are important in catalysis. Within this family it is unique in having a single carbon atom bridging the terminal allyl groups, and therefore incorporates rather more steric strain, apparent in the 48° distortion of C(3)–C(4) out of the plane described by C(1)—C(3).

Surprisingly (17) survives heating in [$^2H_6$] benzene for

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[16] Calculated (MINDO/3) difference in enthalpy 42.6 kJ mol^{-1}, R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1294.

[17] E. Vogel and H. Gunther, *Angew. Chem. Internat. Edn.*, 1967, **6**, 385.

[18] For example, the enthalpy of the hypothetical reaction C_2H_4 + cyclo-$C_3H_6 \longrightarrow$ cyclo-C_5H_{10} is −182 kJ mol^{-1}, whilst that of C_2H_4 + cyclo-$C_2H_4O \longrightarrow$ cyclo-C_4H_8O is −183 kJ mol^{-1}, S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.

[19] *Cf.* J. A. Berson, T. Mayashi, and G. Jones, II, *J. Amer. Chem. Soc.*, 1974, **96**, 3468, and references therein.

[20] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, 1973, **95**, 269; 1972, **94**, 7597; J. A. Berson, P. B. Dervan, and J. A. Jenkins, *ibid.*, p. 7598.

[21] J. M. Brown and D. G. Coles, *J. Organometallic Chem.*, 1973, **60**, C31.

[22] N. W. Alcock and J. A. Conneely, *Acta Cryst.*, 1977, **B33**, 141.

[23] N. W. Alcock, J. M. Brown, J. A. Conneely, and D. H. Williamson, *J.C.S. Chem. Comm.*, 1975, 792.

[24] *Inter alia* T. S. Cameron and C. K. Prout, *Acta. Cryst.*, 1972, **B28**, 2021; R. A. Head, J. F. Nixon, J. R. Swain, and C. M. Woodward, *J. Organometallic Chem.*, 1974, **76**, 393; R. Bussmeier, P. W. Jolly, and G. Wilke, *J. Amer. Chem. Soc.*, 1974, **96**, 4762; G. Ingrosso, R. Porri, G. Pontini, and P. Racanelli, *J. Organometallic Chem.*, 1975, **84**, 75; G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

24 h at 100°, and no rearrangement or isomerisation is apparent. This is in contrast to the (tetrameric) bis-σπ-allyl (18) which rearranges readily at 65°.[23] It does however catalyse the conversion of (19) to cyclohepta-1,4-diene which presumably involves epimerisation to *cis*-divinylcyclopropane. Heating a mixture of (19) and 20 mole % (12) in [$^2H_6$]benzene to 75° gave a solution in which the ^1H n.m.r. resonances of (17) were clearly apparent.

EXPERIMENTAL

N.m.r. spectra were recorded on a Perkin-Elmer R12 machine at 60 MHz, a Varian HA-100 machine at 100 MHz and, in the case of ^{13}C spectra, on a Bruker WH-90 instrument operating at 22.62 MHz. Rate measurements at 100 MHz were recorded at temperatures immediately precalibrated using methanol as reference sample, and we thank Dr. C. Baker of P.C.M.U. for these. Spinning-band distillations were effected with an Annular Teflon still (Nester-Faust). Organometallic complexes were prepared in Schlenck tubes employing vacuum-line techniques under nitrogen prepurified by passage through chromium(III) chloride, sulphuric acid, and over potassium hydroxide pellets. I.r. spectra were taken on a Perkin-Elmer 257 instrument.

cis- *and* trans-2-*Vinylcyclopropanemethanol.*—The addition of ethyl diazoacetate to butadiene was carried out by previously reported methods, with the modification that copper(I) chloride–triphenylphosphite was used as a catalyst in place of copper bronze.[25] The crude mixture of isomers, b.p. 75—90° at 10 mmHg, 35 : 65 *cis* : *trans*, was reduced with lithium aluminium hydride in ether and subjected to spinning band distillation. From crude alcohol (10 g) there was obtained *cis*-2-vinylcyclopropanemethanol (2.1 g), b.p. 47—48° at 5 mmHg, and *trans*-2-vinylcyclopropanemethanol (1.9 g), b.p. 53—54° at 5 mmHg. An intermediate fraction (4.0 g) was predominantly *trans*-isomer and could be obtained pure by refractionation.

cis-2-*Vinylcyclopropanecarbaldehyde.*—To the dark red solution prepared by addition of bispyridinechromium trioxide (2.57 g, 9.9 mmol) to dichloromethane (20 ml.) there was added *cis*-2-vinylcyclopropanemethanol (0.32 g, 3.3 mmol) in dichloromethane (5 ml). The reaction mixture was shaken for 5 min at room temperature and then filtered to remove precipitated chromium salts. The filtrate was distilled to dryness *in vacuo* and washed three times with aqueous nickel chloride (25 ml, 0.5M) followed by two further washings with distilled water. The organic layer was dried (K_2CO_3), and dichloromethane removed at reduced pressure. The residue was bulb-to-bulb distilled *in vacuo* giving *cis*-2-vinylcyclopropanecarbaldehyde [0.625 g, 65% (combined product of three similar runs)]. The product was pure by n.m.r., excepting *ca.* 4% contamination by the *trans*-isomer, δ 9.15 (CHO).

In subsequent work the modified oxidation procedure of Corey and Fleet [9] was used with advantage. To chromium trioxide (1.5 g, 0.15 mol) was added 3,5-dimethylpyrazole (1.44 g, 0.15 mol) in dichloromethane (10 ml) and the mixture stirred for 10 min at room temperature. *cis*-2-Vinylcyclopropanemethanol (0.49 g, 0.05 mol) in dichloromethane (3 ml) was added and the mixture stirred for 30 min followed by addition of pentane (100 ml). Filtration, solvent evaporation, and bulb-to-bulb distillation *in vacuo* gave essentially pure *cis*-isomer.

cis-*Divinylcyclopropane.*—A solution of methyltriphenylphosphonium iodide (5.2 g, 13 mmol) in dimethyl sulphoxide (10 ml) was stirred under nitrogen during addition of dimsyl sodium (2.8 ml, 2.86M in dimethyl sulphoxide, 7.8 mmol). Isopentane (10 ml) was added and the mixture cooled to 7—10°, when a solution of vinylcyclopropanecarbaldehyde (0.625 g, 6.5 mmol) in isopentane (3 ml), precooled to 5°, was added over a period of 20 s. After continuous stirring for 30 s, and a vigorous shake, the mixture was quickly cooled to −20°. The isopentane layer was removed from the frozen slush with a cooled pipette and transferred to a distillation flask at −60°. The cold reaction mixture was shaken with two further portions of precooled isopentane which were combined with the first extract. Isopentane was pumped from the system with the bath at −60°, the distillation column at −50°, and a pressure of 5 mmHg. When the isopentane was thus removed, the head temperature was decreased to −75°, the column to −65°, and the pot maintained at −60°. The pressure was then decreased to 0.01 mmHg. The pot temperature was gradually raised to −40°, and the column temperature increased accordingly until no further distillation occurred. When distillation ceased, nitrogen was bled into the apparatus, the pot was replaced, and the condensed distillate washed down with chlorotrifluoromethane precooled to −20°. This solution was transferred cold to a series of n.m.r. tubes.

Rearrangement of cis-*Divinylcyclopropane to Cyclohepta-1,4-diene.*—Preliminary examination of one n.m.r. sample at 35° demonstrated the presence of a reactive species, decaying to cyclohepta-1,4-diene with a half-life of *ca.* 90 s.

More accurate determination of the rearrangement rate was carried out between 7 and 20°, monitoring changes in the n.m.r. spectrum at 100 MHz. Temperatures were precalibrated by standard methods. The reaction rate was monitored either by following the decay of vinyl resonances due to 1-H in (3) or alternatively the growth of signals at δ 2.3 due to 6- and 7-H in cyclohepta-1,4-diene. At completion of reaction a mixture comprising 90% cyclohepta-1,4-diene and 10% (19) was always observed.

trans-*Divinylcyclopropane.*—To a solution of methyltriphenylphosphonium iodide (15.6 g, 0.04 mol) in dimethyl sulphoxide (35 ml) there was added under nitrogen dimsyl sodium (1.5M in dimethyl sulphoxide, 18 ml, 0.027 mol). The resulting yellow solution was stirred during addition of *trans*-2-vinylcyclopropanecarbaldehyde (1.94 g, 0.02 mol) over 20 min. After a further 30 min, the reaction flask was connected to a vacuum line and volatile material evacuated into a cold trap. Several subsequent bulb-to-bulb distillations at 0° gave *trans*-divinylcyclopropane (1.05 g, 56%), pure by n.m.r., δ(C_6D_6) 4.9 (6 H, m, vinyl), 8.75 (2 H, t, $J_{1,2}$ 6 Hz, 1-H), and 9.3 (2 H, t, 2-H).

Rhodium Complexes of cis- *and* trans-*Divinylcyclopropane.*—Initial attempts at the preparation of acetylacetonate derivatives led to uncrystallisable oils, and therefore the hexafluoroacetylacetonate was investigated. To a solution of freshly recrystallised bisethylenehexafluoroacetonatorhodium(I) (0.301 g, 0.8 mmol) in isopentane (5 ml) held at 0° there was added excess of *trans*-divinylcyclopropane (0.111 g, 1.20 mmol). The resulting orange suspension was stirred for 15 min at 0° and ether (5 ml) added. After a further 25 min at room temperature solvent was removed *in vacuo* and the residue dissolved in isopentane containing a small amount of ether. After filtration to remove a small quantity of insoluble impurities and removal of solvent the

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[25] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

residue was recrystallised from isopentane at −78°. There was thus obtained orange trans-*divinylcyclopropanehexafluoroacetylacetonatorhodium*(I), m.p. 68—69°, (Found: M^+, 403.970 96. $C_{12}H_{10}F_6O_2Rh$ requires M, 403.971 17).

Similarly, with initial addition carried out at −20°, there was obtained from *cis*-divinylcyclopropane the corresponding yellow cis-*complex*, m.p. 79—80° (Found: M^+, 403.970 96).

Thermolyses.—(a) A solution of *trans*-divinylcyclopropane (30 μl) in [$^2H_6$]benzene (0.5 ml) containing bisethylenehexafluoroacetylacetonatorhodium(I) (18 mg, *ca.* 20 mole %) was maintained at 75° and the solution monitored at intervals. After 2 h half the starting material had been converted into cyclohepta-1,4-diene, and after 28 h rearrangement was essentially complete. In a separate experiment employing bisethylene acetylacetonatorhodium(I) (20 mole %) as catalyst, the rate of rearrangement was reduced by a factor of two.

(b) A solution of *cis*-divinylcyclopropanehexafluoroacetylacetonatorhodium(I) (12 mg) in [$^2H_6$]benzene (0.4 ml) was heated to 65° under nitrogen and the n.m.r. spectrum monitored at frequent intervals. Rearrangement to a new compound was apparent, concomitant with 5—10% decomposition revealed by minor, unidentified singlet resonances in the region of δ 5 (acac C–H). The new product was identified as cyclohepta-1,4-dienehexafluoroacetylacetonatorhodium(I) on the basis of its ^1H n.m.r. spectrum. Addition of [$^2H_6$]dimethyl sulphoxide (50 μl) to the reacted solution cleaved the complex, and resonances due to cyclohepta-1,4-diene at δ 2.3 and 3.0 were then readily apparent.

Under the same conditions, and in similar experiments at 100°, the *trans*-isomeric complex proved to be thermally stable.

The above experiment was repeated in the presence of 20 mole % of bisethylenehexafluoroacetylacetonatorhodium(I), the n.m.r. spectrum of the mixture being essentially that of the superimposed pure components. After 24 h at 65°, little rearrangement had occurred.

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