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Vinylcyclopropane Rearrangements

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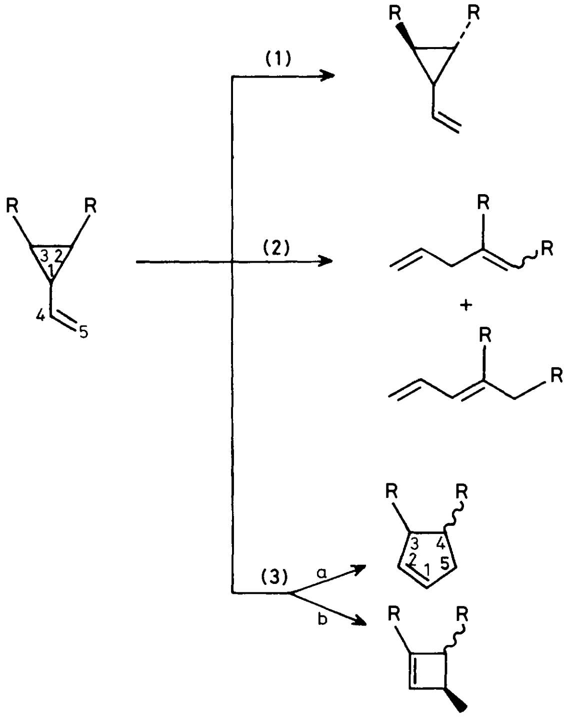
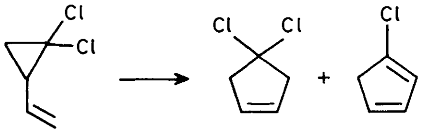
1 Introduction

Vinylcyclopropanes (vcp) can undergo three fundamental types of bond-reorganization processes (Scheme 1): (1) *cis–trans* isomerization; (2) ring opening to pentadienes; (3) ring enlargement to (a) cyclopentenes and (b) methylcyclobutenes. These rearrangement processes can occur by thermal, photochemical, and catalytic routes.



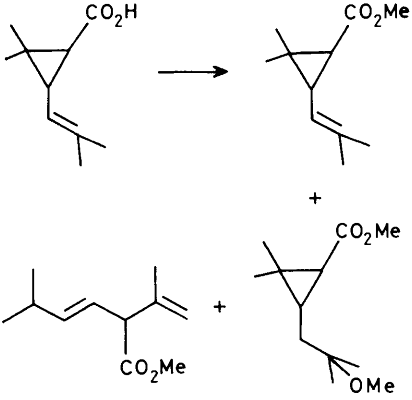
Scheme 1

The first reported vcp rearrangement was the pyrolysis of 2,2-dichlorovinylcyclopropane (1) to a mixture of 4,4-dichlorocyclopentene (2), monochlorocyclopentadiene (3), and unidentified chlorinated hydrocarbons, carried out by



(1) (2) (3)

(1)



Scheme 2

Neureiter in 1959 (equation 1).[1] However, unobserved vcp rearrangements probably occurred as early as 1922 during the preparation of vcp by drastic methods.[2]

On repeating Harper and Reed's acid-catalysed esterification of *trans*-chrysanthemic acid an additional product, the labile methyl ester of lavandulylic acid, was identified (Scheme 2).[3]

This review reflects the recent developments in vcp rearrangements under thermal, acid-catalysed, photochemical, and metal-promoted conditions.

2 Thermal Rearrangements of Vinylcyclopropanes

During the past two decades several reviews[4–10] relating to thermal rearrangements of vcp have appeared. The most recent and the most comprehensive relates only to thermal rearrangements of vcps to cyclopentenes.[11]

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[1] (*a*) N. P. Neureiter, *J. Org. Chem.*, 1959, **24**, 2044; (*b*) U.S. Patent No. 2,951,878 (1960); (*c*) U.S. Patent No. 2,981,756 (1961).

[2] N. J. Demjanow and M. Dojarenko, *Chem. Ber.*, 1922, **55B**, 2718.

[3] S. H. Harper and H. W. B. Reed, *J. Sci. Food Agric.*, 1951, 414. [The mixture of esters obtained was analysed by n.m.r. and it was found that the methyl *trans*-5-methyl-2-propen-2-yl-hex-3-enoate was formed in 10% yield—B. Crammer (1988)].

[4] H. M. Frey, 'The gas phase pyrolyses of some small ring compounds), in *Advances in Physical Organic Chemistry*, 1966, Vol. 4, Ed. V. Gold, Academic Press.

[5] S. Sarel, J. Jovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 5.

Vcps can undergo two kinds of thermal reactions: cleavage of the cyclopropane ring σ-bond followed by H-migration, and a formal 1,3-sigmatropic shift to cyclopentenes (Scheme 1, processes 2 and 3a).

The ring opening process to the dienes (Scheme 1, process 2) occurs with activation energies E_a 52—66 kcal mol^{-1}, which is characteristic of the cyclopropane ring to the alkene process. Cyclopentene formation (Scheme 1, process 3) occurs with E_a 31—63 kcal mol^{-1}. Thermolysis of the parent vcp (4) under adiabatic conditions affords principally cyclopentene (5).[12,13] Minor products that have also been isolated are *cis*-1,3-pentadiene (6), *trans*-1,3-pentadiene (7), isoprene (8), 1,4-pentadiene (9) and cyclopentadiene (10) (equation 2).

Table 1 *Cyclopentene formation from* (11)

*Substituent**	E_a kcal mol^{-1}	*Ref.*
11a R^3 = Me	50.9	13
11b R^1 = Et	50.0	14
11c R^1 = Re = Me	54.6	15
11d R^4 = Me	49.4	16
11e R^3 = Pr	51.1	17
11f R^3 = R^4 = Me	50.5	15
11g R^5 = R^6 = F	40.3	9,18
11h R^5 = Ph	41.0	19
11i R^4 = OMe	44.7	19
11j R^5 = OMe	38.7	19
11k R^1 = $CH{=}CH_2$	44.5	20
11l R^3 = $OSiMe_3$	63.1	21
11m R^5 = NMe_2	31.1	22
11n R^1 = Me, R^3 = Ph	55.0	23

* Remainder R = H

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[6] (*a*) M. R. Willcott, III, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, 1972, **9**, 25; (*b*) M. R. Willcott, III and V. H. Cargle, *J. Am. Chem. Soc.*, 1967, **89**, 723.

[7] R. Breslow, *Molecular Rearrangements*, 1963, **4**, 233.

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

[9] W. R. Dolbier, Jr., *Acc. Chem. Res.*, 1981, **14**, 195.

[10] J. J. Gajewski, 'Hydrocarbon Thermal Isomerizations', in *Organic Chemistry, A Series of Monographs*, Ed. H. A. Wasserman, Academic Press, 1981, p. 5.

[11] T. Hudlický, T. M. Kutchan, and S. M. Naqvi, *Org. React.* (*N.Y.*), 1985, **33**, 247.

[12] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, **1964**, 3547.

[13] H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 1962, 3981.

[14] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, **1964**, 4188.

[15] C. S. Elliot and H. M. Frey, *J. Chem. Soc.*, 1965, 345.

[16] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, **1964**, 959.

[17] G. R. Branton and H. M. Frey, *J. Chem. Soc.*, (*A*), 1966, 1342.

[18] W. R. Dolbier, Jr. and S. F. Sellers, *J. Am. Chem. Soc.*, 1982, **104**, 2494.

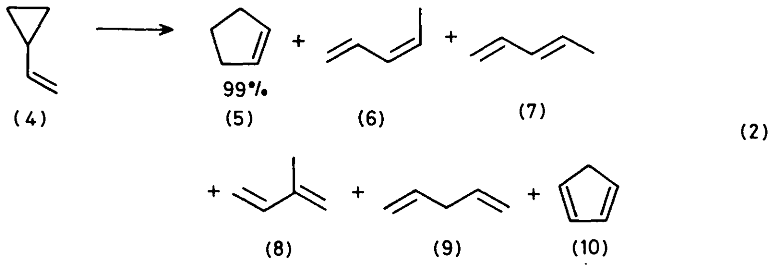
[19] J. M. Simpson and H. G. Richey, Jr., *Tetrahedron Lett.*, 1973, **27**, 2545.

[20] H. M. Frey and J. A. Krantz, *J. Chem. Soc.*, (*A*), 1969, 1159.

[21] B. M. Trost and P. H. Scudder, *J. Org. Chem.*, 1981, **46**, 506.

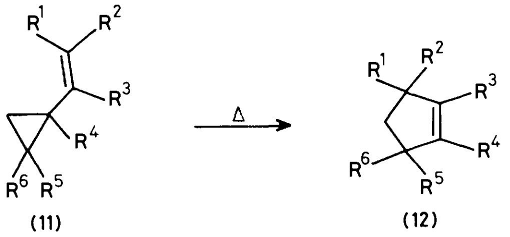
[22] D. W. Shull, *Diss. Abstr. B.*, 1976, **37**, 775.

[23] C. S. Elliot and H. M. Frey, *J. Chem. Soc.*, 1964, 900.



Mono- and di-substituted vcps (11) undergo thermal rearrangement to substituted cyclopentenes (12), Table 1.

Vcps substituted by methoxy and amino groups (11i,j,m) undergo thermal rearrangement to the corresponding cyclopentenes more readily than the alkyl substituted derivatives.[19] Alkenyl- and phenyl-substituted vcps (11h,k) likewise rearrange to cyclopentenes with lower activation energies. R^3-substituted vcps (11a,e,l, and n) apparently hinder cyclopentene formation and require higher activation energies.



Vinylcyclopropanol (13) on heating did not rearrange to the expected cyclopentanone but, instead, produced the 2-methylcyclobutanone (14) as the sole product (equation 3).[24]

cis-2-Methylvinylcyclopropane (15) rearranged on heating *via* a homo-1,5-hydrogen shift (retro-ene reaction) to give, in quantitative yield, *cis*-hexa-1,4-diene (16).[25] At higher temperatures the *trans* isomer (17) gave (16) as the main product [probably *via* initial *cis*/*trans* isomerization to (15)] together with 8% of 4-methylcyclopentene (18).[26] It was also found that the rearrangement of the difluorocyclopropane (19) to *cis*-3,3-difluoro-1,4-hexadiene (20) occurred at even lower activation energies (equation 4).[27]

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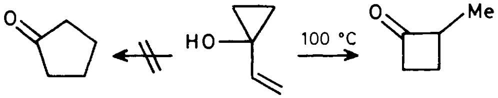
[24] J. Ollivier and J. Salaün, *Tetrahedron Lett.*, 1984, **25**, 1269.

[25] R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 1964, 221.

[26] (*a*) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 1964, 5578; (*b*) Personal communication from H. M. Frey: the 3-methylcyclopentene was incorrectly reported in reference 26*a* and the correct product should be 4-methylcyclopentene. S. W. Benson and H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions', *NSRDS-NBS 21*, 1970, 239, U.S. Dept. of Commerce, Washington, D.C.

[27] W. R. Dolbier, Jr. and S. F. Sellers, *J. Org. Chem.*, 1982, **47**, 1.



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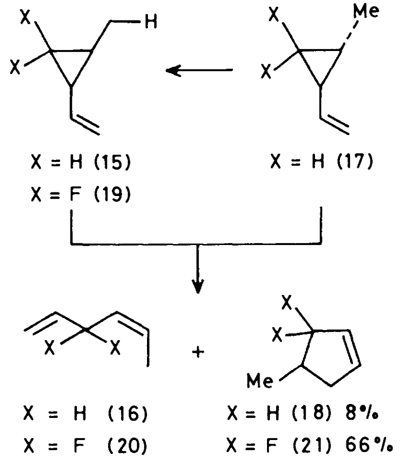

(4)

When the 2-*cis* substituent is methoxy,[19] dimethylamino,[28] acetyl,[29] formyl,[30] or phenyl,[31] the corresponding 3-substituted cyclopentenes are mainly obtained. It was observed that the retro-ene pathway generally competes with other rearrangements when the 2-*cis* substituted groups contain at least one hydrogen atom at the α-position, as in compounds (15), (17), and (19). Similarly the *cis*-(2-vinylcyclopropyl)carbinol (22) rearranges to *cis*-4-hexanal (24), presumably *via* a retro-ene pathway to (23) (equation 5).[32,33]

More drastic conditions are required when chrysanthemol (25) undergoes rearrangement to lavandulol (26) by a 1,5-hydrogen shift from the *cis*-3-methyl (25) with no cyclopentene formation (equation 6).[34]

A. Mechanism of Thermal Rearrangements of vcp.—Although the mechanism of the vinylcyclopropane–cyclopentene thermal rearrangement has been studied in detail for more than twenty years, there is still no definite agreement on the question of concerted *versus* biradical mechanism of the reaction. The difficulty in distinguishing between the two mechanistic pathways by kinetic studies lies in the fact

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[28] H. G. Richey, Jr. and D. W. Shull, *Tetrahedron Lett.*, 1976, 575.

[29] P. Y. Bahural, A. Menet, F. Pautet, A. Poncet, and G. Descotes, *Bull. Soc. Chim. Fr.*, 1971, **6**, 2215.

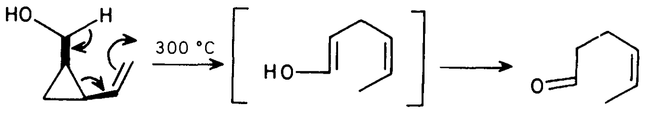
[30] E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 1.

[31] E. N. Marvell and C. Lin, *J. Am. Chem. Soc.*, 1978, **100**, 877.

[32] A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 1964, **49**, 3775.

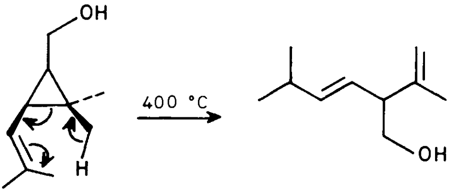
[33] L. H. Zalkow, D. R. Brannon, and J. W. Uecke, *J. Org. Chem.*, 1964, **29**, 2786.

[34] G. Ohloff, *Tetrahedron Lett.*, 1965, **42**, 3795.



(22) (23) (24)

(5)



(25) (26)

(6)

that the activation energies for the rearrangements are not low enough to exclude a nonconcerted biradical mechanism. Thus the E_a of the cyclopropane ring cleavage is about 65 kcal mol^{-1}, decreasing to *ca.* 50 kcal mol^{-1} for vinylcyclopropane. This is close enough to support the involvement of the biradical intermediate (27), since the resonance stabilization energy of the allyl radical is 13 kcal mol^{-1}.[35] Further support for a biradical mechanism comes from a study of the stereomutation of labelled vinylcyclopropane. Thermolysis of *anti-cis*-[2,3,5-$^2H_3$]vinylcyclopropane (28) at 325 °C in the gas phase gave an equilibrium mixture of stereoisomers in a ratio independent of the extent of the reaction. This is consistent with the intervention of the intermediate biradical (29) (equation 7).[35]

It should be noted, however, that although cleavage of the weak allylic σ-bond is the most plausible mechanism, the same kinetic behaviour would result if the reaction involved cleavage of the C(2)–C(3) bond, provided that the internal rotations in the biradical were fast relative to cyclization.[36] Similarly, formation of a mixture of deuterated cyclopentenes (33) and (34) from vinyl-[2-$^2H_1$]-cyclopropane (32) may result by regiochemical homolytic cleavage of the allylic bonds (equation 8).[6]

The same biradical mechanism may explain the formation of 1,4-dienes from vinylcyclopropane[24,37] (equation 9). Since, however, the activation energies of these reactions are in the range of 30—35 kcal mol^{-1} only, an alternative concerted mechanism may be invoked which involves the thermally allowed suprafacial 1,5-H migration (retro-ene reaction).

Whereas kinetic studies may favour a biradical pathway for the vinylcyclopropane–cyclopentene rearrangement, stereochemical analysis of this reaction suggests the occurrence of several concerted processes. Thus, pyrolysis of (+)-

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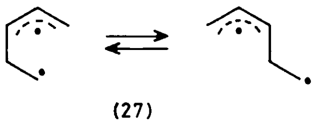
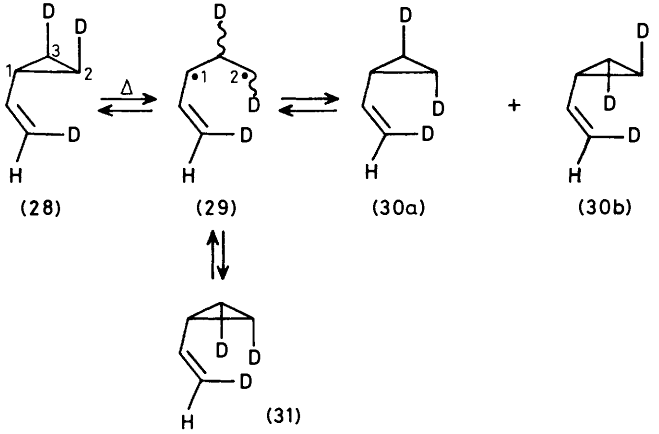
[35] K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, 1964, **86**, 5420.

[36] M. R. Willcott, III and V. H. Cargle, *J. Am. Chem. Soc.*, 1969, **91**, 4310.

[37] (*a*) W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, 1974, **96**, 1168; (*b*) *ibid., J. Am. Chem. Soc.*, 1975, **97**, 5512.





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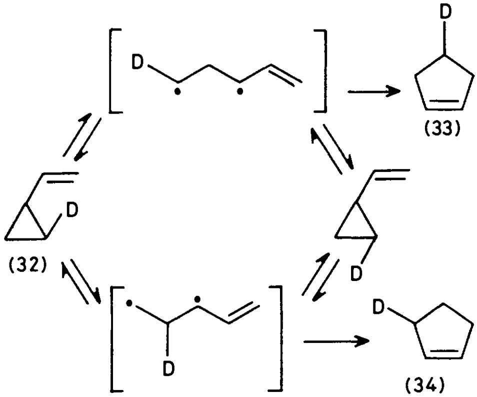

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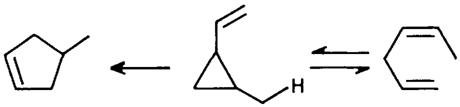

(9)

$(1S,2S)$-*trans,trans*-2-methyl-1-propylcyclopropane (35) gave an optically active mixture of four 3,4-dimethylcyclopentenes (36)—(39) (equation 10).[38]. The high degree of optical purity in the products eliminates the possibility of freely rotating

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[38] G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, 1976, **98**, 6705.

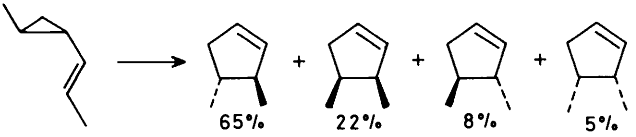
biradical intermediates in the reaction. Consequently, it has been suggested that these 1,3-sigmatropic shifts occur by way of four competing concerted processes.[38,39] The processes allowed by the conservation of orbital symmetry are inversion-suprafacial (is) (36) and retention-antarafacial (ra) (38), whereas those allowed under control of subjacent orbitals are retention-suprafacial (rs) (37) and inversion-antarafacial (ia) (39). Similar results have been reported with the optically active isomers of 2-cyano-isopropenylcyclopropane.[37b]

The mechanism of the degenerate vinylcyclopropane rearrangement in bicyclic compounds was elucidated using the optically active, labelled (−)-[2,2,3-$^{2}H_{3}$]-Δ^{3}-thujene (40).[42] Thermolysis of (40) resulted in both enantiomerization and rearrangements to the racemic mixture of [5,6,6-$^{2}H_{3}$]-Δ^{3}-thujenes (equation 11). Determination of partitioning among the three products reveals that the major reaction pathway is forbidden by orbital symmetry. A high degree of stereochemistry is nevertheless observed in this reaction, suggesting the presence of a small (1.2 kcal mol^{-1}) barrier to conformational equilibrium.[40] The parent bicyclo[3.1.0]hexene (41) undergoes a thermal ring-expansion to a mixture of cyclohexadienes (42) and (43) *via* the usual vinylcyclopropane–pentadiene pathway (equation 12).[41]

In larger bicyclic systems the rearrangement may take another course. For example bicyclo[6.1.0]non-2-ene (44) undergoes a reversible homo-[1,5]-sigmatropic hydrogen shift to *cis,cis*-1,4-cyclononadiene (45) (equation 13).[42,43] The reversed process is the intramolecular, possibly concerted, ene reaction.[44]

The thermolysis of 1-vinyl-spiro[2,4]hepta-4,6-diene (46) at 150 °C gave two products (47) and (48), resulting from an initial 1,3-sigmatropic rearrangement (equation 14).[42]

B. Thermal vcp Rearrangements under Basic Conditions.—If an auxiliary group which has an acidic hydrogen at the α-position is attached to the cyclopropane ring, then treatment with base will produce an anion which is capable of accelerating the thermal vinylcyclopropane–cyclopentene rearrangement. Thus, the lithium salts of 2-vinylcyclopropanols (49) undergo a facile rearrangement at 25 °C to the corresponding 3-cyclopentenols (50) (equation 15).[45]



(35) (36) (37) (38) (39)

(10)

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[39] W. R. Dolbier, Jr., O. T. Garza, and B. H. Al-Sader, *J. Am. Chem. Soc.*, 1975, **97**, 5038.

[40] W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, 1971, **27**, 2005.

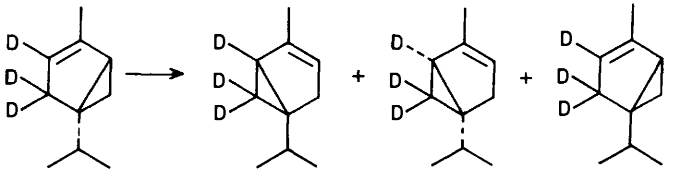
[41] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, (*A*), 1966, 553.

[42] D. S. Glass, R. S. Boikess, and S. Weinstein, *Tetrahedron Lett.*, 1966, 999.

[43] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry', 1970, Verlag Chemie, Weinheim.

[44] H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 556.

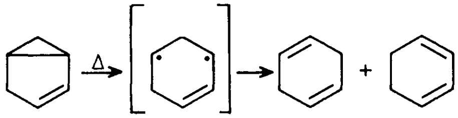
[45] R. L. Danheiser, C. Martinez-Davila, and J. M. Morin, *J. Org. Chem.*, 1980, **45**, 1340.



(40)
(−)-[2,2,3-$^2H_3$]
(−)-Δ-Thujene

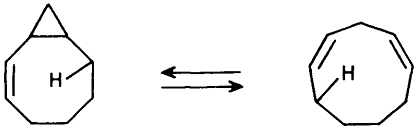
(−)-5,6,6-$^2H_3$ (+)-[5,6,6-$^2H_3$] (+)-[2,2,3-$^2H_3$]

(11)



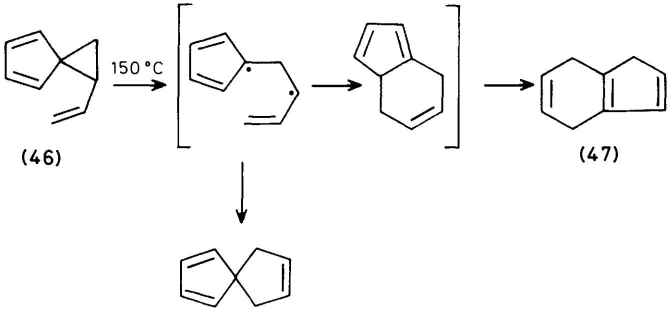
(41) (42) (43)

(12)



(44) (45)

(13)



(46) (47) (48)

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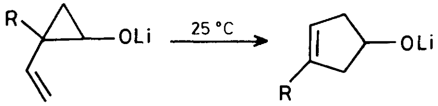

R = Me,Bu^t, Ph

(49) (50)

(15)

The starting cyclopropanols are usually obtained without isolation by treating the corresponding 2-chloroethyl ethers with Bu^{n}Li in THF–hexane–HMPT. The rearrangement generally proceeds with remarkably high stereoselectivity.[46] For

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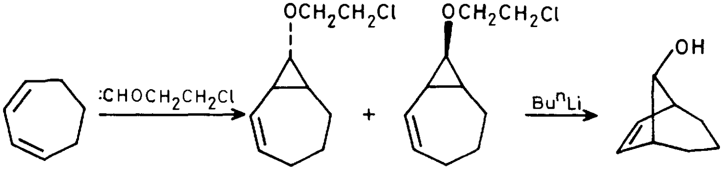
[46] R. L. Danheiser, C. Martinez-Davila, R. J. Auchus, and J. T. Kadonaga, *J. Am. Chem. Soc.*, 1981, **103**, 2443.

example, addition of 2-(chloroethoxy)carbene to cycloheptadiene gave a mixture of the *exo* and *endo* bicyclic isomers (51), which rearrange to the *endo*-bicyclo[3.2.1] octan-8-ol (52) as the only product (equation 16).[45] This is in agreement with a mechanism of either a concerted 1,3-sigmatropic shift, or a stepwise pathway in which the intermediate[45] cyclizes faster than conformational interconversion.

α-Sulphonyl carbanions also accelerate vinylcyclopropane rearrangements stereoselectively.[47] Thus, exposure of the 1-[(phenylsulphonyl)methyl]-2-vinylcyclopropane (53), obtained from *trans,trans*-2,4-hexadiene, to 1.2 equivalents of Bu^{n}Li in 5:1 THF–HMPT at −78 °C provided the corresponding lithium salt, which rearranged smoothly upon warming to −30 °C to afford the *trans,trans*-dimethylsulphone (54) as the only product. This sulphone was trapped by 4-methyliodopent-3-ene, affording, after desulphonylation, the trisubstituted cyclopentene (55) (equation 17).

A related vinylcyclopropane–cyclopentene ring enlargement is observed when 2,2-dibromovinylcyclopropane (56) is treated with MeLi at −78 °C, affording cyclopentadiene (57) and the allene 1,2,4-pentatriene (58) (equation 18).[48,49] The reaction is believed to proceed by initial formation of a vinylcyclopropylidene intermediate which rearranges either to the allene (58) or to the intermediate



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(52)

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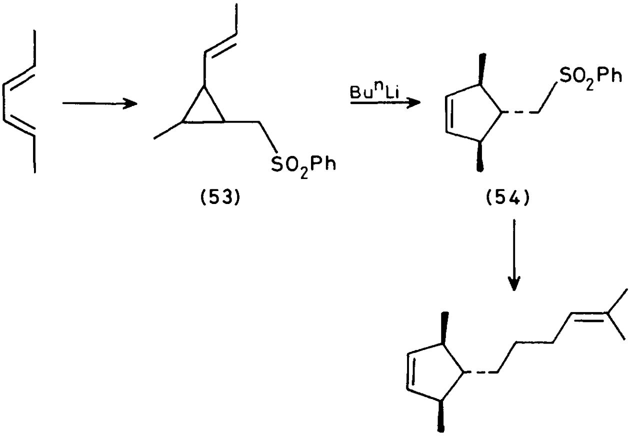

(53)

(54)

(17)

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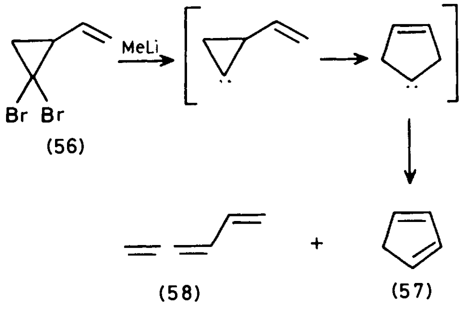
[47] R. L. Danheiser, J. J. Bronson, and K. Okano, *J. Am. Chem. Soc.*, 1985, **107**, 4579.

[48] L. Skattebøl, *Tetrahedron*, 1967, **23**, 1107.

[49] R. Brun, D. S. B. Grace, K. H. Holm, and L. Skatterbøl, *Acta Chem. Scand., Ser. B*, 1986, **40**, 21.

[50] M. S. Baird and I. Jefferies, *Tetrahedron Lett.*, 1986, **22**, 2493.



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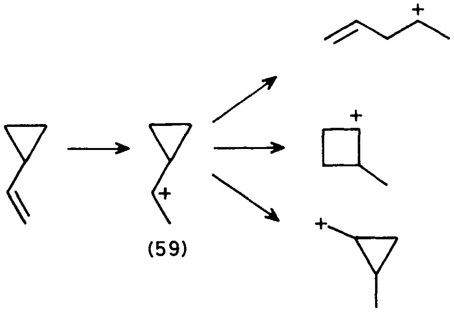

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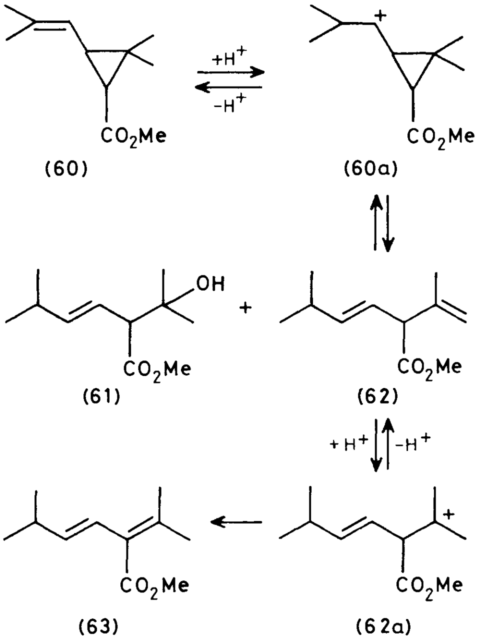


(20)

cyclopentenylidene. The latter subsequently produces cyclopentadiene (57) by a 1,2-hydrogen shift. This mechanism has been confirmed recently by labelling studies.[50]

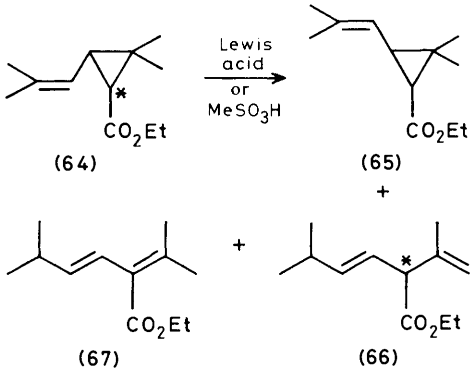
3 Acid-catalysed Rearrangements of vcps

Protonation of vinylcyclopropane leads to the formation of the cyclopropane-stabilized carbonium ion (59).[51] This cyclopropylcarbinyl cation may undergo one of the following rearrangements, before a deprotonation or reaction with nucleophiles (usually the solvent) takes place (equation 19):

(a) cyclopropylcarbinyl–homoallyl rearrangement,
(b) cyclopropylcarbinyl–cyclobutyl rearrangement, and
(c) cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.

The chemistry of cyclopropanes, including vinylcyclopropanes, has been reviewed recently.[52] We shall mainly focus on acid-catalysed rearrangements of vinylcyclopropanes under non-solvolytic conditions.

Chrysanthemyl derivatives are perhaps the best known vinylcyclopropane substrates used for studying the cyclopropylcarbinyl–homoallyl rearrangement. The special interest in these compounds stems from their possible biogenetic relationship with irregular acyclic terpenes, squalene, and higher terpenoids.[53] Methyl *trans*-chrysanthemate (60) rearranges at room temperature, in 50% H_2SO_4–heptane, to a mixture of lavandulyl esters (61)—(63).[54] The kinetic and deuterium exchange studies reveal that (61) and (62) are the primary products of the reaction, obtained from cyclopropylcarbinyl cation (60a) by deprotonation and water addition, respectively. Lavandulyl alcohol (61) and diene (62) equilibrate *via* the tertiary homoallylic carbonium ion (62a), which ultimately deprotonates to the isomeric diene ester (63) (equation 20). Further confirmation for this mechanism comes from the Lewis acid catalysed rearrangement of *cis*-ethyl chrysanthemate



(21)

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[51] (*a*) H. G. Richey, in 'Carbonium Ions', Vol. III, Ed. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1972, 1201.

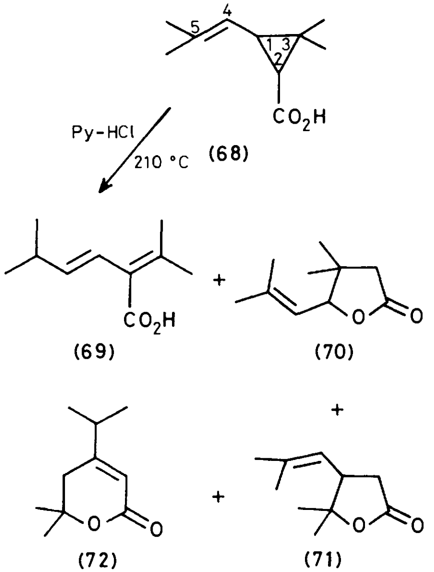
[52] For a recent review see, J. Salaun, 'Rearrangements involving the Cyclopropyl Group' in 'The Chemistry of the Cyclopropyl Group, Part I', ed., Z. Rappoport, Wiley, Chichester, 1987, Ch. 13.

[53] R. M. Coates, *Progress in the Chemistry of Organic Natural Products*, 1976, **33**, 73.

[54] Z. Goldschmidt, B. Crammer, and R. Ikan, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2697.

(64), in aprotic solvents, to the *trans*-isomer (65) and the two lavandulyl esters (66) and (67) (equation 21).[55] It was also established that the chiral carbon of (64) retains its configuration during the rearrangement of optically active ethyl chrysanthemate with methanesulphonic acid as catalyst.[55]

Treatment of *trans*-chrysanthemic acid (68) with pyridine hydrochloride at 210 °C gave a complex mixture of lavandulyl, artemisyl, and santolinyl derivatives, which result from cleavage of either one of the three cyclopropane bonds (equation 22).[56]



(22)

This loss of specificity, achieved under drastic conditions, may result from competitive reaction pathways following protonation at either the double bond or the carboxylic group. Thus protonation at the double bond will lead to the lavandulyl derivative (69) by C(1)–C(3) cleavage, whereas protonation at the carboxylic group will result in cleavage of either the C(1)–C(2) bond to the artemisyl derivative (70), or the C(2)–C(3) bond to form santolinyl derivatives (71) and (72). Specific protonation of the carbonyl group has been reported in the chrysanthemic aldehyde (73a) and ketone (73b) to give the corresponding artemisia dienal (74a) and dienone (74b) (equation 23),[57] and the thiochrysanthemate (75) rearranged under acid catalysis to the thiosantolina diene ester (76) (equation 24).[58] Other mechanistic pathways, such as the direct protonation of the cyclopropane ring and thermal 1,5-H migration from the *gem*-dimethyl groups have also been suggested.[56]

Chrysanthemol (25), like the corresponding carbonyl compounds, rearranges following a preferential protonation at the carbinol functional group, to give (after

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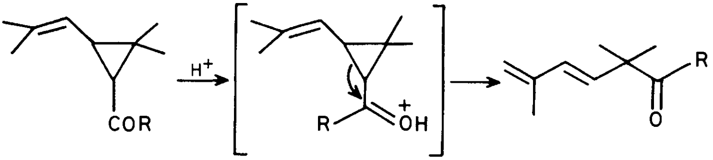
[55] G. Suzukamo, M. Fukao, and M. Tamura, *Tetrahedron Lett.*, 1984, **25**, 1595.

[56] D. A. Otieno, G. Pattenden, and C. R. Popplestone, *J. Chem. Soc., Perkin Trans. 1*, 1977, 196.

dehydration) the analogous artemisia triene (77)[57,59] (equation 25). When, however, the carbinol is allylic (78), protonation occurs at the allylic position, producing the lavandula triene (79) (equation 26).[57]

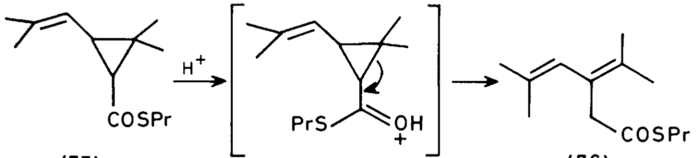
More recently, the solvolytic rearrangements of chrysanthemol derivatives (80) have been studied as a model of the biosynthesis of non-head-to-tail (irregular) terpenes.[60,61] A plethora of products was observed depending on the leaving group and the solvolytic conditions (equation 27). For example, hydrolysis of *N*-methyl-4-chrysanthemyloxypyridinium iodide (80, X = OPyI) gave, in addition to chrysanthemol (25) and the expected artemisyl derivatives (81)—(83), santolinyl triene (84) and dienol (85). The interesting head-to-head dienol (86) was also detected in trace amounts and is believed to be obtained *via* a cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.[60]



(73a) R = H
(73b) R = Me

(74a)
(74b)

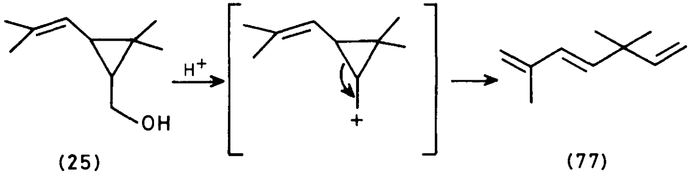
(23)



(75)

(76)

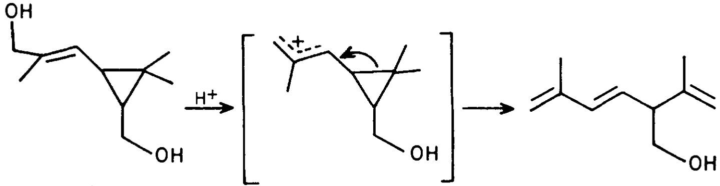
(24)



(25)

(77)

(25)



(78)

(79)

(26)

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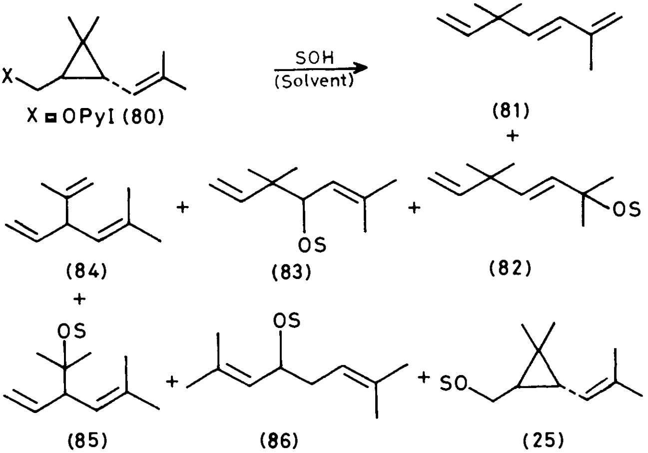
[57] L. Crombie, P. A. Firth, R. P. Houghton, D. A. Whiting, and D. K. Woods, *J. Chem. Soc., Perkin Trans. 1*, 1972, 642.

[58] N. F. Elmore, J. E. Roberts, and G. A. Whitham, *J. Chem. Res. (S)*, 1985, 98.

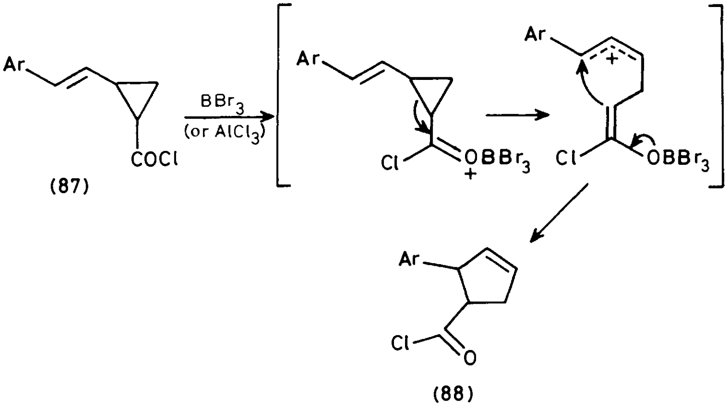
[59] C. D. Poulter, *J. Am. Chem. Soc.*, 1972, **94**, 5515.

[60] C. D. Poulter, L. L. Marsh, J. M. Hughes, J. C. Argyle, D. M. Satterwhite, R. J. Goodfellow, and S. G. Moesinger, *J. Am. Chem. Soc.*, 1977, **99**, 3816.



(27)

The presence of a carbonyl group at position 2 of the vinylcyclopropane, which can react with the acid catalyst, opens up a new rearrangement route—the incipient homoallylic cation can reclose to give a 3-cyclopentenylcarbinyl intermediate. For example, arylvinylcyclopropane-2-carbonyl chloride (87) rearranges in the presence of a Lewis acid such as BBr_3 or $AlCl_3$ to the corresponding 2-arylcyclopent-3-enecarbonyl chloride (88) (equation 28).[62] A similar pathway was utilized by Corey and Myers[63] in the synthesis of the plant hormone Antheridiogen-An (equation 29). Here a lactone vinylcyclopropane (89) underwent this rearrangement pattern to the crucial lactone cyclopentene (90).[63] Yet another



(28)

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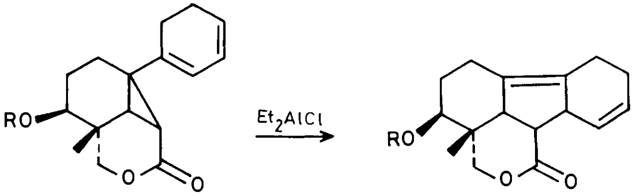
[61] C. D. Poulter and J. M. Hughes, *J. Am. Chem. Soc.*, 1977, **99**, 3830.
[62] Y. Sakito and G. Suzukamo, *Chem. Lett.*, 1986, 621.
[63] E. J. Corey and A. G. Myers, *J. Am. Chem. Soc.*, 1985, **107**, 5574.

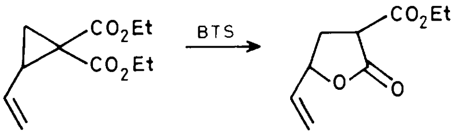
interesting variation of this rearrangement is exemplified in vinylcyclopropane dicarboxylate (91), which gave vinyl butyrolactone (92) when treated with the strong Lewis acid bis(trimethylsilyl) sulphate as the catalyst (equation 30).[64] The initially formed homoallylic carbonium recloses on the oxygen of the other carboxylate group, to form the lactone (92), instead of the α-carbon which would lead to cyclopentene (equation 30).

Cyclopropylcarbinyl–cyclobutyl ring expansions[65] in acid-catalysed vinylcyclopropane rearrangements are facilitated by the presence of oxygen-bonded groups at the allylic position 1. Thus the parent system 1-vinylcyclopropanol (13) undergoes a pinacol–pinacolone type of rearrangement to cyclobutanone (14) in the presence of *p*-TsOH or HBr (equation 31).[66] Similarly, Ollivier and Salaün showed that the diol (93) rearranges in the presence of a Lewis acid catalyst, with dehydration, to 2-vinylcyclobutanone (94) (equation 32).[24] Analogous reactions



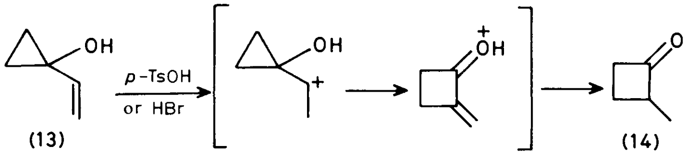
(89) (90)

(29)



(91) (92)

(30)



(13) (14)

(31)

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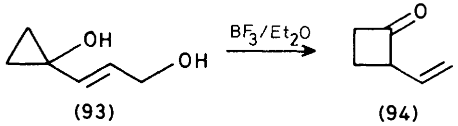
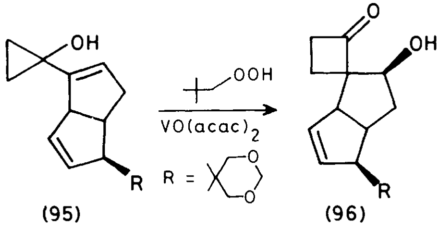
[64] Y. Morizawa, T. Hiyama, and H. Nozaki, *Tetrahedron Lett.*, 1981, **22**, 2297.

[65] K. B. Wiberg, B. A. Hess, and A. J. Ashe, 'Carbonium Ions', Vol. III, Ed. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1972, p. 1295.

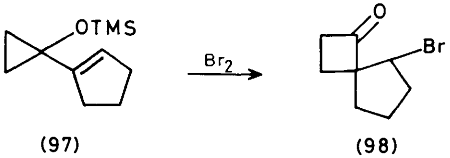
[66] H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Am. Chem. Soc.*, 1969, **91**, 2375.


OH
OH
BF_3/Et_2O
O
(93)
(94)

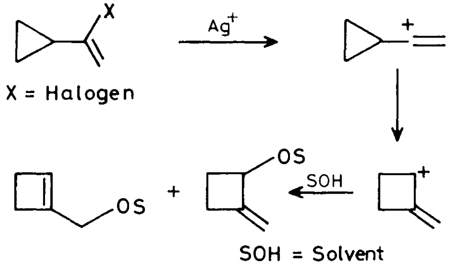
(32)


OH
OOH
VO(acac)$_2$
R =
O
O
R
O
OH
R
(95)
(96)

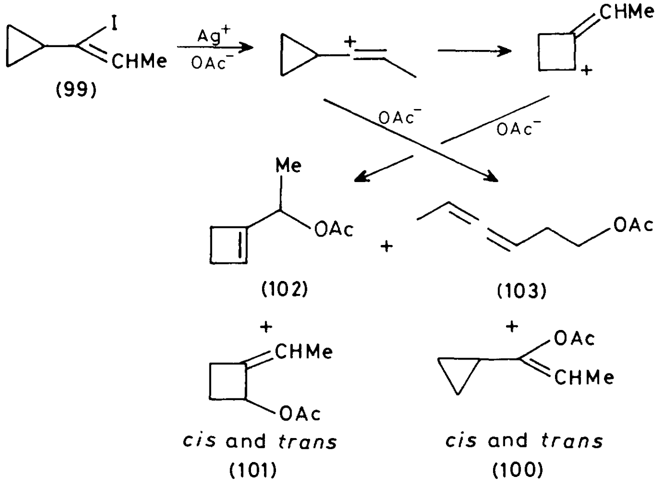
(33)


OTMS
Br_2
O
Br
(97)
(98)

(34)


X
X = Halogen
Ag^+
+
OS
+
OS
SOH
+
SOH = Solvent

(35)

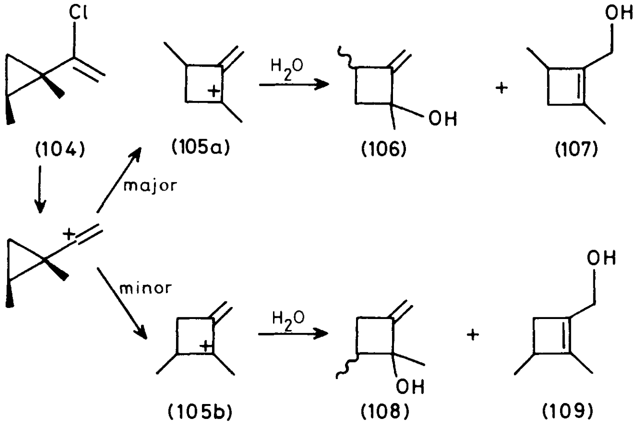

I
CHMe
(99)
Ag^+
OAc^-
+
CHMe
+
OAc^-
OAc^-
Me
OAc
+
OAc
(102)
(103)
+
CHMe
OAc
cis and trans
(101)
+
OAc
CHMe
cis and trans
(100)

(36)

with THP[67] and thioaryl[68] ethers have also been reported.

A modification of these reactions for the synthesis of spiro-cyclobutanones was reported by Trost and Mao,[69] using electrophiles other than proton or Lewis acids. Treatment of vinylcyclopropanol (95) with Bu^tOOH in the presence of $VO(acac)_2$ afforded the hydroxy-spiroketone (96) (equation 33).[69] Analogously, reaction of vinylcyclopropane silyl ether (97) with bromine gave 5-bromo-spiro[3,4]octan-1-one (98) (equation 34).[69]

An exceptional case of cyclopropylcarbinyl–cyclobutyl rearrangement is observed when the 4-halogenovinylcyclopropanes (equation 35, X = halogen, SOH = solvent) is solvolysed in the presence of Ag^+. The solvolysis of either *cis* or *trans* iodovinylcyclopropane (99) with AcOH–AgOAc is non-specific, giving, in addition to both the *cis* and *trans* isomers of (99), a mixture containing acetate derivatives of vinylcyclopropane (100), 2-methylene-cyclobutanols (101), cyclobutene carbinol (102), and the open chain allenol acetate (103) (equation 36).[70] The migratory aptitude of the σ-bond as a function of the substituents was revealed from studies of the hydrolysis of 1,2-dimethyl-4-chlorovinylcyclopropane (104) (equation 37).[71] Of the complex mixture of cyclobutanols (106)—(109) obtained in the reaction, more than 84% were derived from the 2,4-dimethyl-methylenecyclobutyl carbonium intermediate (105a), indicating a regioselective migration of the more substituted cyclopropane C(2).



(37)

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[67] J. P. Barnier and A. J. Salaün, *Tetrahedron Lett.*, 1984, **25**, 1273.

[68] B. M. Trost and L. N. Jungheim, *J. Am. Chem. Soc.*, 1980, **102**, 7910.

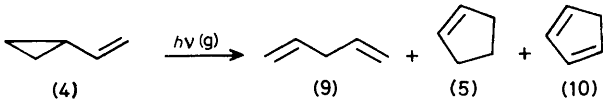
[69] B. M. Trost and M. K. Mao, *J. Am. Chem. Soc.*, 1983, **105**, 6753.

[70] D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, 1971, **93**, 1941.

4 Vinylcyclopropane Photorearrangements

The cyclopropane ring behaves as a moderate auxochrome, causing a 8—15 nm bathochromic shift of the olefinic absorption band. The parent vinylcyclopropane (vcp) (4) and its alkylated derivatives all have absorption maxima for the $\pi \longrightarrow \pi^*$ olefin band in the 189—201 nm region.[72] It is therefore not surprising that the majority of vinylcyclopropanes whose photochemistry has been studied, bear additional chromophoric functional groups which extend the electronic absorption to the experimentally more accessible region of > 254 nm.[73] A limited number of photochemical studies of the parent vcp in the gas phase have nevertheless been reported,[74,75] and the photorearrangements of simple alkyl derivatives, in solution, have also been described.[76,77]

The gas phase vacuum-u.v. photolysis of vcp, using xenon (147.0 nm), krypton (123.6 nm), and argon (106.7—104.8 nm) resonance excitation, gave only fragmentation products.[74] In contrast, the infrared multiphoton irradiation of gaseous vcp, with a CO_2 TEA laser, led to a mixture containing mainly two isomers, 1,4-pentadiene (9) and cyclopentene (5).[75] A substantial amount of cyclopentadiene (10) was also formed, presumably *via* dehydrogenation of 'hot' cyclopentene. This fragmentation process competes with the collisional deactivation of excited (5) to the ground state (equation 38).



(38)

Isopropenylcyclopropane (11a) is the simplest vcp derivative which has been photolysed in solution.[76] Upon direct irradiation in hexane, (11a) rearranges to methylcyclopentene (12a) in 55% yield, with a zero-order rate of 1.1×10^{-3} Mh^{-1} (equation 39). The photosensitized reactions of (11a) with either benzene or acetone gave only traces of (12a) and none was observed with naphthalene as sensitizer. Thus (12a) is derived from the singlet excited state of (11a).

Direct far-u.v. irradiation (185—228 nm) of 2-norcarene in pentane solution gave a mixture of isomeric products.[77] At 214 nm seven isomers were identified, (111)—(117), which constituted 91% of the mixture. The quantum yield for total product formation (at 185 nm) was $\Phi = 0.26 \pm 0.02$. A similar mixture of the

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[71] M. Santelli and M. Bertrand, *Tetrahedron*, 1974, **30**, 243.

[72] C. H. Heathcock and S. R. Poulter, *J. Am. Chem. Soc.*, 1968, **90**, 3766.

[73] S. S. Hixon, *Org. Photochem.*, 1979, **4**, 218; T. Hudlický, T. H. Kutchan, and S. M. Naqvi, *Org. React.*, 1985, **33**, 247.

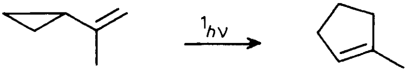
[74] E. Lopez and R. D. Doepker, *J. Phys. Chem.*, 1979, **83**, 573.

[75] W. E. Farneth, M. W. Thomsen, N. L. Schultz, and M. A. Davies, *J. Am. Chem. Soc.*, 1981, **103**, 4001; W. E. Farneth, M. W. Thomsen, and M. A. Berg, *J. Am. Chem. Soc.*, 1979, **101**, 6468.

[76] R. S. Cooke, *J. Chem. Soc., Chem. Commun.*, 1970, 454.

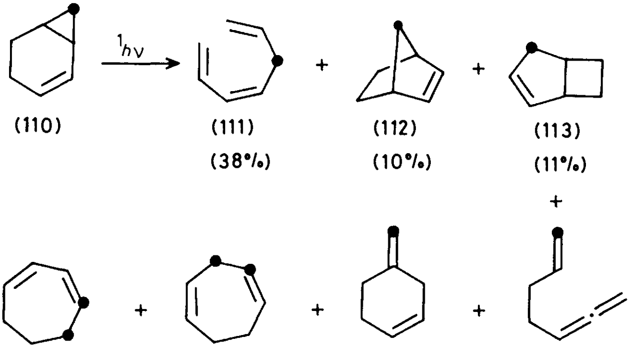
[77] W. J. Leigh and R. Srinivasan, *J. Am. Chem. Soc.*, 1983, **105**, 514.

corresponding dideuterated isomers was obtained when [7,7-$^2H_2$]-2-norcarene was irradiated under the same conditions. The deuterium position in the products is shown in equation 40.



(11a) (12a)

(39)



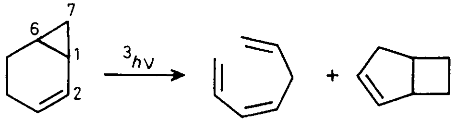
(110) (111) (38%) (112) (10%) (113) (11%)

(117) (7%) (116) (6%) (115) (6%) (114) (13%)

(40)

Photolysis of (110) in the presence of naphthalene as sensitizer did not change the product mixture, indicating that all the products were derived from the singlet excited state. However, isomers (111) and (113) are also products of the triplet state, arising from toluene-sensitized photolysis of (110) in deoxygenated pentane solution (equation 41). Prolonged irradiation resulted, as expected, in *cis–trans* isomerization of (111).

Mechanistically, it is obvious that except for (114) all the observed rearrangements proceed by cleavage of either the internal C(1)–C(6) cyclopropane bond of (110), or the allylic C(1)–C(7) external bond. However, in the absence of stereochemical labels in (110) it is impossible to distinguish whether the reactions are concerted or stepwise. In a stepwise mechanism, the initial intermediates formed are the diradicals (118) and (119). Radical (118) may disproportionate by either a sigma-bond cleavage to (111) or allylic coupling to (113). Alternatively, 1,2-H migrations may lead to either (116) or (117). In a concerted pathway, (111) results from a $\sigma^2 + \sigma^2 + \pi^2$ cycloreversion, and (113) by an alkyl 1,3-sigmatropic shift.[78] Similarly, (112) is obtained either from diradical (119) by recombination, or concertedly *via* 1,3-alkyl migration, whereas (115) may be derived by a 1,2-H shift. There remains the exceptional rearrangement of (110) to allene (114). Since no intermediates could be trapped, it was concluded[77] that (114) is formed concertedly *via* a formal 1,2-migration of the vinyl hydrogen. Alternatively, a short-lived carbene intermediate (120) may first develop, which subsequently rearranges to (114) by a 1,2-H shift.

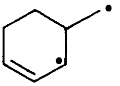


(110) (111) (113)

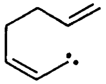
(45%) (55%)

(41)

(118)



(119)



(120)

Except for a few cases, diradicals, analogous to (118)—(120) represent the three major mechanistic pathways which account for most photochemical vcp rearrangements. Clearly, however, the ratio between the products is expected to depend heavily on the nature of the substituents, and usually also on the multiplicity of the reactive excited states (*vide infra*). In addition, fragmentation products are often observed. These result from cleavage of the cyclopropane ring to vinyl carbene and olefin.

There are two additional competing processes for the excited state, which cannot be observed in the absence of appropriate substitution. These are the *cis–trans* isomerizations about an acyclic double bond,[79,80] and about the three-membered ring.[81–89] Vcp esters undergo geometrical isomerization at least 10

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[78] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1970.

[79] M. J. Jorgenson, *J. Am. Chem. Soc.*, 1969, **91**, 6432.

[80] P. H. Mazzocchi and R. C. Ladenson, *J. Chem. Soc., Chem. Comm.*, 1970, 469.

[81] H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, 1965, **98**, 2201.

[82] W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 1968, 129; W. H. Pirkle, S. G. Smith, and G. F. Koser, *J. Am. Chem. Soc.*, 1969, **91**, 1580.

[83] H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, 1969, **91**, 5307.

[84] D. L. Garin and K. O. Henderson, *Tetrahedron Lett.*, 1970, 2009.

[85] H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, 1972, **94**, 8749.

[86] T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, 1968, **33**, 676; *J. Org. Chem.*, 1970, **35**, 790.

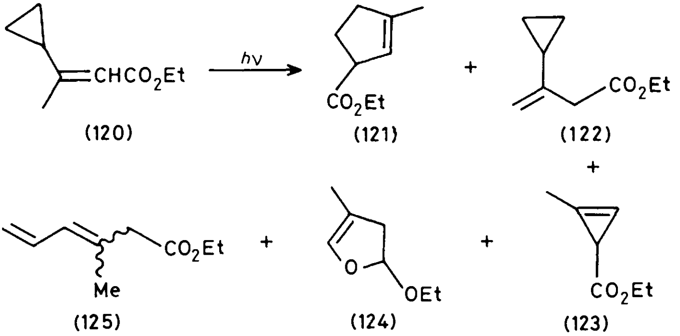
[87] K. Ueda and M. Matsui, *Tetrahedron*, 1971, **27**, 2771.

[88] M. J. Bullivant and G. Pattenden, *Pyrethrum Post*, 1971, **11**, 72.

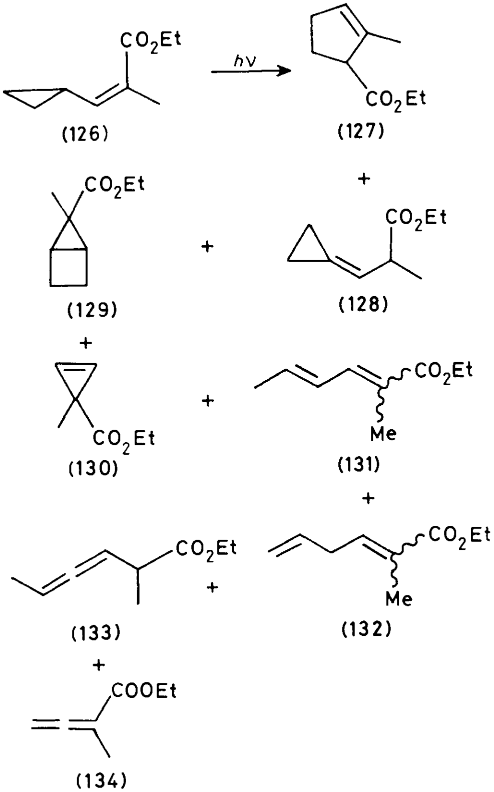
[89] L. O. Ruzo and J. E. Casida, *J. Chem. Soc., Perkin Trans. 1*, 1980, 728.

times faster than irreversible product formation (equations 42 and 43).[79]

Similarly, styryl cyclopropanes undergo *cis–trans* isomerization faster than rearrangement to cyclopentenes (equation 44).[80] Interestingly, however, the esters undergo both isomerization and rearrangement to cyclopentenes upon triplet



(42)

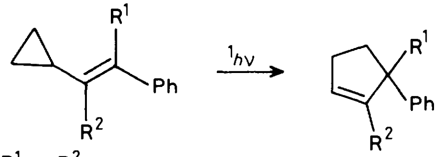


(43)

sensitization, whereas the styryl cyclopropanes only isomerize under these conditions. Upon direct irradiation, esters afford a variety of rearrangement products, including ring enlargement to cyclopentenes (121) and (127), double bond migration to (122) and (128), bicyclo[2.1.0]pentane formation (129)[90] and ring cleavage to diene-esters (125), (131), (132), and (133). In addition, fragmentation of the cyclopropane ring to ethylene and carbene gave cyclopropenes (123) and (130) 2-ethoxyfuran (124), and allene ester (134).

The occurrence of *cis–trans* isomerization during ring cleavage has been reported in a variety of chrysanthemyl derivatives.[86,88] Photochemical isomerization of the natural (+)-*trans*-chrysanthemic acid (135) gave a racemic mixture of all four possible diastereomers, presumably *via* the triplet excited state.[89] This involves a homolytic cleavage of the 1—3 sigma bond, followed by rotation and recombination (equation 44). Ring closure may also occur on oxygen, to give lactone (136).

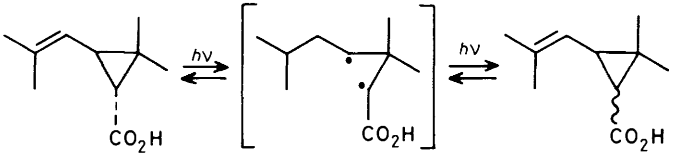
Alternatively, a hydrogen shift takes place in chrysanthemyl alcohol (137) to give the lavandulol (138) (equation 45).[86] Similarly, irradiation of spirocyclohexadienone (139) at 254 nm resulted initially in *cis–trans* isomerization, followed



(44)

$R^1 = R^2 = H$

$R^1 = H$, $R^2 = Me$



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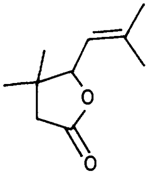

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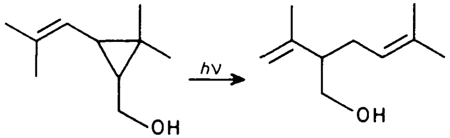

(45)

(137) (138)

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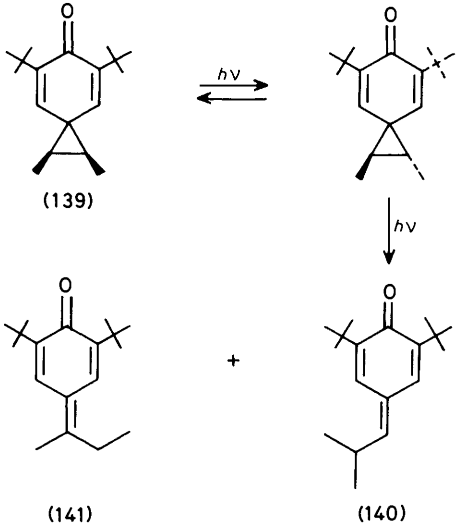
[90] H. Kristinsson and G. S. Hammond, *J. Am. Chem. Soc.*, 1968, **89**, 5970.

by photochemical 1,2-migration of either hydrogen (140) or methyl (141) (equation 46).[82] When (139) is irradiated at lower energies (350 nm) or sensitized by acetophenone, only *cis–trans* isomerization is observed.

Extensive studies have been carried out on the multiplicity dependent photochemistry of condensed cyclopropane systems having either an exocyclic[83] (equation 47) or endocyclic[85] (equation 48) double bond. The ratio between *cis–trans* isomerization (142) $\rightleftharpoons$ (143), hydrogen migration (144) and phenyl migration (145) in 2-methylenebicyclo[3.1.0]hexanes is strongly dependent on the multiplicity of the excited state. Similarly, a multiplicity dependence was observed in the *cis–trans* isomerization (146) $\longrightarrow$ (147) *vs.* the 1,3-sigmatropic migration (147) $\rightleftharpoons$ (148) and (149) $\longrightarrow$ (146) of bicyclo[3.1.0]hex-2-enes (equation 48).



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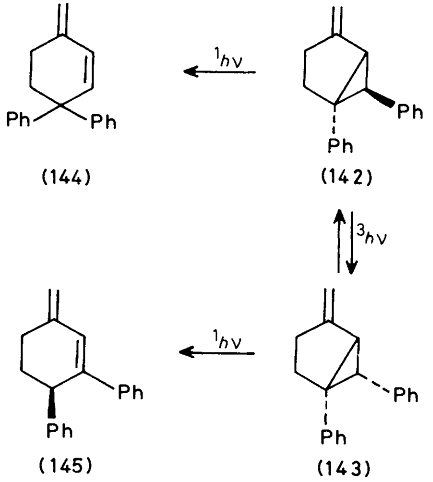
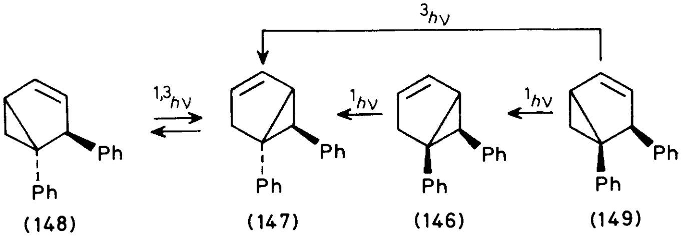


(47)

In general, *cis–trans* isomerizations are favoured from the triplet excited state, 1,3-sigmatropic rearrangements occur from both the singlet and triplet excited states, and hydrogen migrations take place mainly from the singlet state. The selectivity of the 1,3-sigmatropic shift was recently utilized as the key step in the efficient synthesis of grandisol (152), the boll weevil sex pheromone, from (+)-carene (150) (equation 49).[91] The photoproduct (151) proved to be the racemic mixture, indicating the involvement of a triplet diradical intermediate.

By extending the vcp system with an additional chromophore, such as an olefinic or a carbonyl group, a substantial change in the reaction course may occur, especially when the chromophore absorbs in the excitation region. Also, the nature of the excited state (*e.g.* nπ* or ππ*) may often affect the chemoselectivity. One striking example is revealed when the photochemistry of bicyclo[3.1.0]hexen-2-ones is compared with that of the corresponding methylene analogues (homofulvenes). The ketone (153) undergoes rearrangement to cyclohexadienone (155) and phenol (156) (equation 50) presumably *via* the zwitterionic intermediate (154).[92–95] In contrast, homofulvene (157) rearranges mainly to a mixture of



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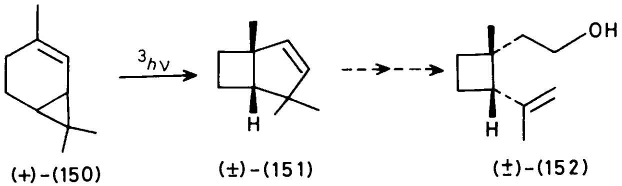

(49)

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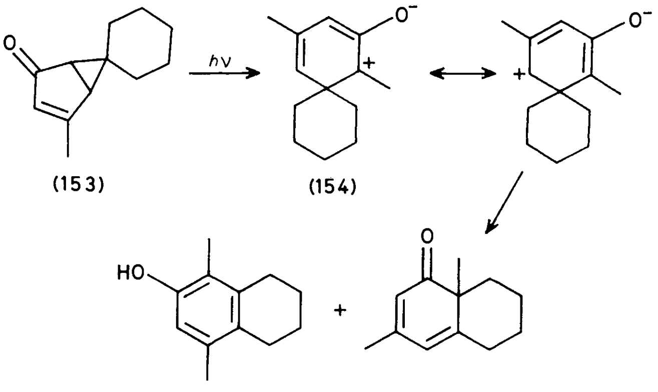
[91] H. R. Sonawane, B. S. Hanjundiah, and M. U. Kumar, *Tetrahedron Lett.*, 1984, **25**, 2245; 1985, **26**, 1097.
[92] P. J. Kropp, *J. Am. Chem. Soc.*, 1964, **86**, 4053; *Org. Photochem.*, 1967, **1**, 1.
[93] H. Durr and P. Heitkamper, *Liebigs Ann. Chem.*, 1968, **716**, 212.
[94] H. Hart and D. C. Lankin, *J. Org. Chem.*, 1968, **33**, 4398.
[95] H. Perst, *Tetrahedron Lett.*, 1970, 3601.

isomeric spiro cyclopentadienes (158) and (159), *via* a walk process, termed the 'bicycle rearrangement'[96–98] (equation 51).

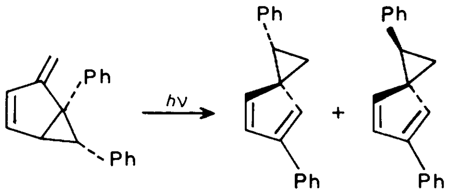
Analogous walking processes were also reported in the norcaradiene[99] (equation 52) and the bicyclo[4.1.1.]octa-2,4-diene systems (equation 53).[100] On the other hand, cleavage of vinylcyclopropanes to aromatic systems was reported in the photochemical interconversion of the strained benzvalenes to benzenes (equation 54).[101,102]

Finally, an interesting case is reported where a change in the relative position of the additional chromophore about the vcp group led to the same formal reaction, but from a different excited-state manifold. Thus, irradiation of bicyclo[5.1.0]oct-5-ene-2-one or its 2-methylene analogue resulted in vcp–cyclopentane rearrangement from the corresponding singlet n,π* and π,π* excited states (equation 55). However, the isomeric bicyclo[5.1.0]oct-2-ene-4-one and its 4-methylene analogue undergo



(153) (154) (156) (155)

(50)



(157) (158)-*anti* (159)-*syn*

(51)

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[96] H. E. Zimmerman, *Chimia*, 1982, **36**, 423.

[97] H. E. Zimmerman, D. F. Juers, J. H. McCall, and B. Schroder, *J. Am. Chem. Soc.*, 1971, **93**, 3662.

[98] T. Tabata and H. Hart, *Tetrahedron Lett.*, 1969, 4429.

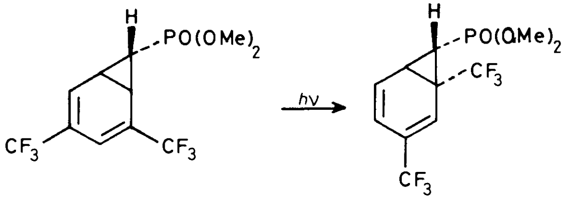
[99] M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 222.

[100] W. T. Borden, J. G. Lee, and S. D. Young, *J. Am. Chem. Soc.*, 1980, **102**, 4843.

[101] M. G. Barlow, R. H. Hazeldine, and R. Hubbard, *J. Chem. Soc., C*, 1970, 1232.

[102] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, 1965, **87**, 4004.

the same formal 1,3-sigmatropic shift from the triplet n,π* and π,π* states, respectively[103] (equation 56).



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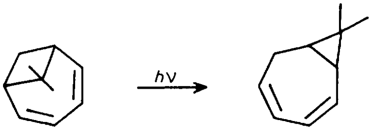

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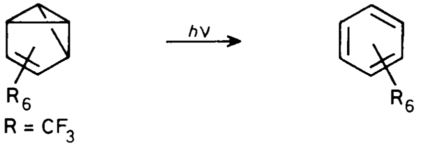

(54)

5 Metal-promoted Rearrangements of Vinylcyclopropanes

Metal-promoted vinylcyclopropane rearrangements can be divided into three categories: (a) metal-catalysed rearrangements, in which the metal is bonded to the organic molecule only during intermediate stages of the reaction; (b) stoicheiometric rearrangements of metal-complexed vcp yielding coordinated isomeric products; and (c) metal-induced rearrangements of non-coordinated vinylcyclopropanes giving metal complexed isomers. Reactions of the type (b) and (c) are frequently useful for mechanistic studies of metal-catalysed rearrangements of vcp. They may also be utilized for synthetic purposes, if the metal fragment is removed subsequent to rearrangement.[11,104,105]

The major pathways of metal-catalysed rearrangements of vcp involve ring cleavage followed by hydrogen migration, presumably *via* a metal hydride intermediate. These reactions closely resemble the metal-catalysed isomerizations observed in saturated small-ring compounds[106] but differ from the vcp–cyclopentene rearrangements that are usually encountered in the absence of a catalyst.

A wide variety of metals has been utilized to induce vcp rearrangements. These usually belong to late transition metal groups. Simple vinylcyclopropanes have been shown to isomerize readily in the presence of catalysts such as

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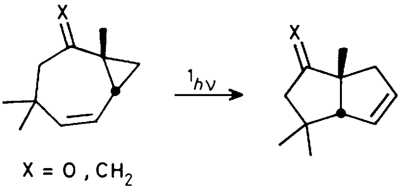
[103] L. A. Paquette, G. V. Meehan, R. P. Henzel, and R. F. Eizember, *J. Org. Chem.*, 1973, **38**, 3250.

[104] S. Sarel, *Acc. Chem. Res.*, 1978, **11**, 204.

[105] H. Alper, *Isr. J. Chem.*, 1981, **21**, 203.

[106] K. C. Bishop, III, *Chem. Rev.*, 1976, **76**, 461.



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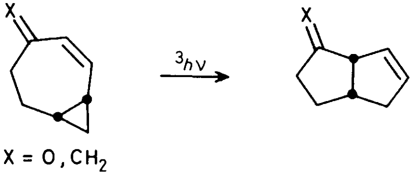

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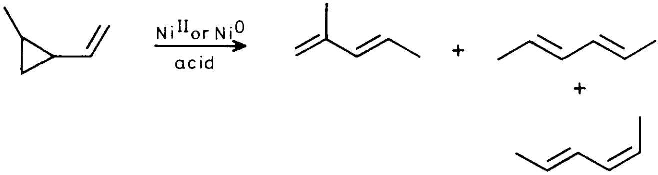

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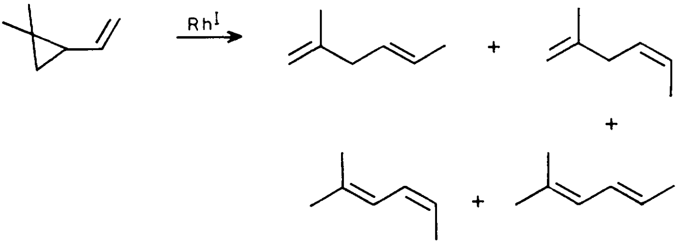

(58)

(Bu$^n{}_3$P)$_2$NiCl$_2$/Bu$^i{}_2$AlCl and [(*o*-tolyl)$_3$P]$_2$Ni(C$_2$H$_4$)$_2$/HCl (equation 57)[107] and [Rh(CO)$_2$Cl]$_2$ (equation 58).[108] With the Ni catalysts, the same mixture of conjugated dienes is obtained from both the *cis* and the *trans* vcp isomers. The Rh^1 catalyst gave a mixture of conjugated and non-conjugated dienes, all of which were primary products of the reaction. However, substitution in the vcp ring with a phenyl or carbethoxy group led only to the corresponding conjugated dienes

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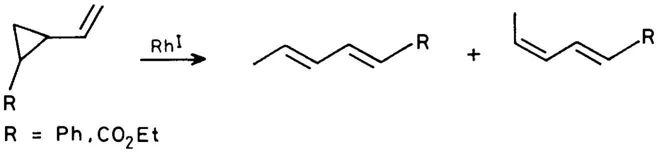
[107] P. A. Pinke, R. D. Stauffer, and R. G. Miller, *J. Am. Chem. Soc.*, 1974, **96**, 422.

(equation 59).[108] The latter reaction could also be induced by Pt^{II} and $Rh_2(OAc)_4$ catalysts.[109]



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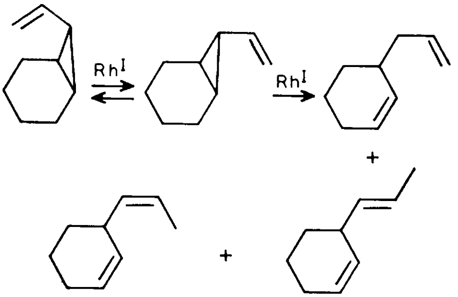
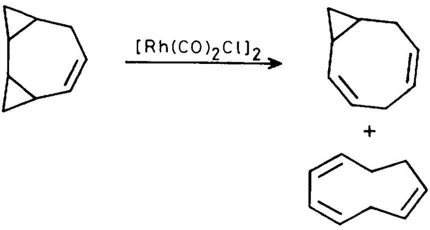


(60)

In both simple and condensed vcp systems *cis–trans* isomerization has been shown to be faster than rearrangement.[108] The *exo* isomer (equation 60) is more reactive than the *endo*. The reaction is therefore not concerted, and both isomers give essentially the same mixture of cyclohexenyl propenes. However, the rearrangement is highly selective, providing only the three non-conjugated dienes shown in equation 60, which neither interconvert nor rearrange to other isomers under the reaction conditions.

Rh^I-catalysed rearrangements also occur when the vcp double bond is endocyclic, providing non-conjugated cyclic dienes in which the bridging cyclopropane sigma bond is preferentially cleaved (equation 61).[110]



(61)

It appears that the typical metal-catalysed rearrangements of vcp proceed in a stepwise mechanism which involves initial double bond coordination to the metal,

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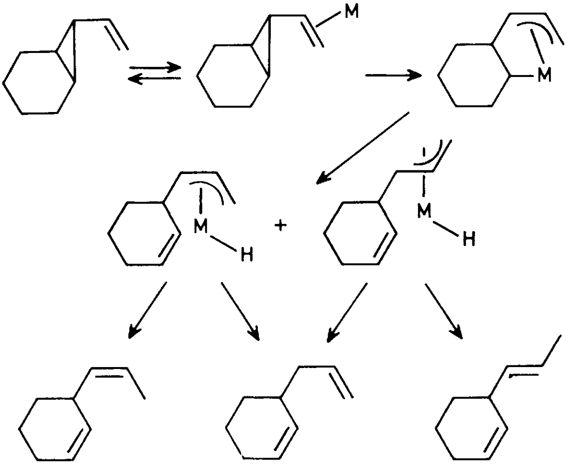
[108] R. G. Salomon, H. F. Salomon, and J. L. C. Kachinski, *J. Am. Chem. Soc.*, 1977, **99**, 1043.

[109] M. R. Doyle and D. van Leusen, *J. Org. Chem.*, 1982, **47**, 5326.

[110] L. A. Paquette and M. R. Detty, *Tetrahedron Lett.*, 1978, 713.

followed by cyclopropane ring cleavage to a σ,π-allylic intermediate. Subsequent intramolecular hydride shift, presumably *via* a metal hydride complex, affords the products (Scheme 3).



Scheme 3

Metal-catalysed valence isomerizations often compete with rearrangements *via* hydride migration when an additional double bond is introduced into the vcp molecule. In these cases, the familiar 1,3-sigmatropic ring enlargement to cyclopentene, observed in thermal and photochemical rearrangements of free vcp, predominates. A variety of catalysts has been used to induce this reaction, including Ni^0 (equation 62),[111] Ni^{II} (equation 63),[112] Rh^I (equations 64—65),[113,114] and Pd^0 (equation 66).[115]

Coordinated vinylcyclopropanes, like their free counterparts, undergo molecular rearrangements with or without hydrogen migration. As in catalysed reactions, hydride shifts are likely to occur when no additional unsaturation is present, whereas valence isomerizations predominate in highly unsaturated vinylcyclopropanes. However, since the majority of stable organometallic complexes have more than one unsaturated functional group coordinated to the metal, the number of cases where hydride migrations occur is small.

A unique example of a 1,3-H migration, which leads to the deconjugation of a vcp function, has been reported for (η^2-9,9-dichlorobicyclo[5.1.0]oct-2-ene)$Fe(CO)_4$ (equation 67).[116] When an additional double bond is present in the η^4-bicyclic

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[111] M. Murukami and S. Nishida, *Chem. Lett.*, 1979, 927.

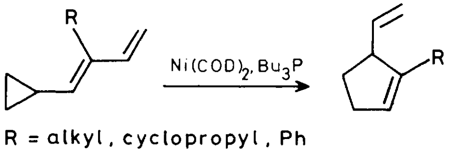
[112] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 715.

[113] R. Grigg, R. Hayes, and A. Sweeney, *J. Chem. Soc., Chem. Commun.*, 1971, 1248.

[114] T. Hudlicky, T. M. Kutchan, F. J. Koszyk, and J. P. Sheth, *J. Org. Chem.*, 1980, **45**, 5020.

[115] Y. Morizawa, K. Oshima, and H. Nozaki, *Isr. J. Chem.*, 1984, **24**, 149.

[116] J. C. Barborak, L. W. Dasher, A. T. McPhail, J. B. Nichols, and K. D. Onan, *Inorg. Chem.*, 1978, **17**, 2936.



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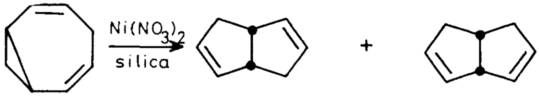

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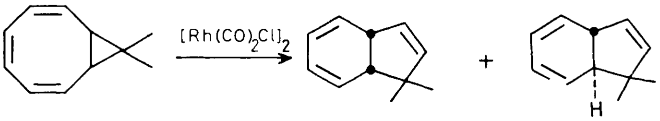

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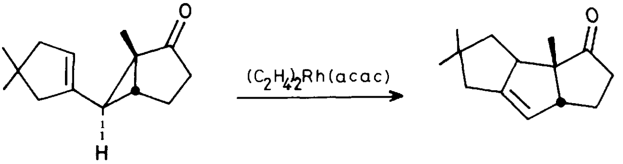

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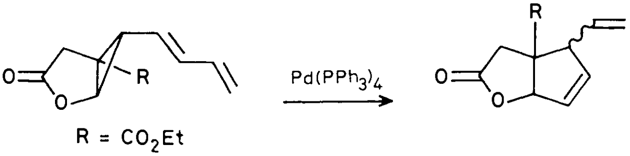

(66)

Fe(CO)$_3$ complex, a circumambulant degenerate rearrangement takes place at 75 °C involving hydrogen, carbon, and metal migrations (equation 68).[117] In each reaction step, an exchange between a sigma-bonded carbon or hydrogen, and a metal fragment occurs over a chain of five conjugated carbon atoms. These reactions may thus be termed sigmahaptotropic rearrangements of the order [5,5].[118] At higher temperatures, an additional rearrangement involving hydrogen migration takes place, giving η^4-(bicyclo[4.2.0]octa-2,4-diene)Fe(CO)$_3$. The isomeric σ,π-allylic complex (equation 69) similarly undergoes a degenerate rearrangement at low temperature (40 °C), and a skeletal rearrangement at higher temperatures (60—70 °C).[117]

Formal [5,5]-sigmahaptotropic rearrangements of (η^6-bicyclo[6.1.0]nonatriene)M(CO)$_3$ (M = Cr, Mo, W) have been reported (equation 70).[119,120] Recent work[121] on the Mo^0 complex has shown that the starting material has the cyclopropane ring in a *syn* rather than the *anti* geometry proposed earlier.[119]

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[117] R. Aumann, *Chem. Ber.*, 1976, **109**, 168.

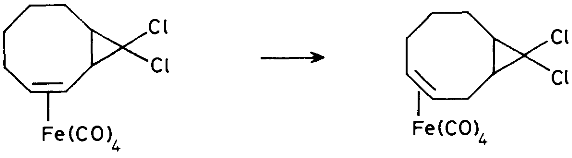
[118] Z. Goldschmidt, H. E. Gottlieb, and D. Cohen, *J. Organomet. Chem.*, 1985, **294**, 219.

[119] W. Grimme, *Chem. Ber.*, 1967, **100**, 113.

[120] A. Salzer, *J. Organomet. Chem.*, 1976, **117**, 245.

[121] F. J. Liotta, Jr. and B. K. Carpenter, *J. Am. Chem. Soc.*, 1985, **107**, 6426.

Hence the proposed pathways for the reaction all involve an intramolecular rearrangement to the unstable *endo*-(η^2,η^4-bicyclo[4.2.1]nonatriene)$Mo(CO)_3$, which attains the final *exo* stereochemistry by a subsequent facile intermolecular exchange process. Deuterium labelling studies showed that a competitive degenerate 1,7-carbon shift also occurs, which does not involve the metal.



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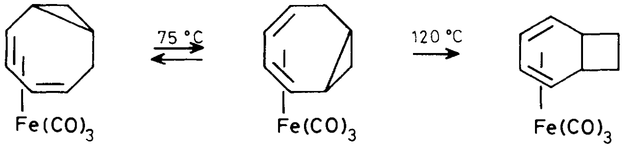

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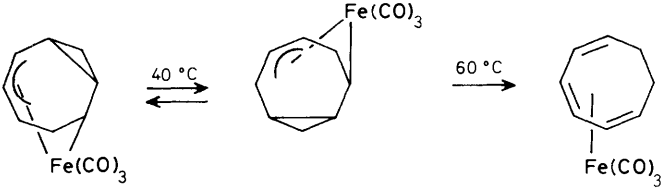

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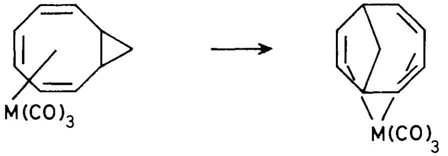
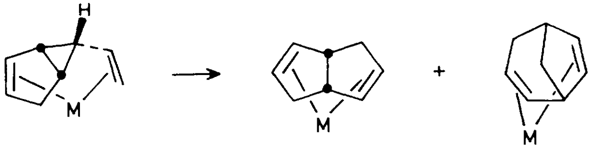


(70)

M = Cr, Mo, W

The η^2,η^2-Rh(acac) complex of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene undergoes a thermal skeletal rearrangement above 80 °C to a mixture of 85% of bicyclo[3.3.0]octa-2,6-diene complex and 15% of the bicyclo[3.2.1]octa-2,6-diene

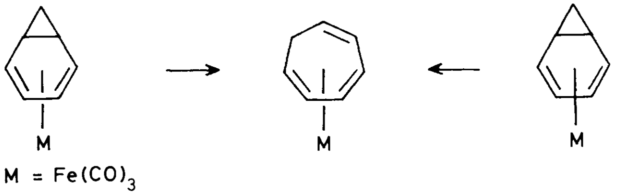


(71)

M = Rh(acac), Rh(hexafluoro-acac), Ir(acac) complex (equation 71)[122] in a formal vcp–cyclopentene (1,3-shift) and Cope (3,3-shift) rearrangement, respectively. The related Rh(hexafluoro-acac) complex rearranges more readily, providing only the first product. The Ir(acac) complex does not rearrange under similar conditions.

It is often observed that metal complexation reduces the energy barrier to rearrangements. An interesting case of the opposite effect has been reported for the electrocyclic ring-opening of both the *exo* and *endo* isomers of (η^4-norcaradiene)$Fe(CO)_3$ complex to (η^4-cycloheptatriene)$Fe(CO)_3$ (equation 72).[123] Here it was found that the energy differences between the cycloheptatriene complex and the isomeric norcaradienes amounts to 21 kcal mol^{-1}, while the difference between the free-valence isomers is estimated[124] to be only *ca.* 4 kcal mol^{-1}.

Finally, we mention two unusual examples of intramolecular oxidative additions in which a cyclopropyl ring carbon migrates to a metal carbonyl ligand. Thus, (η^2-benzvalene)$Fe(CO)_4$ undergoes a facile rearrangement above 10 °C to the isomeric η^1,η^3-$Fe(CO)_3$ σ,π-allylic complex (equation 73).[125] Similarly, the η^4-coordinated (spiro[4.2]heptadiene)$Fe(CO)_3$ compounds were transformed into the corresponding sigma bonded η^1,η^5-(cyclopentadienyl)$Fe(CO)_2$ complexes by a cyclopropane carbon shift to the ligand carbonyl (equation 74).[126]



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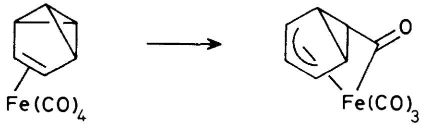
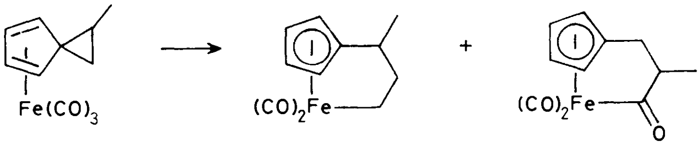


(73)



(74)

Although coordination between vcp and Pd^{II} complexes was detected as early as

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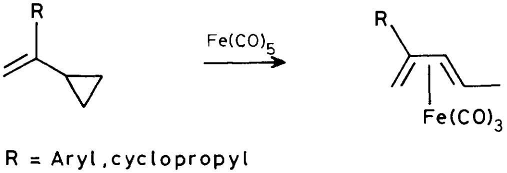
[122] V. Aris, J. M. Brown, J. A. Conneely, B. T. Golding, and D. H. Williamson, *J. Chem. Soc., Perkin Trans. 2*, 1975, 4.

[123] W. Grimme and H. G. Koser, *J. Am. Chem. Soc.*, 1981, **103**, 5919.

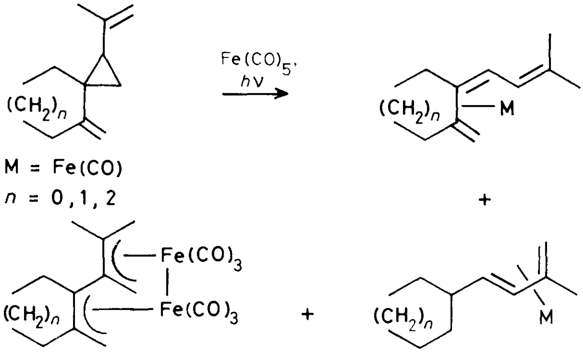
[124] P. M. Warner and S.-L. Lu, *J. Am. Chem. Soc.*, 1980, **102**, 331.

[125] R. Aumann and W. Worman, *Chem. Ber.*, 1979, **112**, 1233.

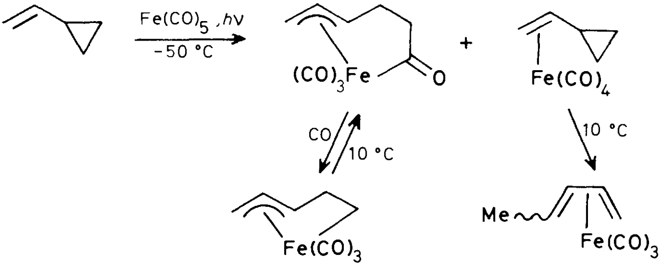
[126] P. Eilbracht and U. Mayser, *Chem. Ber.*, 1980, **113**, 2211.


R
Fe(CO)5
R
Fe(CO)3
R = Aryl, cyclopropyl

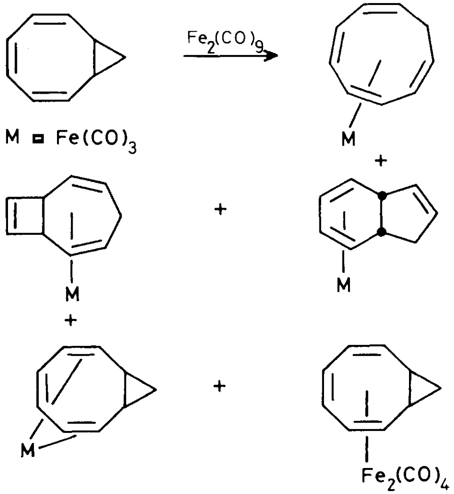
(75)


(CH2)n
Fe(CO)5,
hν
(CH2)n
M
M = Fe(CO)
n = 0, 1, 2
+
Fe(CO)3
(CH2)n
Fe(CO)3
+
(CH2)n
M

(76)


Fe(CO)5, hν
−50 °C
(CO)3Fe
O
+
Fe(CO)4
CO
10 °C
10 °C
Fe(CO)3
Me
Fe(CO)3

(77)


Fe2(CO)9
M = Fe(CO)3
M
+
+
M
M
+
+
M
Fe2(CO)4

(78)

1967[127–129] elucidation of the product structure has remained obscure. On the other hand, a series of (diene)$Fe(CO)_3$ complexes, formed by treatment of acyclic vinylcyclopropanes with iron pentacarbonyl, has been characterized (equations 75—76).[130,131] The reaction mechanism was elucidated by low-temperature irradiation of vcp and $Fe(CO)_5$, giving two unstable $Fe(CO)_4$-coordinated isomers, the η^2-vcp and η^1-acyl-η^3-allylic complexes shown in equation 77.[132] At temperatures above 10 °C, these complexes readily lose a CO molecule to give the ring-opened σ,π-allylic-$Fe(CO)_3$ complex. The latter subsequently rearranges by hydrogen migration to the final diene complexes.

The reaction of bicyclo[6.1.0]nonatriene with $Fe_2(CO)_9$ also gave a mixture of mono and bicyclic coordinated dienes (equation 78).[133,134] Formally, the formation of these complexes requires neither a σ,π-allylic intermediate nor a hydrogen migration. However, evidence from analogous rearrangements of Co (equation 79),[135] Mo (equation 70),[121] and Rh (equation 71)[122] complexes suggests that σ,π-allylic intermediates are indeed involved in this reaction.

Polycyclic olefin systems containing a 1,2-divinylcyclopropane moiety react with $Fe_2(CO)_9$ to give stable mono- and di-nuclear σ,π-allylic complexes, some of which show interesting dynamic properties. Thus, ring-cleavage reactions of this type occur in semibullvalene (equation 80),[136,137] barbaralone (equation 81),[138,139] and bullvalene (equation 82).[140]

Bis(ethylene)rhodium(I) complexes likewise react with *exo*-6-vinylbicyclo-[3.1.0]hex-2-ene to give σ,π-allylic complexes (equation 83)[141] which, depending on the auxiliary ligand, form stable monomers, dimers, or tetramers.

We conclude this section with the reactions of iron and nickel carbonyls with spiro[4.2]heptadienes and its derivatives. The parent compound reacts readily with $Fe_2(CO)_9$ at 25 °C, affording an acyl-bridged cyclopentadienyl complex as the major product, together with an alkyl-bridged dinuclear complex (equation 84).[142] The same reaction occurs in the more complicated spiro-norcaradiene derivative shown in equation 85.[143] In the reaction of 1-vinylspiro[4.2]heptadiene with $Ni(CO)_4$, both alkyl-and acyl-bridged cyclopentadienyl complexes were observed

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[127] A. D. Keteley and J. A. Braaz, *J. Organomet. Chem.*, 1967, **9**, P5.

[128] T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, 1968, **33**, 1876.

[129] E. Vedejs, *J. Am. Chem. Soc.*, 1968, **90**, 4751.

[130] S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Am. Chem. Soc.*, 1965, **87**, 2417; R. Ben-Shoshan and S. Sarel, *J. Chem. Soc., Chem. Commun.*, 1969, 883.

[131] S. Sarel and M. Langbeheim, *J. Chem. Soc., Chem. Commun.*, 1979, 73.

[132] R. Aumann, *J. Am. Chem. Soc.*, 1974, **96**, 2631.

[133] E. J. Reardon, Jr. and M. Brookhart, *J. Am. Chem. Soc.*, 1973, **95**, 4311.

[134] G. Deganello, H. Maltz, and J. Kozarich, *J. Organomet. Chem.*, 1973, **60**, 323.

[135] H. R. Beer, P. Bigler, W. von Philipsborn, and A. Salzer, *Inorg. Chim. Acta*, 1981, **53**, L49.

[136] R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Am. Chem. Soc.*, 1971, **93**, 6709.

[137] D. Entholt, A. Rosan, and M. Rosenblum, *J. Organomet. Chem.*, 1973, **56**, 315.

[138] A. Eisenstadt, *Tetrahedron Lett.*, 1972, 2005.

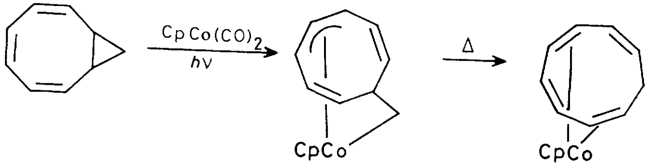
[139] A. H. Wang, I. C. Paul, and R. Aumann, *J. Organomet. Chem.*, 1974, **69**, 301.

[140] R. Aumann, *Chem. Ber.*, 1975, **108**, 1974.

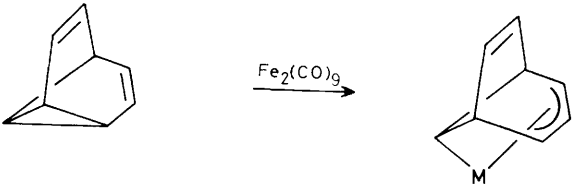
[141] N. W. Alcock, J. M. Brown, J. A. Conneely, and D. H. Williamson, *J. Chem. Soc., Perkin Trans. 2*, 1979, 962.

[142] P. E. Eilbracht and P. Dahler, *Chem. Ber.*, 1980, **113**, 542.

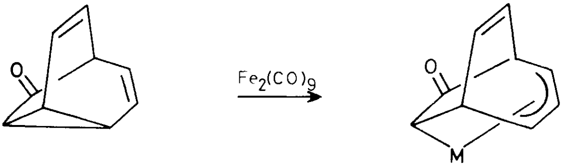
[143] R. M. Moriarty, K. N. Chen, M. R. Churchill, and S. W. Y. Chang, *J. Am. Chem. Soc.*, 1974, **96**, 3661.



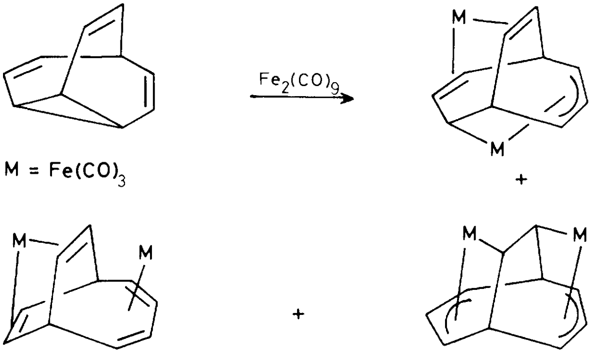
(79)



(80)

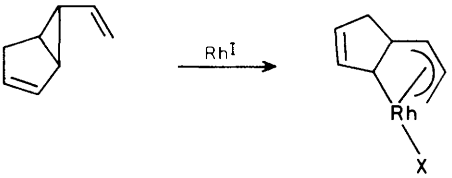


(81)



(82)

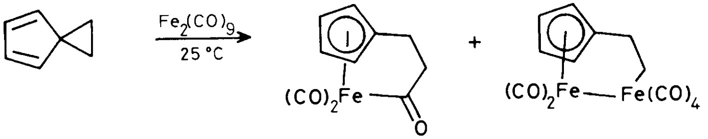
M = Fe(CO)$_3$



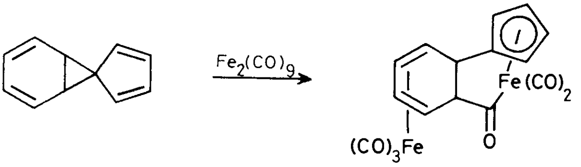
(83)

X = cyclopentadienyl (monomer)
X = acac (dimer)
X = hexafluoro-acac (tetramer)

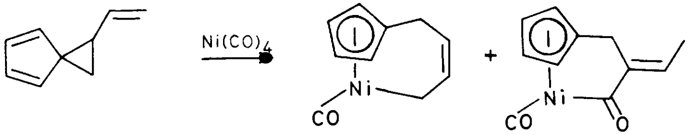
(equation 86).[144] In these reactions, as in those of the non-spiro counterparts, the initial step consists of coordination of the organic π-system with the metal. This is followed by cyclopropane ring-cleavage giving either alkyl or acyl σ,π-allylic complexes. Here, the allylic group and the additional double bond join to form the cyclopentadienyl ligand.



(84)



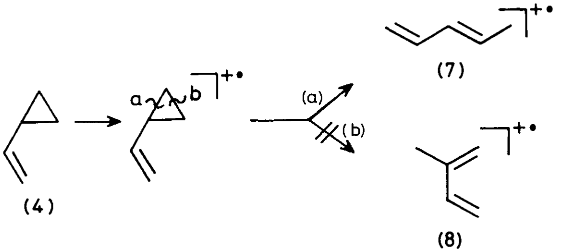
(85)



(86)

6 Conclusions

Recently, rearrangements of the vcp radical-cations have become a subject of interest. Collisional ionization studies of vcp (4) in the gas phase indicate cleavage of the cyclopropane ring *via* pathway (a) to the 1,3-pentadiene radical-cation (7) and not by pathway (b) to the isoprene radical-cation (8) (Scheme 4).[145]



Scheme 4

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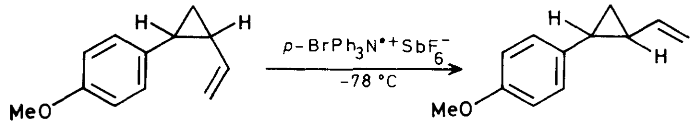
[144] P. E. Eilbracht, *Chem. Ber.*, 1976, **109**, 3136; P. E. Eilbracht, U. Mayser, and G. Tiedtke, *Chem. Ber.*, 1980, **113**, 1420.

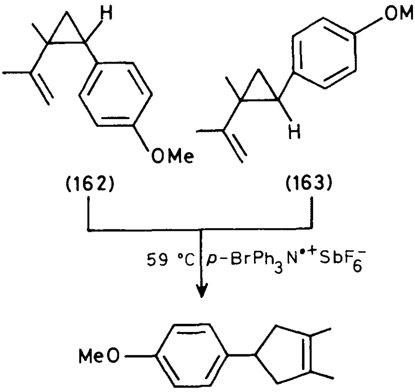
[145] C. Dass, D. A. Peake, and M. L. Gross, *Org. Mass Spectrom.*, 1986, **21**, 741.

Vinylcyclopropyl radical-cations were proposed as intermediates in the *cis–trans* isomerization of *cis*-1-*p*-anisyl-2-vinylcyclopropane (160) to the *trans* isomer (161) by one-electron chemical oxidants such as, for example, p-BrPh$_3$N$^{\bullet+}$SbF$_6^-$at temperatures as low as −90 °C (equation 87).[146]

The same one-electron oxidant caused the rearrangement of either the *cis*-vcp (162) or the *trans*-vcp (163) to the 1,2-dimethyl-4-*p*-anisyl cyclopentene (164) at 59 °C in 86% yield (equation 88)[147] It should be noted that the thermal rearrangement of either (162) or (163) in the absence of such oxidants proceeded only above 200 °C, to yield (164).[147]



(160) (161) 84% (87)



(162) (163) (88)

(164) 86%

It can be seen that vcp rearrangements have been extensively studied for more than two decades, principally from a mechanistic viewpoint. Recently, however, the thermal pathways involving vcp-cyclopentene rearrangements have been utilized in the total syntheses of antheridiogen-An,[63] aphidicolin,[148] zizaene,[149] and 11-deoxyprostaglandin E.[150] Acid-catalysed rearrangement of chrysanthemic acid esters are important intermediates to lavandulols which are used as fragrants.[151]

A new route utilizing trimethyl iodide (TMSI) which induces the vinylcyclopropane–cyclopentene rearrangement has been developed. For example the vcp (165) under carefully controlled reaction conditions either rearranged

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[146] J. P. Dinnocenzo and M. Schmittel, *J. Am. Chem. Soc.*, 1987, **109**, 1561.

[147] J. P. Dinnocenzo and D. A. Conlon, *J. Am. Chem. Soc.*, 1988, **110**, 2324.

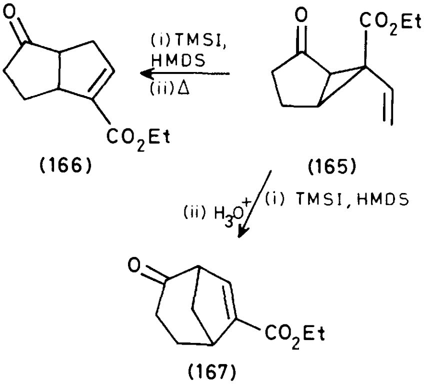
[148] B. M. Trost, Y. Nishimura, K. Yamamoto, and S. S. McElvain, *J. Am. Chem. Soc.*, 1979, **101**, 1328.

[149] E. Piers and J. Bauville, *J. Chem. Soc., Chem. Commun.*, 1979, 1138.

[150] J. Salaün and J. Ollivier, *Nouv. J. Chim.*, 1981, **5**, 587.

[151] G. Suzukamo and M. Tamura, Sumitomo Chemical Co., U.S. Patent No. 4,547,586 (1985).

to the annulated cyclopentene (166) or to the bicyclo[3.2.1]octene (equation 89).[152]



(89)

This review has attempted to highlight the broad versatility and utility of vcp rearrangements. It is hoped that such rearrangements will encourage further developments in the use of vcps as precursors in organic and natural product syntheses.

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[152] A. Fleming, G. Sinai-Zingde, M. Natchus, and T. Hudlický, *Tetrahedron Lett.*, 1987, **28**, 167.