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1,2-DICHLORO-3,3-DIMETHYLCYCLOPROPENE AS A SOURCE OF 1,2-DICHLORO-3-METHYLBUT-2-ENYLIDENE AT AMBIENT TEMPERATURE

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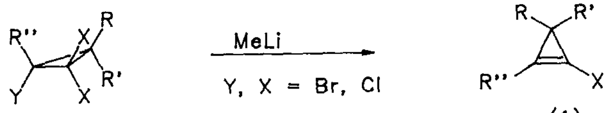
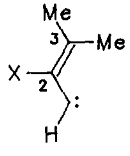
Reaction of 2–bromo–1,1,2–trichloro–3,3–dimethylcyclopropane with one mol.equiv. of methyl lithium at –90 to 0 °C leads to 1,2–dichloro–3,3–dimethylcyclopropene. This is stable for several hours at 20 °C in chloroform or benzene solution but in the presence of an electron–rich or electron–poor alkene reacts in 15 m to 2 h under these conditions to give products apparently derived by reaction of these with 1,2–dichloro–3–methylbut–2–en–1–ylidene (4). The corresponding products are also obtained when 1,1,2–trichloro– or 1,1,2,2–tetrachloro–3,3–dimethylcyclopropanes are treated with methyl lithium in the presence of alkenes at 0 – 20 °C. The cyclopropene (3) is stable in ether solution for more than 10 days at –30 °C, but at ambient temperature reacts in 18 h to give the product of insertion of the carbene (4) into the C–H bonds adjacent to oxygen.

The reaction of a range of 1,1,2-trihalocyclopropanes with methyl lithium leads to 1,2-elimination, with the formation of a cyclopropene (1):[1]



(1)

When R″ = H, R = R′ = Me, the cyclopropenes (1) rearrange at ambient temperature and above to produce alkynes. One explanation for this is a formal ring-opening to the carbene (2, X = Cl, Br), followed by a 2,3-halogen shift.[2,3] Although the carbene could not be trapped by an added alkene, there are several examples of related 3,3-dimethylcyclopropenes bearing an electron withdrawing substituent at C-1 ring-opening to carbenes at or below ambient temperature, and of the trapping of these by alkenes.[4] This may be contrasted with the ring-opening of 3,3-dimethylcyclopropene itself,[5] of tetrachlorocyclopropene,[6] and of a number of other cyclopropenes,[7] which proceed at a reasonable rate only at ca. 150-180 °C. We now report the preparation of a related cyclopropene, 1,2-dichloro-3,3-dimethylcyclopropene (3), and its ring-opening to a vinyl carbene, 1,2-dichloro-3-methylbut-2-en-1-ylidene (4).*



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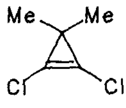

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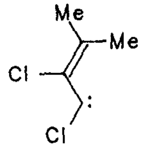

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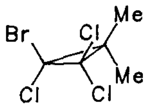

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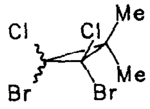
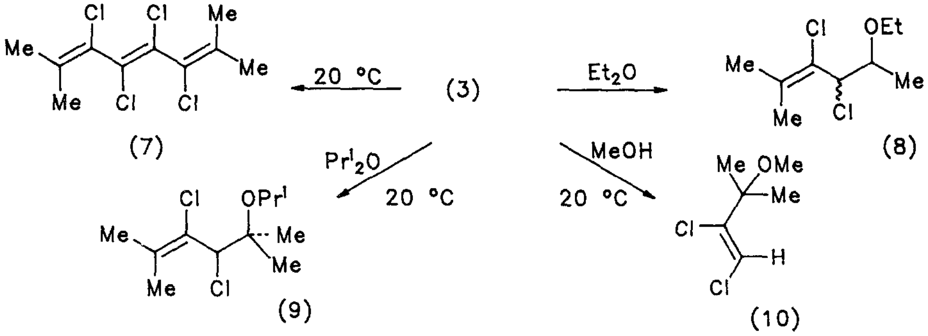


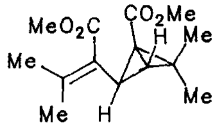
(6)

Reaction of the bromotrichloride (5) with a slight excess of methyl lithium in ether at -78 °C, followed by warming to 0 °C for 5 m led to the cyclopropene (3) which could be separated from the solvent by removal of the latter at - 30 to -40 °C and 0.1 mm Hg. Although the yield of (3) in a concentrated ethereal solution could be estimated as 88%, this was reduced to 61% on removal of all the solvent, because of the volatility of the product. The cyclopropene showed a single peak at δ 1.24 in the ^{1}H n.m.r., while the ^{13}C spectrum showed quaternary carbon signals at δ 118.1 and 40.2, together with a methyl signal at 25.0. If the reaction of (5) with methyl lithium was carried out at -90 to -100 °C for 1 m, and the solution was treated directly with bromine in carbon tetrachloride, a 4:3 mixture of Z- and E- isomers of (6) was obtained.[#] The ^{1}H n.m.r showed one singlet for the E-isomer at 1.53 and two for the Z-isomer at δ 1.57 and 1.51, while the ^{13}C spectrum showed three primary signals at δ 21 - 28 and three quaternary ones at 38.5 (which is assumed to arise by accidental overlap of the two C-3 signals), 62.7 and 62.8; the latter positions are close to those for C-1 in other 1-bromo-1-chlorocyclopropanes.[8]

The cyclopropene (3) decomposed in 18 h at 20 °C to give (7) (86%), the ^{1}H n.m.r. spectrum of which showed just two methyl signals, and the ^{13}C n.m.r. just two methyl groups and three quaternary alkene carbons. The stereochemistry about the centre double bond is assumed to be E-; a similar E-product has been isolated from the decomposition of methyl 3,3-dimethylcyclopropenecarboxylate, and an apparent intermediate bicyclobutane (11) was isolated.[9] By analogy, the formation of (7) may involve ring opening of (3) to the carbene (4), addition of this to the starting cyclopropene and then rearrangement of the derived bicyclo[1.1.0]butane. In the present case, however, the presumed bicyclic intermediate was not detected.



Cyclopropene (3) remained unchanged after more than 10 days at -30 °C in ether. However, complete reaction occurred in 18 h at 20 °C to give a 1:1 mixture of diastereoisomers of (8) (65%). Thus the ^{1}H spectrum included two doublets at δ 4.85 and 4.73 (>CHCl), and the ^{13}C spectrum showed seventeen of the expected eighteen signals including four quaternary carbons in the alkene region, and four tertiary carbons at δ 78.5, 76.5, 64.7 and 62.7. This compound is again apparently derived from the carbene (4), which inserts into the C-H bond of ether α- to oxygen. Such reactions have been reported for a number of other carbenes, and in particular for the vinyl carbene (12).[6,10] Treatment of the cyclopropene (3) with di-isopropyl ether for 18 h at 20 °C led to the ether (9), the ^{1}H n.m.r. of which included a singlet for the -CHCl- group at δ 4.8, while the ^{13}C-spectrum showed three quaternary, two tertiary and six primary carbons; the diastereotopic carbons of the -CMe$_2$- and isopropyl groups are therefore distinguished.



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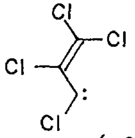

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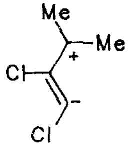

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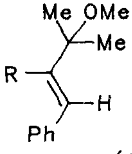
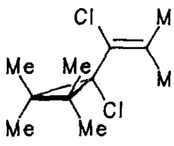


(14)

The cyclopropene (3) also decomposed when allowed to stand in other solvents.** In benzene or chloroform, the reaction led to a complex mixture which was not separated but which did appear to contain the triene (7). In methanol, a single major product, the ether (10), was obtained after 18 h at 20 °C. This was identical to a sample prepared independently, the Z-configuration of which was established by an n.O.e. study;[11] the reaction could involve trapping of the dipolar form of the carbene, i.e. (13), by proton abstraction from the solvent to give an allyl cation followed by methanolysis, or indeed by direct attack of methanol at C-3 of the carbene, although a direct acid catalysed ring opening of (3) has not been excluded. A minor product (ca. 6%), which was not present in the crude reaction mixture, was 2-chloro-3-methylbut-2-en-1-al;[12] this could be derived by trapping of the intermediate allyl cation at C-1 rather than C-3, followed by acid catalysed fragmentation of the derived α-chloroether on chromatography. Photolysis of 1,2-diphenyl-3,3-dimethylcyclopropene in methanol also leads to ring-opened allylic ethers which have been explained in terms of protonation of an intermediate vinylcarbene, though the product distribution is rather different from that observed in acid induced methanolysis which leads to (14, R = Ph).[13] Silver induced methanolysis of 2-phenyl-1,3,3-trimethylcyclopropene also leads to (14, R = Me) as one of the products.[14]

The above reactions apparently involve the intermediacy of vinylcarbene (4). This could also be trapped by an added alkene (see Table). The reactions occurred more rapidly than (3) was consumed in the absence of alkene, suggesting a reversible cyclopropene - carbene rearrangement. Thus on reaction of (3) with 2,3-dimethylbut-2-ene for 30m at 20 °C, (15) was obtained in good yield. Compound (15) showed four distinct ring methyls by both ^{1}H and ^{13}C n.m.r. spectroscopy, consistent with a preferred twisted conformation as shown, and rotation about the exocyclic C-C bond which is slow on the n.m.r. time scale.[6,15,20] There was no material change in the 90 MHz ^{1}H spectrum on heating to 60 °C. The same cyclopropane (15) was obtained by reaction of either 1,1,2-trichloro- or 1,1,2,2,-tetrachloro-3,3-dimethylcyclopropanes with methyl lithium at 20 °C in the presence of 2,3-dimethylbut-2-ene, presumably in each case through 1,2-elimination of HCl or Cl_2 respectively to produce (3), followed by ring-opening.



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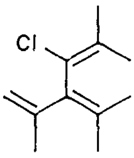

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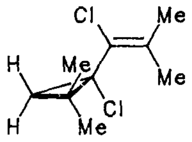
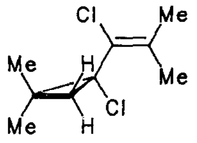


(17a)



(17b)

Attempted purification of (15) by preparative g.l.c. led to elimination of hydrogen chloride to give the triene (16), presumably by cyclopropyl-allyl ring-opening with loss of chloride ion, followed by the loss of a proton.

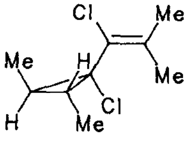
In the presence of 2-methylpropene, the cyclopropene (3) was converted to (17). The ^{1}H and ^{13}C n.m.r. spectra at ambient temperature showed twice the expected number of signals and corresponded to a 2:3 mixture of two rotamers (17a) and (17b). On heating to 343K the ^{1}H n.m.r. at 90 MHz became much simpler and included four singlets of equal size at δ 1.91, 1.86, 1.33 and 1.13, the latter obscuring a number of small signals; presumably under these conditions rotation is rapid on the n.m.r. timescale. The $\Delta G^{\#}$ for the process was estimated as 17.5 kcal/mol using the approximation developed by Gunther [$\Delta G^{\#} = 4.57\ T_C(9.97 + \log(T_C/\delta\nu)$ cal/mol)].[16]

TABLE

Reactions of Cyclopropene (3) with alkenes

Alkene	Products	Ratio	Yield
2,3-dimethylbut-2-ene	(15)	-	75%
2-methylpropene	(17)	-	42%
trans-but-2-ene	(18)	-	52%
cis-but-2-ene	(19),(20)	5.5:1	37%
2-methylbut-2-ene	(21)	7:1(Z:E)	51%
methyl acrylate	(29)	-	77%
methyl methacrylate	(25)	-	85%
dimethyl fumarate	(34)	-	38%
dimethyl maleate	(34),(35)	3:2	15%
ethyl vinyl ether	(22)	-	83%
methyl β,β-dimethylacrylate	(31),(30)	1:1	58%
3-methylbut-2-en-1-ol trimethylsilyl ether	(33),(32)	7.5:1	85%

Trapping by *trans*-but-2-ene led to (18). In this case the ^{13}C spectrum at ambient temperature showed only nine signals and was consistent either with the presence of a single preferred rotamer, or of rapid rotation. However, several of the signals were unusually broad - in particular those at δ 32.7 and 29.6; moreover the ^{1}H n.m.r. spectrum, which had very broad peaks at ambient temperature, showed two sets of signals in ratio 1:2.3 when determined at 235K. Addition to *cis*-but-2-ene led to a mixture of two products in ratio 5.5:1 which could be distinguished by capillary g.l.c., but not separated on a preparative scale. The ^{13}C n.mr. showed seven major signals consistent with the isomer (19). The ^{1}H n.m.r. was complicated, but at both 300 MHz and 233K and 200 MHz and 303K the ring protons of the major isomer appeared as a broad multiplet at δ 1.33, and the ring methyl groups appeared as a broad singlet, while the olefinic methyl groups appeared as two sharp singlets. This is again consistent with the isomer (19), with rapid rotation on the n.m.r. time scale even at 233K. Minor signals at 233K included two doublets (J 6.7 Hz and 6.6 Hz) at δ 1.08 and 1.05 which could be assigned to the ring methyl groups in the minor isomer (20); these appeared as a broad signal at 200 MHz and 303K. They appeared upfield of those in (19), in agreement with their position in the shielding zone of the vinyl group. The cyclopropane hydrogens appeared as two double quartets with a coupling between them of 10.6 Hz, in agreement with their *cis*-relationship; they appeared downfield of the corresponding hydrogens in the major isomer, in agreement with the latter being in the shielding zone of the vinyl-group. A similar downfield shift in the hydrogens *trans*- to the vinyl-group has been observed in the two adducts of *cis*-butene with the carbene (10).[6]



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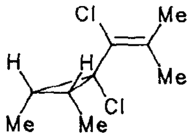

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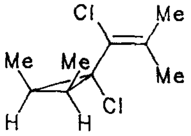

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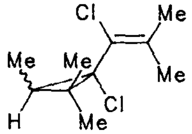
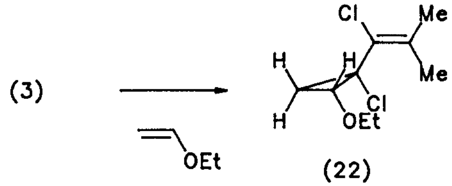


(21)

There was no evidence for the presence of any *trans*-isomer (18) in the reaction of (3) with *cis*-butene, nor of any (19) or (20) in its reaction with *trans*-butene. This is consistent with a concerted addition of a singlet carbene;[17] no e.s.r. signals were observed when the cyclopropane was allowed to stand at ambient temperature either neat, as a 50% solution in ether or as 2% solutions in ether, benzene or carbon tetrachloride.

Not surprisingly, the reaction of cyclopropene (3) with 2-methyl-but-2-ene was complex, but apparently led to a mixture of Z- and E-(21) in ratio ca 7:1 by capillary g.l.c., which could not be separated by preparative g.l.c. The ^{13}C spectrum showed two major sets of signals in ratio ca. 1:1, including quaternary carbons at δ 136.1, 134.3, 121.0, 117.4, 58.9 and 58.5, two tertiary carbons at 31.9 and 28.9 and ten primary carbons at higher field. The ^{1}H n.m.r. spectra at 293 or 233 K were very similar and included three singlets at δ 1.87, 1.86 and 1.85 in ratio ca.1:1:2; these integrated to a total of six hydrogens when compared with ten protons in the higher field region between δ 1.04 and 1.22, though this latter region could not be fully interpreted. There were also a number of smaller signals possibly corresponding to rotamers of the minor isomer.

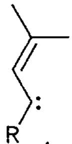
Reaction of the cyclopropene (3) with ethyl vinyl ether led to a single product in good yield:



(22)

The ^{1}H n.m.r. spectrum in CDCl$_3$ showed two doublets of quartets in the region δ 3.6 - 4.0, coupled to each other with J 9.3 Hz, corresponding to the diastereotopic methylene hydrogens of the ethyl group. In addition there were two methyl singlets at δ 1.95 and 1.83, together with a three-hydrogen triplet at 1.29, in agreement with the structure proposed. The signals for the ring hydrogens, a sharp single-hydrogen triplet at δ 3.36 (separation 6.5 Hz), and a sharp two-hydrogen doublet at 1.52 (separation 6.5 Hz), were less easy to explain. However, when the spectrum was run in benzene, the three cyclopropane hydrogens each appeared as double doublets at δ 3.36 (J 5.2, 7.9 Hz), 1.68 (J 5.2, 7.4 Hz) and 1.35 (J 7.4, 7.9 Hz). The signal at δ 1.68 may be assigned to the hydrogen *cis*- to the ethoxy group on the basis of the smaller vicinal coupling constant (5.2 Hz).[17,18] Ethyl vinyl ether is reported to react with 1,3,3-trichloroprop-2-en-1-ylidene to give both E- and Z-adducts in ratio 2:1.[19] In the E-isomer, the hydrogen *cis*- to the ethoxy group appears 0.19 ppm at higher field, whereas in the Z-isomer the two hydrogens are very close in chemical shift (δ 1.36 and 1.39). Moreover, only in the case of the Z-isomer are the two hydrogens of the methylene group of the ether non-equivalent. On this basis, and on steric grounds, the isomer obtained above is believed to be Z-; either the reaction is highly stereoselective or the E- isomer is unstable to the reaction conditions or to the work up. Addition of (23, R = SEt) to ethyl vinyl ether is reported to give two isomeric cyclopropanes in moderate yield; the major isomer was separated, though no stereochemistry was assigned.[21] Addition of (23, R = SOEt) to the same alkene apparently leads to a single isomer of the corresponding cyclopropane; this is represented as (24), although no proof of stereochemistry is given.[4b]

The carbene (4), or a related species, derived from cyclopropene (3), also reacted with electron poor alkenes. When allowed to stand for 18 h at 20 °C with methyl methacrylate a single product was obtained in good yield (85%). The ^{13}C n.m.r. at 20 °C showed a single carbonyl carbon at δ 171.2, two alkene signals and five other sharp peaks at 54.9, 52.2, 22.1, 21.1 and 17.6 respectively; in addition there was an extremely broad signal at δ 30–33. The ^{1}H n.m.r. was also complex at 303K, but at 233K and 300 MHz was consistent with the presence of two rotamers in ratio ca. 1:1. There were a number of other very minor peaks, including two singlets at δ 3.87 and 3.83 (integrating together to about 5 % of the methoxy peaks for the major product), but these could not be interpreted in terms of a stereoisomeric minor product. Since the cyclopropane (17), with a methyl-group syn- to the alkene showed slow rotation on the n.m.r. time scale even at 303K, it seems likely that the ester-group in the present case is syn- to the alkene, rather than the methyl-group, i.e. the compound is assigned the structure (25). In support of this, reaction of the carbene (26, X = Ph) with methyl methacrylate has been shown to lead to (27, X = Ph), and the structure has been proved by X-ray crystallography;[22] the positions and coupling constants of the ring hydrogens for (25) are close to those in (27, X = Ph). Moreover, the carbene (10) can also add to place the vinyl-group syn to the ester;[6] it is interesting to note, however, that dimethoxycarbene (28), which leads to a syn-product with methyl acrylate, gives a 1:1 mixture of stereoisomers on reaction with methyl methacrylate.[23]



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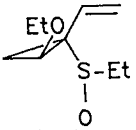

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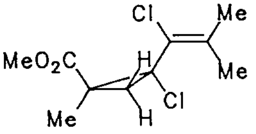

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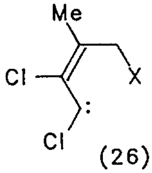

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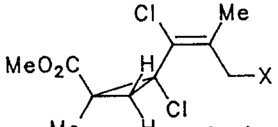
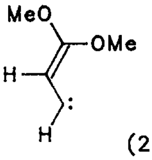


(27)

Treatment of (3) with methyl acrylate for 18 h at 20 °C also led to a single product (29). The ^{1}H n.m.r. at 303K showed just one methoxy-group and the ^{13}C spectrum showed only nine signals in the expected positions, although the signals for the secondary and tertiary ring carbons at δ 26.8 and 32.9 were rather broad. However, in the ^{1}H spectrum at 300 MHz and 233K the methoxy signal was split into two peaks and a triplet for one of the ring hydrogens which appeared at 2.47 (J 5.3 Hz) at 303 K was split into two similar triplets at 2.6 and 2.31 (ratio 1:3); this is in agreement with slow rotation on the n.m.r. time scale at this temperature, and the formation of two preferred rotamers in ratio 1:3. This is again consistent with a *cis*-arrangement of ester and vinyl-group. The coupling constants for the signals at δ 2.6 and 2.31 in the two rotamers are typical of geminal and trans-couplings in cyclopropanes. These signals are therefore assigned to H_a. The chemical shifts are then close to those of the doublets at δ 2.42 and 2.24 in the spectrum of (25), which presumably result from the corresponding hydrogen; hydrogens *cis*- to ester groups in cyclopropanes are shifted downfield.[24] There was a small additional singlet in the methoxy region (< 5% of the signal for (29)) but no signals could be discerned at higher field to correspond to a minor isomer.



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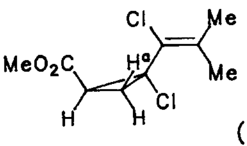


(29)

The reaction of (3) with methyl β,β-dimethylacrylate followed a rather different course, leading to an ca. 1:1 mixture of (30) and (31). These ran together on column chromatography but could be distinguished by capillary g.l.c. The ^{1}H n.m.r. spectrum was complicated because of the presence of two rotamers of each diastereoisomer. Four singlets appeared in the region δ 3.58 - 3.67 in ratio ca. 8:14.5:11:9, corresponding to the methoxy-group in each of the four forms. In addition there were a large number of singlets in the region 2.14 - 1.22, integrating in total to thirteen protons compared to a total of three in the region 3.58 - 3.67. Some of these peaks corresponded in area to those in the methoxy-region, but a complete analysis was not carried out. Reduction of the mixture of esters to the corresponding alcohols by reaction with lithium aluminium hydride followed by silylation gave a mixture of (32) and (33), which showed one spot on t.l.c. and one peak on g.l.c. The ^{1}H n.m.r. spectrum at ambient temperature showed signals for two rotamers of each compound. Thus the region 3.5 - 4.3, where the methylene hydrogens adjacent to oxygen appeared, clearly showed six double doublets and one triplet (Fig. 1); a further multiplet was partly obscured. In addition there were four trimethylsilyl-signals. The spectrum could be analysed by comparison with a mixture of (32) and (33) prepared independently by reaction of the trimethylsilylether of 3-methylbut-2-en-1-ol with cyclopropene (3). The methylene region of the n.m.r. of this showed all same peaks as those from the previous mixture, but in different ratios (Fig. 2). The cyclopropane prepared in this way apparently consists of one major diastereoisomer and one minor one in ratio 7.5:1; the product of this reaction has previously been described as an ca. 2:1 mixture of Z- and E-isomers.[25] The major diastereoisomer existed in two rotameric forms in ratio ca.3:2. The double doublets labelled A and B for one of the methylene hydrogens in each of the rotamers are clearly visible; the second pair of double doublets overlap somewhat, but are labelled C and D.[24] A comparison with Fig.1 indicates that the mixture obtained indirectly from (30) and (31) consists of two diastereoisomers in ratio ca. 1:1.

Fig. 1
300 MHz ^{1}H nmr spectrum of (30) and (31) prepared from 3-methylbut-en-1-ol trimethylsilyl ether in the region of δ4.

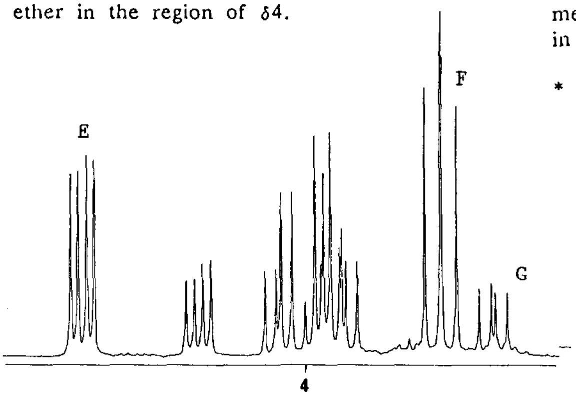
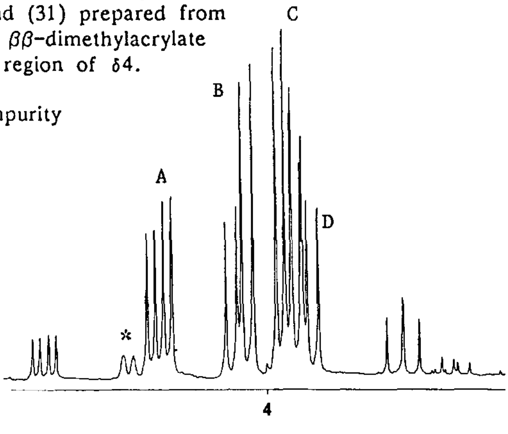


Fig. 2

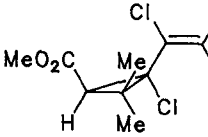
300 MHz ^{1}H nmr spectrum of (30) and (31) prepared from methyl $\beta\beta$-dimethylacrylate in the region of δ4.

* = impurity

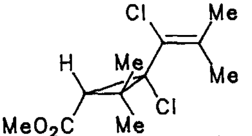


The second diastereoisomer exists in two rotameric forms in ratio ca.4:1; the major rotamer gives rise to the double doublet labelled E and the triplet F, while the minor rotamer gives the double doublet G, and a second multiplet which is largely obscured by by the signals of C. Unlike the reaction with methyl acrylate or methacrylate, the addition of (3) to the more highly substituted methyl β,β-dimethylacrylate seems therefore to give a 1:1 mixture of diastereoisomers. This may be caused by the effect of the β-methyl group in hindering the approach of the carbene (3) or a related species *cis-* to the ester group. It seems most likely the reaction of the silyl ether with

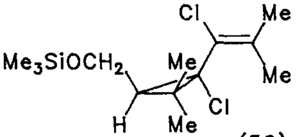
(3) leads predominantly to the cyclopropane with vinyl and ether groups *trans*– to each other, (33). In agreement with this, the methylene signals at highest field (F and G), which are larger in the mixture of (32) and (33) derived from (30) and (31), could be in the shielding zone of the vinyl group. The addition of carbene (10) to esters of β,β–dimethylacrylic acid has been reported to lead to both E– and Z– isomers,[6] as does reaction with 1–trimethylsilyloxy–3–methyl but–2–ene;[15c] addition of 1,3,3–trichloroprop–2–en–1–ylidene to the latter silyl–ether leads predominantly to the E– adduct (ratio 5:1).[20] The addition of these carbenes to esters of acrylic or methacrylic acid generally leads predominantly to Z–cyclo– propanes, ie., the ester and vinyl groups are trans–related,[6,15c] in marked contrast to the corresponding additions of (4) described above. However, it is noteworthy that the carbene (28) adds to methyl acrylate to place ester and vinyl groups entirely *cis*–, but with methyl methacrylate leads to a 1:1 mixture of stereoisomers.[23] Clearly the stereochemical outcome of the reactions is highly dependent on the nature of the substituents on both the carbene and the alkene.



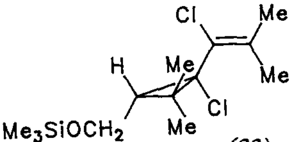
(30)



(31)

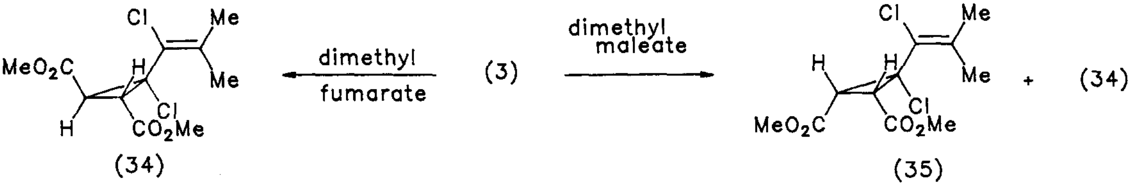


(32)



(33)

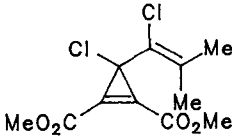
The cyclopropene (3) also reacted with diesters. With dimethyl fumarate in ether a single adduct (34) was obtained, albeit only in moderate yield (38%); a second product was the ether (9). The ^{13}C n.m.r. spectrum of (34) showed eleven signals at 303K, including two carbonyl carbons and one alkene; the ^{1}H n.m.r. was also consistent with a single rotamer at 293K, and included two single hydrogen doublets at δ 2.99 and 2.90, each with a coupling constant of 7.3 Hz, for the ring hydrogens. On cooling to 230 K, these signals were split into two pairs of doublets, at δ 3.08 and 2.91 and 3.0 and 3.17 respectively, in ratio ca. 4:1. Small shoulders also appeared on two of the methyl signals at δ 3.74 and 1.90, but the complete spectrum of the minor rotamer could not be seen. Reaction of dimethyl maleate with the cyclopropene proceed even less efficiently, to produce a 3:2 mixture of the above adduct (34), and an isomer, in overall 15% yield, as well as the ether insertion product (9) (50%). The two isomers could not be separated, and the structure of the minor one is therefore inferred from the n.m.r. spectra.



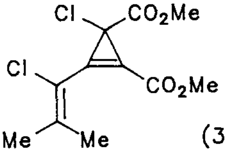
The ^{13}C n.m.r. spectrum at 230 K showed eleven signals in addition to those for (34), in each case close to those of (34) and with the same multiplicity. The ^{1}H spectrum at this temperature showed four methyl singlets, two in the methyl–ester region and two at high field; in addition there were two doublets at δ 3.01 and 2.78 with a coupling constant of 10.9 Hz, consistent with a cis–1,2–coupling in a cyclopropane. This compound is therefore characterised as (35), although it is not clear whether the alkene is cis– or trans– to the esters. The fact that the ^{1}H and ^{13}C spectra both became very broad in the region of the ring–hydrogens and the carbonyl groups respectively on warming to 300 K, suggests that restricted rotation is occurring at 230 K. Since the ring-hydrogens of (35) are sharp at this temperature, whereas those of the trans-ester are still slightly broadened, the barrier to rotation is apparently higher in (35) than in (34); this may be evidence for an all cis-geometry - though the possible effect of restricted rotation of the cis-ester groups makes this assignment provisional. Whatever the stereochemistry of (35), the key observation is that the reaction of (3) with dimethyl maleate is not stereospecific.

The loss of configuration in this addition could be explained in terms of a triplet carbene; the fact that the reaction of (4) with electron rich alkenes does lead to retention of configuration suggests that this is not likely. An alternative explanation could be that the reaction with electron poor alkenes is not concerted but is better described as a Michael addition followed by ring closure. Loss of stereochemistry in additions to maleates has also been reported in the addition of 3,3-dimethoxyvinylcarbene,[24,26] (23, R = SEt)[21] and phenylhalocarbenes,[27] and in the latter case carbene - adduct complexes have been invoked as intermediates.

The reaction of (3) with dimethyl acetylene dicarboxylate proceeded in reasonable yield to give a product assigned as (37).



(36)



(37)

This showed four singlets in the ^{1}H n.m.r., including two at δ 2.22 and 2.16. The ^{13}C spectrum showed eleven peaks including four primary carbons at δ 54.0, 53.1, 23.9 and 22.7. The remaining seven carbons were quaternary, although some long range coupling was observed. Two signals at δ 168.3 and 157.8 were assigned to the two carbonyl groups. Two singlets at 124.4 and 106.4, which showed no long range coupling, were assigned to the carbons of the cyclopropene double bond. The remaining two olefinic carbons appeared at δ 155.0 and 114.4 and each showed long range coupling to more than one methyl group. The final signal, for C_3 of the ring, appeared at δ 50.7. Two ester bands were observed in the i.r. spectrum, at 1750 and 1728 cm^{-1}. These data could be consistent with the structure (36) if, like the corresponding vinylcyclopropanes, this adopted a preferred conformation in which the vinyl-group does not bisect the ring and restricted rotation leads to all the carbons being different on the n.m.r. timescale, or that the two ester groups are not both coplanar with the cyclopropene double bond. However, the related dimethyl 3-naphthyl-3-methylcyclopropene-1,2-dicarboxylate, with a similar large substituent at C-3, shows only one ester band in the i.r. spectrum, and only one type of methyl ester by n.m.r.[28] An alternative explanation is that, although (36) is the primary product, an allylic rearrangement has occurred to produce (37); a similar reaction is reported when 3,3-dichloro-1,2-bis(trifluoromethyl)cyclopropene is heated to 180 °C, or on treatment with antimony pentafluoride or aluminium trichloride at ambient temperature.[29] Indeed such a rearranged product has also been reported in the reaction of (23, R = SEt) with dimethyl acetylenedicarboxylate.[21]

Experimental Section

Unless otherwise stated all new compounds were homogeneous by t.l.c. and/or g.l.c.; n.m.r.

spectra were run in $CDCl_3$ solution and recorded for ^1H at 200 or 300 MHz on Bruker Spectrospin instruments, and ^{13}C spectra were recorded at the corresponding carbon frequency on the same instruments. Infra-red spectra were obtained on a Nicolet F.T. instrument, while mass spectra were measured on an AEI MS9 or a Kratos MS80 using the E.I. method; where mass measurements are quoted for chlorine containing species, they refer to ^{35}Cl isotope peaks. Melting points are uncorrected.

All experiments involving methyl lithium were carried out under dry nitrogen. Petrol refers to the fraction boiling between 40 and 60 °C.

1,2-Dichloro-3,3-dimethylcyclopropene

A solution of 2-bromo-1,1,2-trichloro-3,3-dimethylcyclopropane[8b] (5) (1.0 g) in ether (4.0 ml) was treated with methyl lithium (2.9 ml, 1.5 M, 1.1 mol eq) at -78 °C. The solution was allowed to warm to 0 °C and after 5 min the product was flash distilled together with ether at 20 °C/1.0 mm Hg. Evaporation of ether at -30 to -40 °C/0.1 mm Hg afforded a colourless liquid identified as *1,2-dichloro-3,3-dimethylcyclopropene* (3) (0.33 gm, 61%; 0.48 gm, 88% in ether solution) (Found M^+ 135.9854. $C_5H_6Cl_2$ requires 135.9846) which showed δ_H (C_6D_6): 1.24 (6H, s): δ_H(C_6D_6, 230 K): 1.28 (6H, s); δ_C (C_6D_6, 230 K) 118.14s (fine coupling, allylic C), 40.18s (fc), 25.0q; ν_{max} (film): 750, 1123, 1447, 1977 cm^{-1}; m/e: 121 (M-Me), 101 (M-Cl).

The tetrahalide (250 mg) in ether (15 ml) was treated with methyl lithium (2ml, 1.2 M) at -90 °C to -100 °C over 1 m. Bromine (600 mg) in CCl_4 (0.5 ml) was added at - 90 °C. Removal of the solvent and excess bromine gave a solid (230 mg) which was recrystallised from methanol and was a mixture of E- and Z-1,2-dibromo-1,2-dichloro-3,3-dimethylcyclopropanes which showed one peak on t.l.c. or g.l.c. (Found: C, 19.25; H, 1.91. Calculated for $C_5H_6Br_2Cl_2$: C, 18.93; H, 1.91) which showed δ_H (E) 1.53 (s) (Z) 1.57 (3H, s), 1.51 (3H, s) (ratio ca 3:4); δ_C 21.0q, 24.5q, 27.9q, 38.5s, 62.7s, 62.8s.

Thermal Stability of 1,2-Dichloro-3,3-dimethylcyclopropene

a) A solution of dichloro-3,3-dimethylcyclopropene in ether (in ratio 4:6, by volume) was allowed to stand at -30 °C, monitoring the reaction by nmr spectroscopy; after 10 days the compound survived unchanged, showing the same proton spectrum as the starting material.

b) The cyclopropene (100 mg) was allowed to stand for 18 h at 20 °C in a sealed tube. The ^1H nmr spectrum then showed complete rearrangement. Column chromatography over silica gel eluting with petrol and ether (9.5:0.5) gave *2,7-dimethyl- 3,4,5,6-tetrachloro-2,4,6-octatriene* (7) (86 mg, 86%) as a colourless oil (Found M^+: 271.9666. $C_{10}H_{12}Cl_4$ requires: 271.9693), which showed δ_H 1.84 (6 H, s) 1.87 (6 H, s); ν_{max} 742, 1063, 1440, 2917 cm^{-1}; m/e: 257 (M-Me), 237 (m-Cl), 222 (M- CH_3Cl); δ_C 21.3, 22.37, 119.55, 131.44, 138.07.

c) The dichlorocyclopropene (64 mg) was allowed to stand in hexadeuterobenzene (0.5 ml) at 20 °C, monitoring the reaction by n.m.r. spectroscopy. The signal for the starting material was replaced over a period of ca. 20 h by a complex set of signals in the region of δ 1.0 - 2.0. The t.l.c. showed several spots, one of which corresponded to the triene (7).

d) The cyclopropene (64 mg) was allowed to stand at 20 °C in deuterochloroform (0.5 ml), and the reaction was monitored by n.m.r. spectroscopy. The signal for the starting material was replaced over a period of ca 10.5 h by a complex set of signals in the region δ 1.0 - 2.0. The t.l.c. showed several spots, including one which corresponded to the triene (7).

Ethyl 5-Methyl-3,4-dichlorohex-4-en-2-yl Ether

1,1-Dichloro-3,3-dimethylcyclopropene was prepared as above from (5) (0.5 g) and methyl lithium (1.45 ml, 1.5 M, 1.1 mol eq). Dry ether (1.0 ml) was added and the solution was stirred overnight at 20 °C, when the tlc showed one spot. Evaporation of the ether at 20 °C/14 mm Hg gave an oil which was an ca 1:1 mixture of two diastereoisomers of *ethyl 5-methyl-3,4-dichlorohex-4-en-2-yl ether* (0.27 gm, 65%) (Found M$^+$: 210.0591. Calculated for $C_9H_{16}Cl_2O$: 210.0578) which showed δ_H 4.85 (1 H, d, J 8.8 Hz), 4.73 (1 H, d, J 8.8 Hz), 3.85-3.40 (6H, complex), 1.92 (3 H, s), 1.893 (3H, s), 1.892 (3H, s), 1.88 (3H, s), 1.36 (3H, d, 6.1 Hz), 1.24 (3H, t, 7.0 Hz), 1.15-1.08 (6H, complex); δ_C 134.2 s, 133.9s, 126.7s, 125.95 s, 78.5 d, 76.5 d, 66.1 t, 65.6 t, 64.7 d, 62.7 d, 22.6 t, 22.3, 20.7, 18.05, 17.3, 15.6, 15.5; ν_{max} 750, 1121, 1977 cm^{-1}; m/e 175 (M-C_2H_5O).

Isopropyl 3,4-dichloro-2,5-dimethylhex-4-en-2-yl Ether

1,1-Dichloro-3,3-dimethylcyclopropene was prepared as above from (5) (0.5 g) and methyl lithium (1.45 ml, 1.5 M, 1.1 mol eq); remaining ether was removed by careful distillation at -40 °C and 1 mmHg. Di-isopropyl ether (1.5 ml) was added at 20 °C and the solution was stirred for 18 h. Evaporation of excess di-isopropyl ether at 20 °C gave a colourless oil (0.40 g, 85%). Flash chromatography using silica and eluting with petrol and ether (9:1) afforded *isopropyl 3,4-dichloro-2,5-dimethylhex-4-en-2-yl ether* (0.32, 68%) (Found M$^+$-Me: 223.0655. Calculated for $C_{10}H_{17}Cl_2O$: 223.0656) which showed δ_H (CCl_4); 4.8 (1H, s), 3.77 (1H, sep, J 6 Hz), 1.85 (6H, s), 1.41 (3H, s), 1.2 (3H, s), 1.05 (6H, d, J 6 Hz); δ_C 134.1s, 125.8s, 78.8s, 66.8 d, 64.3 d, 25.0 q, 24.9 q, 24.1 q, 23.1 q, 22.7 q, 21.6 q; ν_{max} 735, 910, 2997 cm^{-1}.

Methyl 3,4-Dichloro-2-methylbut-3-en-1-yl Ether

1,1-Dichloro-3,3-dimethylcyclopropene was prepared as above from (5) (0.5 g) and methyl lithium (1.45 ml, 1.5 M, 1.1 mol eq). The product and the solvent were flash distilled at 20 °C/0.1 mm Hg giving a clear solution. Dry methanol (2.0 ml) was added and the solution was stirred at 20 °C overnight. Evaporation of the volatile compounds at 14 mm Hg/ 20 °C produced a colourless oil; column chromatography eluting with petrol and ether (9:1) gave methyl 3,4-dichloro-2-methylbut-3-en-1-yl ether (0.2 g, 60%) [Found M$^+$: 168.0100. Calculated for $C_6H_{10}OCl_2$: 168.0109], which showed δ_H 1.28 (6H, s), 2.99 (3H, s), 6.24 (1H, s); δ_C 141.5 s, 116.5 d, 78.05 s, 50.6 q, 25.3 q; ν_{max} 783 m, 1074 s, 1178 m, 2987 s, 3150 m, cm^{-1}; m/e 153 (M-Me), 133 (M-Cl), 101(M- CH_4OCl). This was identical by n.m.r. and i.r. to an authentic sample.[11] A minor product (15 mg., 6.4%) was identified as 2-chloro-3-methylbut-2-en-1-al,[12] and showed δ_H 9.75 (1 H, s), 2.25 (3H, s), 2.10 (3H, s).

2-Chloro-2-(1-chloro-2-methylprop-1-enyl)-1,1-dimethylcyclopropane

a) A solution of (5) (0.5 g) and isobutylene (3.0 ml) in dry ether (3.0 ml) was treated with methyl lithium (2.0 ml, 1.5 M, 1.4 mol.eq.) at -78 °C. The mixture was allowed to warm to 20 °C and after 2.0 h water (2.0 ml) was added at - 20 °C and the product was extracted with ether (2 x 10 ml), washed with water (3 x 10 ml) and dried ($MgSO_4$). Removal of the solvent at 14 mm Hg and 20 °C and flash distillation at 40 °C/0.2 mm Hg to produced colourless oil (0.16 g, 42%), showing one peak by glc, characterised as *2-chloro-2-(1-chloro-2-methylprop-1-enyl)-1,1-dimethylcyclopropane* (17) (Found M$^+$: 192.0492. $C_9H_{14}Cl_2$ requires: 192.0472) which showed δ_H (200 MHz, ambient) (lst rotamer) 1.95 (3H, s), 1.84 (3H, s), 1.35 (3H, s), 1.25 (1H, d, J 6 Hz), 1.19 (3H, s) (the final signal for this rotamer was presumably obscured by other signals), (2nd rotamer) 1.87 (3H, s), 1.86 (3H, s), 1.40 (3H, s), 1.15 (1H, d, J 6.4 Hz), 1.08 (3H, s), 1.00 (1H, d, 6.4 Hz) (ratio of rotamers 2:3); δ_C 136.9 s, 135.3 s, 129.5s, 127.9 s, 54.7 s, 54.1 s, 32.9 t, 30.1 t, 29.6 s, 25.1 s, 23.3 q, 23.0 q, 22.9 q, 22.8 q, 22.4 q, 21.9 q, 21.5 q; ν_{max} 712, 1081, 1446, 2922 cm^{-1}; m/e 177 (M-Me), 157 (M-Cl), 141 (M-CH_4Cl). The 90 MHz ^{1}H n.m.r. spectrum in CCl_4 was similar to that reported above in $CDCl_3$; on heating to 343 K the peaks at δ 1.95 - 1.84 became two 3H-singlets at 1.91 and 1.86 while those at 1.0 - 1.4 became two singlets at 1.33 and 1.13, the latter obscuring some additional signals.

b) 1,1,3-Trichloro-2,2-dimethylcyclopropane (2.0 g) was stirred at -40 ^{o}C with isobutene (2.0 g) in ether (10 ml) under a dry ice condenser. Methyl lithium (22 ml, 1.25 M) was added over 1 m and the temperature was allowed to increase until a gently refluxing occurred, when a heavy white precipitate appeared. After 30 m, the products were quenched with water and worked up as above. Removal of the solvent gave a residue (950 mg) which showed a single peak on g.l.c. Bulb-to-bulb distillation at 100-110 ^{o} and 14 mm Hg gave (17) identical to that in (a) (739 mg, 35%).

c) Methyl lithium (6 ml, 1.25 M) was added over 1 m to a stirred solution o 3,3-dimethyl-1,1,2,2-tetrachlorocyclopropane (1.0 g) in ether (10 ml) at -30 ^{o}C. The product were allowed to reach 20 ^{o}C, stirred for 30 m, quenched with water, and worked up as above The solvent was removed at 760 mm and then at 14 mm Hg, and the residue was purified b bulb-to-bulb distillation at 80-100 ^{o}C/mm to give (17) identical to that above (458 mg, 50 %).

3-Chloro-3-(1-chloro-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane

a) Compound (5) was treated with methyl lithium in ether as in (a) above, replacin 2-methylpropene by 2,3-dimethylbut-2-ene, except that the products were quenched with wate at -40 ^{o}C and then allowed to reach ambient temperature. Removal of the solvent at 14 mmH gave a solid which was one peak by g.l.c. Recrystallisation from methanol gave *3-chloro-3-(1-chloro-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane* (15) (70 %), m.p. 56 - 57 ^{o} (Found: C, 59.71; H, 8.10. Required for $C_{11}H_{18}Cl_2$: C, 59.73; H, 8.21) which showed δ_H 1.84 (3H s), 1.82 (3H, s), 1.24 (3H, s), 1.17 (3H, s), 1.11 (3H, s), 1.19 (3H, s); δ_C 136.5, 129.6, 61.6, 30. 27.3, 22.1, 21.8, 20.7, 19.6, 19.5.

An attempt to collect this compound by preparative g.l.c. (2 M SE30 column, 170 ^{o}C) led to single product characterised as *4-chloro-3-(prop-1-en-2-yl)-2,5-dimethylhexa-1,3-diene* (1 (Found M$^+$: 184.1018. Required for $C_{11}H_{17}Cl$: 184.1019) which showed δ_H 5.0 (1H, br.s), 4.7 (1H br.s), 1.85 (3H, s), 1.75 (3H, s), 1.65 (6H, s).

b) Methyl lithium (18 ml, 1.25 M) was added over 2 - 3 min to a stirred solution o 1,1,2-trichloro-3,3-dimethylcyclopropane ((2.0 g) in ether (10 ml) in the presence o 2,3-dimethylbut-2-ene (2.2 g). After 5 min, the products were quenched with water and worke up as above; work up gave (15) (1.1 g) identical to that obtained above.

c) Methyl lithium (5 ml, 1.25 M) was added over 2 - 3 min to a stirred solution o 1,1,2,2-tetrachloro-3,3-dimethylcyclopropane (1.0 g) in ether (10 ml) in the presence o

2,3-dimethylbut-2-ene (1.0 g). After 15 min, the products were quenched with water and worked up as before to give a residue which was a single peak by g.l.c., and was identical by n.m.r. and g.l.c. to (15) obtained in (a) (776 mg, 75 %).

Trans-1,2-dimethyl-3-chloro-3-(1-chloro-2-methylprop-1-enyl)cyclopropane

Methyl lithium (1.98 ml, 1.5 M, 1.5 mol eq) was added at -78 °C to a solution of (5) (0.5 g) and excess *trans*-but-2-ene (2.2 g,) in dry ether (2.0 ml). The solution was allowed to warm to 20 °C and after 3.0 hours, water (2.0 ml) was added at -20 °C and the product was worked up as above to give an oil (0.35 g, 65.4% crude); bulb-to-bulb distillation at 85 °C/1.3 mm Hg, gave a colourless oil, which showed only one peak by glc., identified as *trans-1,2-dimethyl-3-chloro-3-(1-chloro-2-methylprop-1-enyl)cyclopropane* (18) (0.28 g, 52%) (Found M$^+$: 192.0481. Calculated for $C_9H_{14}Cl_2$: 192.0469), which showed δ_H (235K) (rotamer 1): 1.97 (3H, s), 1.87 (3H, s), 1.27 (3H, d, J 6.1 Hz), 1.1 (1H, m), 1.07 (3H, d, J 6.1 Hz), 0.97 (1H, q, J 6.1 Hz); (rotamer 2): 1.86 (6 H, s), 1.35 (3H, d, J 6.1 Hz), 1.1 (4H, complex), 1.0 (1 H, q, J 6.1) (ratio of rotamers 1: 2.3) (the peaks were not completely resolved and these assignments must be regarded as tentative); ν_{max} 746 s, 1451 s, 1643 cm^{-1}; m/e 177 (M-Me), 157 (M-Cl); δ_C (293K); 136.6 s (broad), 128.5 s(broad), 54.1 s, 32.7 br. d, 29.6 br. d, 22.3 q, 21.6 q, 15.3 q, 14.3 q.

The g.l.c., ^{1}H, and ^{13}C spectra showed only *trans* cyclopropane (18), and no evidence of *cis*-products (19) or (20).

Cis-1,2-dimethyl-3-chloro-(3-1-chloro-2-methylprop-1-enyl)cyclopropane

a) Methyl lithium (1.98 ml, 1.5 M, 1.5 mol. eq) was added slowly to a solution of (5) (0.5 g) and *cis*-butene (3.0 ml) in dry ether (2.0 ml) at -78 °C. The mixture was allowed to warm to ambient temperature and after one hour, water (2.0 ml) was added and the product was worked up as before. Flash distillation (35 °C/0.1 mm Hg) gave a colourless oil (0.24 gm, 37%), identified as *cis-1,2-dimethyl-3-chloro-3-(1-chloro-2-methylprop-1-enyl)cyclopropane* (Found M$^+$: 192.0490. $C_9H_{14}Cl_2$ requires: 192.0472), which showed δ_H(200 MHz)(293K) 1.12-1.09 (6H, complex) 1.35-1.30 (2H, complex), 1.81 (3H, s), 1.86 (3H, s); (300 MHz) (233K): 1.87 (3H, s) 1.83 (3H, s), 1.33 (2H, m), 1.12 (6H, complex); δ_C 134.6 s, 131.6 s, 54.7s, 25.3 d, 21.9 q, 21.0 q, 8.6 q,. In addition signals for a minor isomer (ratio ca. 1:5.5) were seen at δ_H(293 K) 1.95 (s) and 1.03 - 1.06 (v.broad); δ_H(233 K) 1.97 (3H, s), 1.77 (1H, dq, J 10.6, 6.7 Hz), 1.53 (1H, dq, J 10.6, 6.7 Hz), 1.08 (3H, d, J 6.7 Hz), 1.05 (3H, d, J 6.6 Hz); δ_C 138.9 s, 127 s, 50 s, 29 d, 9.8 q. The mixture showed ν_{max} 731, 1460, 2931, cm^{-1}; m/e (177 M-Me), 157 (M-Cl) 141 (M-CH_4Cl).

b) When the reaction above was repeated on the same scale and the mixture was stirred overnight at 20 °C before addition of water, and the crude product was subjected to column chromatography using petrol as eluant, pure product was obtained in better yield (0.30 g, 78.8%)

2-Chloro-2-(1-chloro-2-methylprop-1-enyl)-1,1,3-trimethylcyclopropane

Methyl lithium (2.0 ml, 1.5 M, 1.5 mol eq) was added to a solution of (5) (0.5 g) and 2-methyl-2-butene (3.0 ml) and dry ether (3.0 ml) at -78 °C. The mixture was allowed to warm to 20 °C and after 1.3 h water (2.0 ml) was added at - 20 °C and the product was worked up as before. Flash distillation at 35 °C/0.1 mm Hg gave a colourless oil (0.21 g, 51%), identified as a mixture of 2-chloro-2-(1-chloro-2-methylprop-1-enyl)-1,1,3-trimethylcyclopropanes in ratio 7:1 by g.l.c. [Found M$^+$: 206.0641. $C_{10}H_{16}Cl_2$: 206.0629] which showed δ_H 1.86 (s), 1.85 (s), 1.84 (s) [ratio 1:1:2, total integral 6H], 1.04 - 1.22 (complex, 10H, including large peaks at 1.19, 1.17, 1.12, 1.10, 1.08); δ_C 136.16s, 134.4s, 130.9s, 129.0s, 58.9s, 58.5s, 31.9d, 30.7d, 28.9q, 26.4q, 24.8q, 24.4q, 22.1q, 21.9q, 21.8q, 21.2q, 17.0q, 16.9q, 9.6q, 9.5q; additional smaller peaks were seen at 137.6, 137.4, 121.0, 117.4, 35.8, 32.9, 30.7, 29.4, 25.8, 25.6, 23.5, 23.0, 22.8, 18.4, 17.4, 11.0q, 10.6q; ν_{max} 756, 1455, 2916 cm^{-1}; m/e 191 (M-Me), 171 (M-Cl).

1-Chloro-1-(1-chloro-2-methylprop-1-enyl)-2-ethoxycyclopropane

A solution of (5) (0.5) in dry ether (2.0) was treated with methyl lithium (1.45 ml, 1.5 M, 1.1 mole. eq.) at -78 °C. The mixture was allowed to warm to 0 °C and the product was distilled together with solvent at 20 °C and 1.0 mm Hg. Vinyl ethyl ether (1.0 g, 7.0 mole. eq.) was added at -20 °C and the solution was stirred at 20 °C overnight. Evaporation of the volatile material at 14 mm Hg/20 °C afforded an oil (0.34 g, 83% crude yield). The ^{1}H n.m.r. spectrum of the crude material showed no signals at low field. The t.l.c. showed one major spot; g.l.c. showed one major and one minor peak close together. The major one was separated by preparative g.l.c. and was identified as *1-chloro-1-(1-chloro-2-methylprop-1-enyl)-2-ethoxycyclopropane* (Found M$^+$: 208.0405. Calculated for $C_9H_{14}OCl_2$: 208.0422) which showed δ_H (CCl_4): 3.88 (1H, dq, J 9.3, 7.1 Hz), 3.69 (1H, dq, J 9.3, 7.1 Hz), 3.36 (1H, t, J 6.5 Hz), 1.92 (3H, s), 1.80 (3H, s), 1.52 (2H, d, J 6.5 Hz), 1.29 (3H, t, J 7.1 Hz); δ_H ($CDCl_3$) 4.06 (1H, dq, J 9.1, 6.5 Hz), 3.72 (1H, dq, J 9.3, 6.5 Hz), 3.36 (1H, dd, J 5.2, 7.9 Hz), 1.79 (3H, s), 1.78 (3H, s), 1.68 (1H, dd, J 5.2, 7.4 Hz), 1.40 (3H, t, J 6.5 Hz), 1.35 (1H, dd, J 7.4, 7.9 Hz); ν_{max} 789, 1198, 2979 cm^{-1}; m/e 193 (M-Me), 172 (M-Cl); δ_C(C_6D_6) .

6-Chloro-6-(1-chloro-2-methylprop-1-en-1-yl)-2-oxabicyclo[3.1.0]hex-3-ene

A solution of (5) (0.5 g) in dry ether (2.0 ml) was treated with methyl lithium (2.0 ml) 1.5 M, 1.5 mol eq) at -78 °C and the mixture was allowed to warm to -20 °C for 5 min. Water (0.2 ml) was added at -40 °C to destroy the excess of methyl lithium, followed by addition of furan (1.44 ml, 10 mol eq) at -40 °C. The mixture was stirred overnight at 20 °C and worked up as before. Evaporation of ether at 20 °C/ 24 mm Hg afforded a brown-yellow oil which gave one spot on t.l.c. (0.36 g, 88%) identified as 6-chloro-6-(1-chloro-2-methylprop-1-en-1-yl)-2-oxabicyclo[3.1.0]hex-3-ene which showed δ_H(CD_3COCD_3, 233 K) (major) 6.53 (1H, d, 2.6 Hz), 5.41 (1H, t, 2.7 Hz), 5.12 (1H, d, 6.0 Hz), 2.90 (1H, dd, 2.9 Hz), 1.94 (3H, s), 1.78 (3H, s), δ_H (minor) 6.57 (1H, d, 2.5 Hz), 5.46 (1H, t, 2.8 Hz), 4.78 (1H, d, 5.9 Hz), 3.29 (1H, dd, 3.0 Hz), 2.04 (3H, s), 1.90 (3H, s); δ_C(CD_3COCD_3, -40 °C): (major) 148.8 d, 141.4s, 121.7s, 103.3 d, 73.3 d,44.9 s, 39.1 d, 22.0 q, 20.8 q; (minor): 149.9d, 135.7s, 127.8s, 102.4 d, 69.7 d, 43.3 d, 22.6 q, 20.6 q; ν_{max} 722, 1149, 1595, 2918 cm^{-1}; m/e: 169 (M-Cl). This compound gave no molecular ion and was too unstable to obtain a microanalysis, polymerising within a few minutes at ambient temperature to give a heavy black oil which showed a complex nmr spectrum.

Methyl 2-chloro-2-(1-chloro-2-methylprop-1-enyl)-1-methylcyclopropanecarboxylate

A solution of (5) (0.5 g) in dry ether (3.0 ml) was treated with methyl lithium (2.0 ml, 1.5 M, 1.5 mol eq) at -78 °C. The mixture was allowed to warm to -10 °C, and after 5 min methyl methacrylate (1.0 g, 5 mol eq) was added slowly and the reaction mixture was stirrred overnight at 20 °C. Work up as before gave an oil showing only one peak by glc and identified as *methyl 2-chloro-2-(1-chloro-2-methylprop-1-enyl)-1-methylcyclopropanecarboxylate* (0.40 g, 85%) (Found M+: 236.0382. Calculated for $C_{10}H_{14}O_2Cl_2$: 236.0371), which showed δ_H($CDCl_3$, 30 °C): 3.7 (3H, br, s), 2.29 (1H, br.d, J 6.6 Hz), 2.00–1.24 (4H, very complex), 1.82 (3H, s), 1.60 (3H, s); δ_H($CDCl_3$, –40 °C): (rotamer 1): 3.72 (3H, s), 2.33 (1H, d, J 6.4 Hz), 2.0 (3H, s), 1.85 (3H, s), 1.57 (3H, s), 1.58 (1H, d, J 6.4 Hz): (rotamer 2): 3.64 (3H, s), 2.24 (1H, d, J 6.7 Hz) 1.83 (3H, s), 1.77 (3H, s), 1.63 (3H,s), 1.34 (1H, d, J 6.7 Hz) (the ratio of rotamers was ca. 16:15; two very small singlets were present at δ 3.87 and 3.83, in total ca 5 % of the major methoxy signals); δ_C (303K) 171.2, 136.4 (broad), 126.4, 54.9br, 52.2br, 30–33 (very broad), 22.1, 21.1, 17.6; ν_{max} 711, 1299, 1733, 2949 cm^{-1}; m/e: 221 (M–Me), 201 (M–Cl).

Methyl 2-chloro-2-(1-chloro-2-methylprop-1-enyl)cyclopropanecarboxylate

Methyl lithium (1.45 ml, 1.5 M, 1.1 mol eq) was added at –78 °C to a solution of (5) (0.5 g) in dry ether (2.0 ml) under nitrogen. The mixture was allowed to warm to –20 °C for 10 min., followed by addition of water (0.2 ml). Methyl acrylate (1.7 g, 10 mol eq) was added at –20 °C and the mixture was allowed to stir overnight at ambient temperature. Work up as before afforded an oil; column chromatography using silica gel and eluting with petrol and ether (9:1) produced *methyl 2-chloro-2-(1-chloro-2-methylprop-1-enyl)cyclopropanecarboxylate* (0.34 g, 77%) [Found M+: 222.0205. $C_9H_{12}O_2Cl_2$ requires: 222.0214] which gave a single peak on capillary g.l.c. and showed δ_H (303K, 200 MHz): 3.71 (3H, s), 2.47 (1H t, J 5.3 Hz), 2.1–1.85 (8H, complex) (including 1.96 (s, 3H), 1.86 (3H, s), (a minor additional singlet was also seen at 3.8 (ca. 0.05 of that at 3.71)); (233K) the signals at 3.71 and 2.47 were split into 3.65(s) and 3.61(s), and 2.6(t) and 2.31(t) in ratio 9:3:1:3; δ_C (303 K) 169.2 s, 137.8 s, 124.5 s, 52.2 q, 48.9 s, 32.9 d (broad), 26.8 t (broad), 22.2 q, 21.1 q; ν_{max} 1204, 1374, 1738 cm^{-1}; m/e: 207(M–Me), 187(M–Cl).

Methyl 3-chloro-3-(1-chloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate

Methyl lithium (5.8 ml, 1.5 M, 1.1 mol.eq.) was added to (5) (2.0 g) in dry ether (10 ml) at – 78 °C. The products were allowed to reach 0 °C and then codistilled with solvent as before. The distillate was treated with methyl β,β-dimethylacrylate (0.91 g, 1.0 mol.eq.) at – 20 °C and the mixture was stirred at 20 °C for 18 h. Evaporation of the solvent and flash distillation of the remaining acrylate at 120 °C and 1 mmHg gave an oil which was purified by chromatography over silica eluting with petrol and ether (9:1); the product was one spot by t.l.c. but showed two peaks on capillary g.l.c., and was characterised as an ca. 1:1 mixture of methyl E- and Z-3-chloro-3-(1-chloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropanecarboxylates (1.15 g, 58 %) (Found: 250.0535. Required for $C_{11}H_{16}O_2Cl_2$: 250.0527) which showed ν_{max} 1743 cm^{-1}. The ^{1}H and ^{13}C n.m.r. spectra of the mixture were very complicated, and suggested the presence of two rotamers of each of the isomers, with slow rotation on the n.m.r. timescale. Thus the methoxy region of the former included four singlets 3.67, 3.65, 3.61 and 3.58 (ratio 9:11:14.5:8); additional peaks, integrating in total to 13 hydrogens compared to 3 in the region 3.58 – 3.67, appeared at δ 2.14 – 1.69 (7H), and 1.46 – 1.22 (6H), including 1.46 (12), 1.44 (15), 1.40 (9), 1.39 (8), 1.36 (14), 1.35 (9), 1.13 (11.5), 1.22 (8).

2-Chloro-2-(1-chloro-2-methylprop-1-enyl)-1,1-dimethyl-3-(trimethylsilyloxymethyl)

cyclopropane

(a) The above experiment was repeated, except that the distilled solution of (3) in ether was allowed to stand for 5 h at 20 °C with the trimethylsilylether of 3-methylbut- 2-en-1-ol (1.5 g, 1.2 mol.equiv.). Removal of the volatile material at 20 - 25 °C and 1 mmHg gave an oil which was subjected to column chromatography over silica eluting with petrol and ether (9:1) to give *2-chloro-2-(1-chloro-2-methylprop-1-enyl)-1,1-dimethyl-3-(trimethylsilyloxymethyl)cyclopropane* (2.0 g, 85 %) (Found M^+: 294.0948. Calculated for $C_{13}H_{24}Cl_2OSi$: 294.0973) which was one peak by g.l.c. but was a mixture of Z- and E-isomers in ratio 7.5:1 by ¹H n.m.r. (Fig.1). The major isomer was present as two rotamers in ratio ca. 4:3. The major rotamer showed δ_H 0.26 (9H, s), 3.94 (1H, dd, J 5.9, 11.1 Hz), 4.06 (1H, dd, J 7.5, 11.1 Hz) and the minor one showed δ 0.28 (9H, s), 3.91 (1H, dd, J7.9, 11.2 Hz), 4.24 (1H, dd, J 5.6, 11.2 Hz); in addition there were three-hydrogen singlets at δ 1.93, 1.76, 1.39, 1.34, 1.33 and 1.08 and a double doublet at 1.51 (1H, J 5.6, 7.9 Hz). A further double doublet was partly hidden by a signal from the minor isomer at δ 1.72. The signals for the two rotamers coalesced and broadened on heating to 363 K in deuteronitrobenzene.

(b) Lithium aluminium hydride (182 mg) was added to the mixture of methyl E- and Z-3-chloro-3-(1-chloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropanecarboxylates obtained above (0.6 g) in ether (30 ml). After 30 m, t.l.c. showed that no starting material remained. Excess reducing agent was destroyed by the addition of ethyl acetate and the products were worked up in the normal way to give a colourless oil (0.52 g), which was one spot by t.l.c. but two peaks by g.l.c. in ratio ca. 3:2. The oil was dissolved in dichloromethane (30 ml) and treated with triethylamine (0.47 g, 2 mol.eq.) followed by addition of trimethylsilylchloride (0.38 g, 1.5 mol.eq.) at - 20 °C. After standing overnight at 20 °C the products were treated with 5 % HCl (30 ml) and extracted with dichloromethane (30 ml), washed with water (3 x 30 ml) and dried ($MgSO_4$). Removal of the solvent at 14 mmHg gave an oil (0.45 g, 64 %) which was one major spot on t.l.c. This was purified by column chromatography as in (a) to afford an oil which was one spot on t.l.c. and one peak by g.l.c., identical in retention time to the product from (a). The 300 MHz n.m.r. spectrum contained all the signals seen for the product in (a) but in different ratios, corresponding to a mixture of two isomers in ratio 1:1, each isomer appearing as a mixture of rotamers. The second compound, corresponding to the minor isomer in (a) showed δ_H(rotamer 1): 0.22 (9H, s), 3.68 (1H, t, J 11 Hz), 4.5 (1H, dd, J 5.2, 11 Hz), 1.724 (3H, s), 1.719 (3H, s), 1.56 (3H, s), 1.25 (3H, s); (rotamer 2) 3.56 (1H, dd, J 8.2, 11 Hz), 3.98 (1H, partly obscured), 1.86 (3H, s), 1.57 (3H, s), 1.42 (3H, s), 0.19 (9H, s) (ratio of rotamers 4:1).

Dimethyl 3-chloro-3-(1-chloro-2-methylprop-1-enyl)cyclopropane-*trans*-dicarboxylate

Methyl lithium (1.74 ml, 1.5 M, 1.1 mole. eq.) was added to a solution of 1-bromo-1,2,2-trichloro-3,3-dimethylcyclopropane (0.6 g) in dry ether (2.0) at -78 °C, under nitrogen. The mixture was allowed to warm up to 0 °C followed by flash distillation of the product and the solvent at 20 °C/1.0 mm Hg. Dimethyl fumarate (0.14 g, 1.0 mole. eq.) was added at 20 °C and the solution was stirred overnight. Evaporation of all the volatiles at reduced pressure afforded an oil which was purifed by column using silica and eluting with petrol and ether (9:1, then 7:3). The first compound isolated was identical by ¹H n.m.r. to (9) (1.85 mg, 35%). The second (250 mg, 38%) was characterised as *dimethyl 3-chloro-3-(1-chloro-2-methylprop-1-*

enyl)cyclopropane–trans–1,2–dicarboxylate [Found M$^+$: 280.0264. $C_{11}H_{14}O_4Cl_2$ requires 280.0269] which showed δ_H(200 MHz, 293 K); 3.78 (3H, s) 3.69 (3H, s), 2.99 (1H, d, J 7.3 Hz), 2.90 (1H, br. d, J 7.3 Hz), 1.96 (3H, s), 1.83 (3H, s); δ_C 167.6 s, 166.3 s, 138.4 s, 123.6 s, 52.8 q, 52.6 q, 51.3 s, 37.8 d, 36.3 d, 22.4 q, 21.1q. On cooling to 233 K, two rotamers could be seen in ratio ca. 4:1, δ_H ($CDCl_3$, -40 °C)(rotamer 1) 3.86 (3H, s), 3.78 (3H, s), 3.08 (1H, d, J 7.14 Hz), 2.91 (1H, d, J 7.14 Hz), 2.07 (3H, s), 1.90 (3H, s); (rotamer 2) 3.74 (shoulder), 3.17 (br.d, J ca. 7 Hz), 3.00 (br.d, J ca. 7 Hz), 1.85 (shoulder); δ_C ($CDCl_3$, 230 K) 167.8 s, 166.9 s, 138.8 s, 123.0 s, 53.3 q, 53.2 q, 50.8 s, 38.2 d, 35.0 d, 23.3 q, 22.7 q; ν_{max} 1331, 1729, 2955 cm^{-1}; m/e 265 (M–Me), 245 (M–Cl). The n.m.r. and g.l.c. showed no evidence for the presence of any of the *cis*–isomer.

Reaction of 1,2–dichloro–3,3–dimethylcyclopropene with dimethyl maleate

A solution of (5) (0.6 g) in ether (2.0 ml) was treated with methyl lithium (1.74 ml, 1.5 M, 1.1 mol. eq.) as in the previous experiment. Dimethyl maleate (0.14 gm, 1.0 eq.) was added at 20 °C* and the solution was stirred overnight. Evaporation of the solvent produced a heavy oil. Chromatography over silica gel and eluting with petrol and ether (9:1, then 7:3) afforded two products. The first one was identical by ^1H n.m.r. to (9) (250 mg, 50%); the second was a mixture of carbene adducts in ratio ca. 3:2 (100 mg, 15%), the major one of which showed identical n.m.r. spectra to those obtained for (34). The two compounds could not be separated by t.l.c or column chromatography, but the mixture showed a molecular ion at m/z 280.0262; the n.m.r. spectrum indicated that the second isomer, characterised as (35), showed δ_H($CDCl_3$, 300 K) 3.71 (6H, s), 2.7 - 3.0 (2H, very broad), 2.03 (3H, s), 1.92 (3H, s); (230 K) 3.76 (3H, s). 3.73 (3H, s), 3.01 (1H, d, 10.9 Hz), 2.78 (1H, d, 10.9 Hz), 2.06 (3H, s), 1.95 (3H, s); δ_C ($CDCl_3$, -40 °C) 166.4 s, 165.3 s, 143.4 s, 118.7 s, 53.1 q, 52.6 q, 51.0 s, 38.4 d, 34.4 d, 22.4 q, 21.4 q (when the spectrum was obtained at 300 K, the signals at 166.4 and 165.3 appeared as a very broad singlet at ca. 166, and those at 38.4 and 35.4 were very broad.

Dimethyl 3–chloro–2–(1–chloro–2–methylprop–1–enyl)cyclopropene–1,3–dicarboxylate

A solution of (5) (0.5 g) in ether (2.0 ml) was treated with methyl lithium (1.45 ml, 1.5 M, 1.1 mol. eq.) as above. Dimethyl acetylenedicarboxylate (0.84 g, 3.0 mol.eq.) was added and the solution was stirred for 18 h. Removal of the solvent at 14 mmHg and bulb–to–bulb distillation gave unreacted acetylene followed by a colourless oil, b.p. 120 - 125 °C at 0.2mmHg, characterised as *dimethyl 3–chloro–2–(1–chloro–2–methylprop–1–enyl)cyclopropene–1,3–dicarboxylate* (37) (0.26 g, 47 %) (Found M$^+$: 278.0130. Required for $C_{11}H_{12}O_4Cl_2$: 278.0113) which showed δ_H(CCl_4) 3.85 (3H, s), 3.75 (3H, s), 2.22 (3H, s), 2.16 (3H, s); δ_C($CDCl_3$) 168.3s^a, 157.8s^a, 155.0s^b, 124.4s^c, 114.4s^b, 106.4s^c, 54.0q, 53.1q, 50.7s, 23.9q, 22.7q (a - small long range quartet coupling; b - large long range coupling to two methyl groups; c - no long range coupling); ν_{max} 760, 1155, 1245, 1266, 1605, 1750, 1728, 1818 cm^{-1}; m/z 263 (M - Me), 243 (M - Cl).

References

1. M.S. Baird, W. Nethercott and H.H. Hussain, *J.Chem.Soc., Perkin Trans.*1, 1986, 1845.
2. M.S. Baird, and W. Nethercott, *Tetrahedron Letts.,* 1983, 605.
3. M.S. Baird, S.R. Buxton and H.H. Hussain, *J.Chem.Res.,* 1986, S310.

4. See eg., (a) M. Franck-Neumann and J-J.Lohmann, *Angew.Chem.Int.Edn.Engl.,* 1977, *16*, 323; (b) *Tetrahedron Letts,* 1979, 2397; (c) M.S.Baird, H.H.Hussain and W.Clegg, *J.Chem.Soc., Perkin Trans.I*, 1987, 1609.
5. R.Walsh, S.Untiedt, M.Stohlmeier and A.deMeijere, *Chem.Ber.*, 1989, *122*, 637; R.Srinivasan, *J.Chem.Soc., Chem.Comm.*, 1971, 1041.
6. W. Weber and A. de Meijere, *Angew. Chem.Int.Edn.Engl.,* 1980, *19*, 138; *Chem.Ber.*, 1985, *118*, 2450; T.Liese, S.Teichmann and A.deMeijere, *Synthesis,* 1988, 25.
7. For recent reviews, see eg., M.G.Steinmetz, R.Srinivasan and W.J.Leigh, "Reactive Intermediates in the Interconversions of C_3H_4 Hydrocarbons", in *Reviews of Chemical Intermediates*, 1984, *5*, 57; B.Halton and M.G.Banwell, "Cyclopropenes", in *The Chemistry of the Cyclopropyl Group,* Part 2, Ed. Z.Rappoport, 1223, Wiley, 1987.
8. (a) P. Weyerstahl, *Cyclopropanes*, in "The Chemistry of Functional Groups", Suppl.D., Eds., S. Patai and Z. Rappoport, Wiley; (b) M.S. Baird, W. Nethercott and P.D. Slowey, *J.Chem.Res.,* 1985, S 370, M 3815.
9. M.S. Baird, H.H. Hussain and W. Clegg, *J.Chem.Res.,* 1988, S110.
10. E.V.Dehmlow and Naser-ud-Din, *J.Chem.Res.*, 1981, S144.
11. M.S. Baird and H.H. Hussain, *J.Chem.Res.*, 1988, S292.
12. L.Skattebol. *J.Org.Chem.,* 1966, *31,* 1554.
13. J.A.Pincock, R.Morchat and D.R.Arnold, *J.Amer.Chem.Soc.*, 1973, *95*, 7536.
14. A.Padwa, T.J.Blacklock and R.Loza, *J.Org.Chem.*, 1982, *47*, 3712.
15. (a) A. de Meijere and W. Luttke, *Tetrahedron,* 1969, *15*, 2047; (b) H. Gunther, H. Klose and D. Wendisch, *ibid,* 1969, *25*, 1531; (c) T.Liese and A.de Meijere, *Chem.Ber.,* 1986, *119*, 2995.
16. H.Gunther, N.M.R. Spectroscopy, Thieme, Stuttgart, 1973.
17. W. Kirmse, Carbene Chemistry, 2nd Edn., *Academic Press.*
18. J.D.Graham and M.T.Rogers, *J.Amer.Chem.Soc.*, 1962, *84*, 2249.
19. K.B.Wiberg, D.E.Barth and D.H.Schertler, *J.Org.Chem.*, *38*, 378.
20. W.Gothling, S.Keyaniyan and A.deMeijere, *Tetrahedron Letters*, 1984, 4101; S.Keyaniyan, W.Gothling and A.deMeijere, *Chem.Ber.*, 1987, *120*, *395.*
21. M.Franck-Neumann and J.J.Lohmann, *Tetrahedron Letters*, 1979, 2075.
22. J.Al-Dulayymi, M.S.Baird and W.Clegg, *Tetrahedron Letters*, 1988, 6149.
23. D.L.Boger and C.E.Brotherton, *Tetrahedron Letters,* 1984, 5611; see also ibid., *J.Amer.Chem.Soc.,* 1986, *108*, 6695.
24. P.Binger and B.Biedenbach, *Chem.Ber.,* 1987, *120,* 601.
25. W.Gothling, Dissertation, University of Hamburg, 1985.
26. P.Binger, J.McMeeking and H.Schafer, *Chem.Ber.*, 1984, *117*, 1551.
27. M.P.Doyle, J.W.Terpstra and C.H.Winter, *Tetrahedron Letters*, 1984, 901.
28. L.Schrader, *Chem.Ber.*, 1971, *104*, 941.
29. M.Birchall, K.Burger, R.N.Haszeldine and S.N.Nona, *J.Chem.Soc.,Perkin Trans.I*, 1981, 2080.

\# Although the E- and Z-nomenclature should, under the IUPAC convention, strictly only be applied to alkenes, it has been used widely in describing cyclopropane stereochemistry; this terminology is used throughout this paper.

* A preliminary account including some aspects of this work has already appeared (M.S. Baird, S.R. Buxton and J.S. Whitley, *Tetrahedron Letters,* 1984, 1509).

** The cyclopropene (3) also reacted with acetone; the results will be described elsewhere.