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GENERATION AND TRAPPING OF VINYLCARBENES AT AMBIENT TEMPERATURE: A ROUTE TO FUNCTIONALISED VINYL- AND ALLYLIDENE-CYCLOPROPANES

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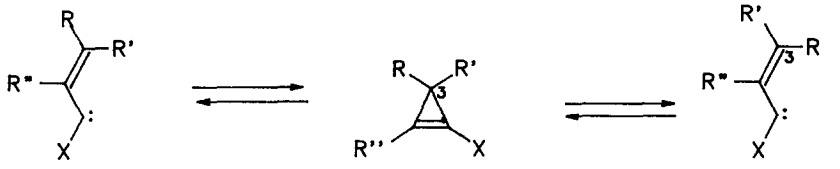
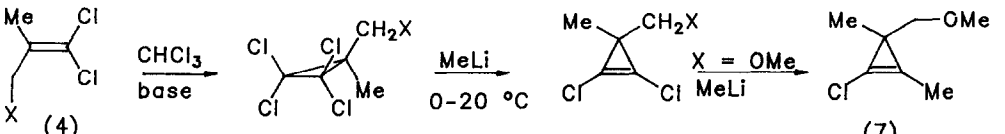
1,2-Dehalogenation of tetrachlorocyclopropanes (5, X = Cl, OMe, NPr$^i_2$, SAllyl) by methyl lithium leads to dichlorocyclopropenes (6, X = Cl, OMe, NPr$^i_2$, SAllyl); the first two of these react with electron rich and electron poor alkenes at 20 °C to give cyclopropanes which are apparently derived by trapping of vinylcarbenes (8) rather than (20). Reaction of the derived vinylcyclopropanes with base leads either to ethyl cyclopropyl ketones or to allylidenecyclopropanes.

The ring-opening of a cyclopropene (1) to a vinylcarbene,[1] which is reported in several cases to be reversible, involves a formal monorotation at C_3 and could, provided (2) and (3) are reasonable representations of the product, lead to *E*- or *Z*-isomers about the alkene:[1+]



(2) (1) (3)

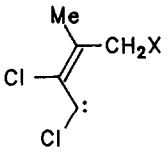
There are several examples of intramolecular trapping of the carbene by a 3-substituent which require these to be *Z*-related;[2] this may arise by stereocontrolled ring-opening but could be the result of a reversible process and selective trapping of one isomer.[3] Most reported intermolecular trappings of vinylcarbenes derived from cyclopropenes do not distinguish between the 3-substitutents of the latter, though thermolysis of 3-methyl-3-phenylcyclopropene at 180 °C does lead to trapping of the *E*-carbene (2, X = R" = H, R = Ph, R' = Me) by alkenes, albeit in low yield.[4] Moreover, the metal induced ring-opening of (1, X = R" = H, R = Ph, R' = Me) leads to the trapping of both *E*- and *Z*- 'carbene' isomers.[5] We have shown that cyclopropenes (6, X = H)[6] and (6, X = Ph)[7] rearrange at 0 - 20 °C to give vinylcarbenes (8, X = H, Ph) which are trapped by alkenes. We now describe the preparation of a number of cyclopropenes (6), and the trapping of derived vinylcarbenes (8, X = Cl, OMe).#



(4) (5) (6) (7)

The trichloride (4, X = Cl)[8a] and derived ethers, eg. (4, X = OMe)[8b] or amines, eg. (4, X = NPr$^i_2$), were converted to the corresponding cyclopropanes (5) using chloroform and aqueous base under phase transfer conditions. Treatment of (5, X = Cl) with the sodium salt of allylthiol

in dimethylformamide led to the corresponding thioether (5, X = $SCH_2CH{=}CH_2$).



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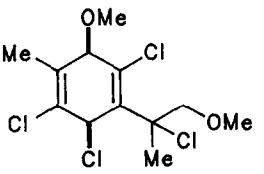

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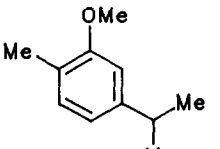
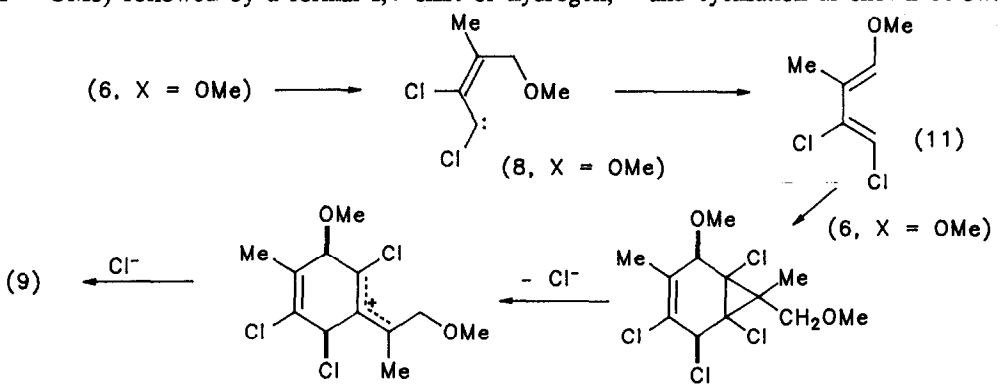


(10)[5]

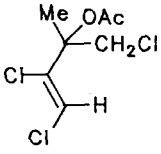
Reaction of the pentachloride (5, X = Cl) with a slight excess of methyl lithium for 30 m at 0 °C led to the cyclopropene (6, X = Cl) (82 %). This showed two singlets in the ^{1}H n.m.r., at δ 3.6 and 1.4 in ratio 2:3, while the ^{13}C n.m.r. showed quaternary carbons at δ 113.8 and 41.9 as well as a methylene carbon at 51.6, and a methyl carbon at 19.4; it may be derived by lithium – chlorine exchange at one of the gem-dichlorides, followed by 1,2-elimination of lithium chloride,[6,7] a process apparently preferred over 1,3-elimination,[8] which would lead to a 1-chlorobicyclo[1.1.0]butane. The reaction of (5, X = OMe) with methyl lithium was more difficult to control because the cyclopropene (6, X = OMe) reacted relatively rapidly with methyl lithium to produce (7), apparently by an addition – elimination process promoted by coordination of the lithium to the ether oxygen. Careful addition of just over one equivalent of methyl lithium to (5, X = OMe) provided the purest sample of (6, X = OMe), though this still contained a small amount of (7); additional reagent (2 mol.equiv.) increased the yield of (7) to 40 %, but more then led to a complex mixture of products. The cyclopropene (6, X = Cl) was relatively stable in ether or deuterochloroform solution at 20 °C, surviving unchanged for ca. 10 h. However, when allowed to stand for 48 h at 20 °C in deuterochloroform, (6, X = OMe) dimerised to give (9) (61 %); this was also obtained when (6, X = OMe) was allowed to stand for 10 h in ether at 20 °C. It showed the expected twelve signals in the ^{13}C spectrum, including four singlets in the olefinic region, four methyl groups (including two in the methoxy region), a CH_2-group adjacent to oxygen, and two tertiary carbons at δ 80.1 and 63.7. The ^{1}H spectrum showed two single-hydrogen singlets at δ 5.44 and 4.82, a two hydrogen singlet at 3.52, two methoxy-groups and two other methyl groups, one at δ 2.02 and one at 1.17. The overall structure was confirmed by reaction of (9) with lithium – ^{t}butanol – tetrahydrofuran when carvacrol methyl ether (10) was obtained.[10] The formation of (9) may involve ring-opening of (6, X = OMe) to the carbene (8, X = OMe) followed by a formal 1,4-shift of hydrogen,[11] and cyclisation as shown below.



The selective loss of only one of the cyclopropyl chlorines in the final step presumably reflects

detailed steric interactions in the transition state for cyclopropyl – allyl rearrangement.The stereochemistry of (9) is not certain both in respect of the methoxy and chlorine substituents in the six-membered ring and the relative configuration of the side chain; however, (6, X = Ph) has been shown to rearrange to E,Z-1,2-dichloro-3-methyl-4-phenylbuta-1,3-diene at ambient temperature,[7] and it is likely therefore that (11) has the stereochemistry indicated, and that Diels-Alder addition leads to cyclohexene with the methoxy and chlorine substituents cis-related.

The cyclopropene (6, X = Cl) also reacted with acetic acid, giving the acetate (12). This may arise either by protonation of the cyclopropene and ring-opening to an allylic cation,** or by trapping of the carbene (8, X = Cl) by the acetic acid; the stereochemistry is assigned as Z- by analogy with the corresponding reaction of (6, X = H) with methanol.[6b,13] In contrast, a solution of (6, X = Cl) in ether or chloroform remained largely unchanged after 10 h at 20 °C. However, addition of 2,3-dimethylbut-2-ene led to complete reaction in ca. 2 h and the formation of one cyclopropane (13a) (See Table), suggesting either that the alkene promoted the ring-opening of the cyclopropene, or that a reversible ring-opening to a carbene was occurring and this was trapped by the added alkene. The ^{1}H n.m.r. of the product showed five methyl signals and an AB pattern for the methylene group (J 11.6 Hz); this is in keeping with a preferred twisted conformation, and rotation about the exocyclic carbon- carbon bond which is slow on the n.m.r. timescale. Similar results have been reported for (14, X = Y = Me),[6] and (14, X = Me, Y = CH_2Ph),[7] while extensive studies of rotation barriers in tetrachlorides such as (14, X = Y = Cl) have also been performed.[12] In the same way (6, X = OMe) reacted with 2,3-dimethylbut-2-ene to give the cyclopropane (15a). There was no evidence in either case for the presence of a second stereoisomer. The stereochemistry about the alkene was assigned as E- because an n.O.e. examination of (15a) showed an enhancement in the methylene rather than the olefinic methyl signal when a signal for a methyl group at δ 1.07 was irradiated; it is the same as that reported for the major stereoisomer of the product in the reaction of (6, X = Ph) with 2,3-dimethylbut-2-ene,[7] although the selectivity in the present cases is much higher.



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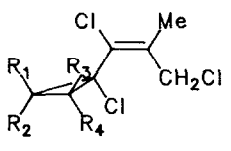

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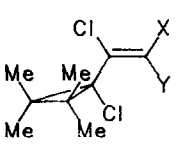

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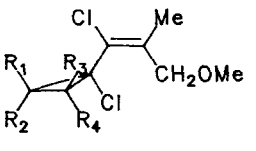

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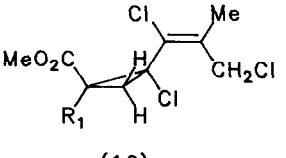
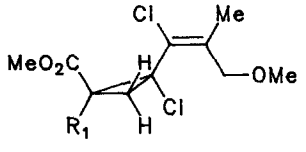


(16)

Treatment of (6, X = Cl, OMe) with other alkyl-substituted alkenes also led to cyclopropanes (See Table). Reaction with 2-methylpropene led to a single compound from each cyclopropene, (13b) and (15b), though in each case the n.m.r. spectrum was complicated by the presence of two rotamers. Addition of (6, X = OMe) to E-but-2-ene gave a single product, but the ^{1}H n.m.r. at ambient temperature included a number of broad signals; on cooling to -40 °C the spectra of two rotamers of the adduct (15e) were observed. In the case of addition to Z-but-2-ene, n.m.r. and g.l.c. analyses revealed the presence of two adducts in ratio ca. 6:1; the major isomer showed only one doublet for the ring methyls and a multiplet for the ring hydrogens even at -40 °C, indicating a low barrier to rotation about the exocyclic bond, and was assigned as (15c). The signals for the minor isomer were not clearly resolved, but since the MeO-substituent appears only in the E-configuration in the above adducts (ie., 13a/b, 15a/b), it

was characterised as (15d). G.l.c. analysis showed that no (15e) was produced in this experiment; in the same way no (15c) was obtained from the reaction of (6, X = OMe) with E-but-2-ene, as expected for a singlet carbene. Addition of (6, X = Cl) to ethene in a high pressure vessel at 20 °C resulted in the formation of the parent cyclopropane (14g) in low yield, but a complex mixture of other products was also formed.



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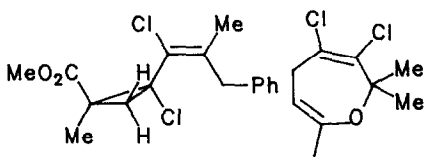

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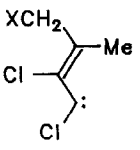


(20)

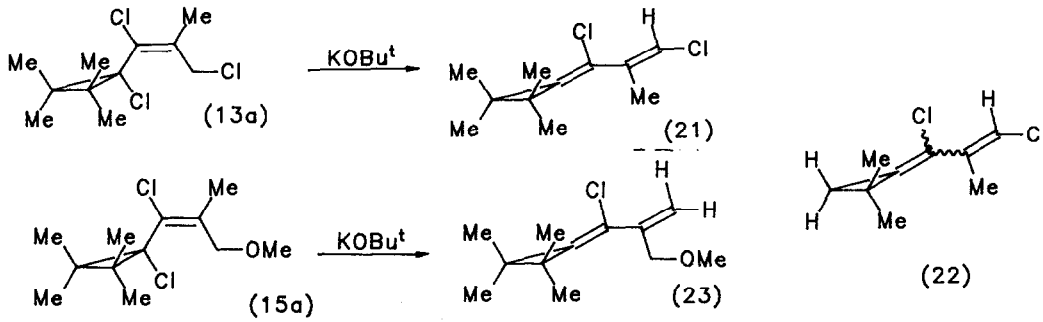
Table **Reactions of Cyclopropenes (6, X = Cl, OMe) with Alkenes**

Alkene	Cyclopropane									
	R_1	R_2	R_3	R_4	X	No	%*	X	No	%
$Me_2C = CMe_2$	Me	Me	Me	Me	Cl	13a	77	OMe	15a	69
$Me_2C = CH_2$	Me	Me	H	H	Cl	13b	70	OMe	15b	68
Z-Me CH = CH Me	H	Me	H	Me }	Cl	13c	76	OMe	15c	56
	Me	H	Me	H }	Cl	13d		OMe	15d	
E-Me CH = CH Me	Me	H	H	Me				OMe	15e	54
$Me_2C = CH$ Me	Me	Me	Me	H				OMe	15f	68
	Me	Me	H	Me				OMe	15g	
$H_2C = CH_2$	H	H	H	H	Cl	13g	15			
$CH_2 = CH\text{-}CO_2Me$	H	-	-	-	Cl	16a	75	OMe	17a	75
$CH_2 = CMe\text{-}CO_2Me$	Me	-	-	-	Cl	16b	82	OMe	17b	84

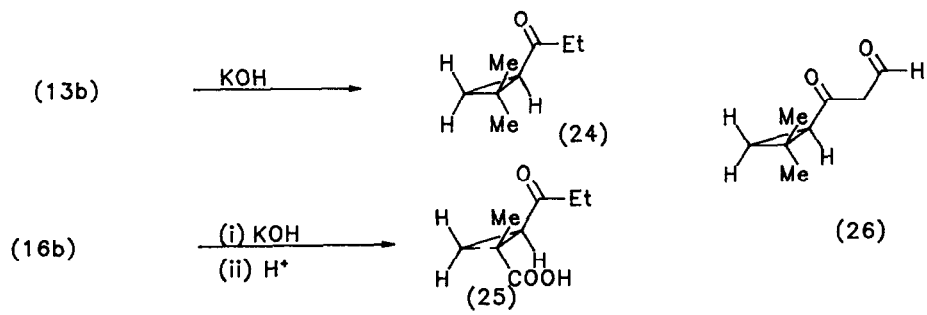
The cyclopropanes (16a,b) and (17a,b) were also formed when (6, X = Cl, OMe) were treated with methyl acrylate or methacrylate at 20 °C. The single diastereoisomers formed in each case showed temperature variable ^1H n.m.r. spectra. Thus the spectrum of (17a) was very broad at 303 K but two sets of signals were observed at 230 K, corresponding to two rotamers in ratio 7:3; although there were some additional signals, these only amounted to ca. 5% of the product and could not be assigned to alternative stereoisomers. The rotation barriers for (17a) and (17b) are similar to those for (18),[7] suggesting that the ester group is again cis- to the alkene.[14] This may arise by stereocontrol in a concerted cyclopropanation or by dipolar attraction in a Michael-type addition of the delocalised carbene; indeed formation of a methoxydihydro-oxepine, eg. (19), followed by a Claisen rearrangement would offer a possible explanation in the present case.

The above additions gave E-alkenes derived by trapping of carbenes (8, X = Cl, OMe). It is not clear why the alternative, but possibly less hindered, carbene (20), if formed, should be trapped less efficiently by the alkene. It would appear, therefore, either that the carbene (8) is formed selectively from (6), or that the representation of these species in two geometrical forms is not correct and that more subtle factors control the geometry of addition. Whatever the detailed mechanism, the cyclopropenes (6, X = Cl, OMe) do provide a convenient source of functionalised isoprenoid carbenes (8, X = Cl, OMe) which are trapped by both electron rich and electron poor alkenes. In contrast, compounds (6, X = NPr^i_2, SAllyl), which were stable for several hours at

-40 °C, decomposed rapidly when allowed to reach 0 – 20 °C; no products of intramolecular trapping of a carbene by the amine or thioether were isolated. When this was carried out in the presence of 2,3-dimethylbut-2-ene, no cyclopropanes were isolated. Reaction of the trichloro-cyclopropanes, eg. (13a) with nucleophiles did offer a possible route to introduce other substituents into the allylic position of the side chain. Thus treatment of (13b) or (16b) with sodium methoxide in methanol gave (15b) or (17b) respectively. However, reaction with potassium t-butoxide led instead to the elimination of hydrogen chloride and the formation of a single allylidene-cyclopropane (21),[$,17] apparently derived by removal of the allylic hydrogen adjacent to chlorine. The stereochemistry at the terminal alkene is assigned as E- on steric grounds. A similar elimination occurred with the cyclopropane (13b), although two stereoisomeric allylidene-cyclopropanes (22) were obtained in ratio 1:1; these were characterised as Diels-Alder adducts with tetracyanoethene. The regioselectivity of the above processes was reversed in the reaction of the ether (15a), elimination of the proton occurring from the methyl- rather than the methoxymethyl- group:



Similar reactions occur readily for a range of 3-chloro-3-(2-chlorovinyl)cyclopropanes; these, and the reactions of derived allylidenecyclopropanes will be described elsewhere. An alternative transformation was seen on reaction of (13b) and (16b) with potassium hydroxide in water:



The stereochemistry of the acid (25) was assigned as E- because the signals for the two hydrogens on C-3 of the cyclopropane appeared at very similar chemical shift, whereas in the Z-compound a large shift difference would have been expected.[14] A reasonable explanation of these processes would involve the formation of a 1,3-dicarbonyl compound, eg. (26) and fragmentation by attack of hydroxide ion at the aldehyde carbon followed by loss of formic acid to produce the enolate of (25). A number of mechanisms may be written to produce compound (26). One logical intermediate would be a diene of type (22); however, treatment of the mixture of stereoisomers of (22) under the reaction conditions did not give (24)!

We wish to thank the Government of Iraq for the award of a grant to J.A-D.

Experimental

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 instruments, and ^{13}C spectra were recorded at the corresponding carbon frequency on the same instruments. Infra-red spectra were obtained on a Nicolet 20SX, 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. Organic layers were dried with $MgSO_4$ before removal of the solvent. Column chromatography was carried out over silica eluting with (a) petrol, (b) 10:0.5 , (c) 10:1 and (d) 10:2 petrol and ether or (e) ether.

1,1-dichloro-3-methoxy-2-methylpropene.

1,1,3-Trichloro-2-methylprop-1-ene (4.3 g) was added over 5 min. to a stirred solution of sodium methoxide (3.5 g) in methanol (50 ml). After refluxing for 2 h, the products were treated with water (50 ml) and extracted with dichloromethane (2 x 50 ml). The solvent was removed at 14 mm Hg; flash distillation of the residue gave *1,1-dichloro-3-methoxy-2-methylpropene*,[8b] b.p 20-22 °C at 0.3 mm Hg (3.1 g, 74 %) which showed δH 4.0 (2H, s), 3.22 (3H, s), 1.85 (3H, s).

3,3-dichloro-2-methyl-2-propenyl di-isopropyl amine

1,1,3-Trichloro-2-methylprop-1-ene (5 g) was refluxed with diisopropylamine (30 ml) in ethanol (50 ml). After 30h the solvent and excess amine were removed at 14 mm Hg and the residue was dissolved in ether (50 ml) and extracted with 4M hydrochloric acid. The aqueous layer was brought to pH 10 by addition of 4M sodium hydroxide and extracted with ether (2 x 50 ml). Removal of the solvent at 14 mm Hg gave an oil; flash distillation gave *3,3-dichloro-2-methyl-2-propenyl di-isopropyl amine*, b.p 54-56°C at 0.4 mm Hg (4.6 g, 65 %) (Found M^+: 223.0901. Required for $C_{10}H_{19}NCl_2$: 223.0895) which showed δH 3.2 (2H, s), 2.85 (1H, septet, J ca. 6 Hz), 1.8 (3H, s), 0.92 (6H, d, J 6 Hz); ν_{max} 2966, 1674, 1621, 1462, 1379, 1180, 895 cm^{-1}.

1,1,2,2-Tetrachloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropane

Sodium hydroxide (10 g) in water (10 ml) was stirred vigorously with 3,3-dichloro-2-methylprop-2-en-1-yl di-isopropylamine (5.0 g) and cetrimide (0.8 g) in chloroform (40 ml). After 48 h at 20 °C the products were extracted with dichloromethane (3 x 30 ml) and the combined organic layers were evaporated at 14mmHg. Chromatography[a] gave *1,1,2,2-tetrachloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropane* (2.5 g, 36 %), m.p. 57 - 59 °C (Found M^+: 305.0265. $C_{11}H_{19}Cl_4N$ requires: 305.0272) which showed δH 2.95 (2H, septet, J 6 Hz), 2.75 (2H, s), 1.4 (3H, s), 1.0 (12H, d, J 6 Hz); ν_{max} 2967s, 2932m, 1458m, 1385m, 1190m, 852s cm^{-1}.

3-Chloromethyl-3-methyl-1,1,2,2-tetrachlorocyclopropane

Sodium hydroxide (45 g) in water (45 ml) was added to a rapidly stirred solution of 1,1,3-trichloro-1-propene (30 g) and cetrimide (3 g) in chloroform (150 ml). After 48 h at 20 °C, work up as before gave *3-chloromethyl-3-methyl-1,1,2,2-tetrachlorocyclopropane* (5, X =

Cl), b.p. 48 °C at 0.4–0.5 mm Hg (28 g, 61.5%) (Found M^+: 239.8853. C_5H_5Cl requires: 239.8833) which showed δ_H 3.78 (2H, s), 1.65 (3H, s); ν_{max} 862 vs, 762 m, 737 m cm^{-1}.

1,1,2,2-Tetrachloro-3-methoxymethyl-3-methylcyclopropane

Sodium hydroxide (15 g) in water (15 ml) was stirred with 3,3-dichloro-2-methylprop-2-en-1-yl methyl ether (5 g) and cetrimide (0.4 g) in chloroform (50 ml). After 48 h, work up as before gave *1,1,2,2-tetrachloro-3-methoxy-3-methylcyclopropane* (5, X = OMe), b.p. 50–52 °C at 0.5 mm Hg (5.04 g, 70%) (Found: C, 30.54, H, 3.26. $C_6H_8Cl_4O$ requires: C, 30.28; H, 3.38) which showed δ_H 3.55 (2H, s), 3.36 (3H, s), 1.52 (3H, s); ν_{max} 1117 s, 858s cm^{-1}.

1,1,2,2-Tetrachloro-3-methyl-3-(allylthiomethyl)cyclopropane

Allylmercaptan (1.83 g, 0.024 mole) was added slowly to a stirred solution of sodium ethoxide (1.68 g, 0.024 mole) in DMF (15 ml). After 0.5 h, (5, X = Cl) (5 g, 0.021 mole) was added slowly, when a yellow precipitate formed; the reaction was heated to 50 °C for 2h, stirred at room temperature for 12h, and then diluted with water (100 ml) and extracted with ether (2 x 100ml). The combined organic layers were washed with aq. 5% sulphuric acid (100 ml), and water (2 x 50 ml). Evaporation of the solvent at 760 mm Hg and chromatography[a] gave *1,1,2,2-tetrachloro-3-methyl-3-(allylthiomethyl)cyclopropane* (5, X = SAllyl) (4.2 g, 73 %) (Found M^+: 277.9235. $C_8H_{10}SCl_4$ requires: 277.9257) which showed δ_H 5.7 (1H, m), 5.05 (2H, m), 3.18 (2H, d, J ca 6 Hz), 2.8 (2H, s), 1.53 (3H, s); ν_{max} 1635w, 1451m, 1381m, 1228m, 921m, 860s cm^{-1}.

1,2-Dichloro-3-chloromethyl-3-methylcyclopropene

Methyl lithium (3.2 ml, 1.5 M) was added over 1 m to a stirred solution of (5, X = Cl) (1.0 g, 4.1 mmole) in ether (10 ml) at 0 °C. After 0.5 h the products were quenched with water (1 ml) at −40 °C; the organic layer was washed with water (1 ml) at that temperature, the solvent was removed carefully at 14 mmHg and the residue was flash distilled at 20 °C and 14 mmHg to give *1,2-dichloro-3-chloromethyl-3-methylcyclopropene* (6, X = Cl) (0.57 g, 82 %) (Found M^+: 169.9472. $C_5H_5Cl_3$ requires: 169.9457) which showed δ_H 3.6 (2H, s), 1.4 (3H, s); δ_C 113.8s, 51.6t, 41.9s, 19.4q; ν_{max} 1795w, 1445m, 1377m, 1266m, 933vs, 733m cm^{-1}.

1,2-Dichloro-3-methyl-3-(allylthiomethyl)cycloprop-1-ene.

Methyl lithium (1.5 ml, 1.2 eq.) was added to a rapidly stirred solution of (7, X = SAllyl) (0.51 g, 1.8 mmol) in ether (8 ml) at 0 °C. After 2 m, a yellow precipitate formed; after 0.5h, the products were quenched with water at −40 °C and the solvent was removed at −30°C and 0.4 mm Hg to give *1,2-dichloro-3-methyl-3-(allylthiolmethyl)cycloprop-1-ene* (6, X = SAllyl) (0.25 g, 65 %) which showed δH (300 MHz, −40 °C) 5.72 (1H, m), 5.1 (2H, m), 3.19 (2H, d, J 7.3 Hz), 2.72 (2H, s), 1.4 (3H, s). The crude product was pure by n.m.r.; however, within minutes of reaching 0 °C, a solution in $CDCl_3$ darkened and the ^1H n.m.r. spectrum became complicated.

Preparation of 1,2-dichloro-3-methyl-3-methoxymethyl-1-cyclopropene

Methyl lithium (3.2 ml, 1.5 M) was added over 2 min to (5, X = OMe) (1.0 g) in dry ether (15 ml) at 0 °C. After 30 min, the products were quenched with water (2 ml) at −40 °C and shaken at −40 °C until a clear solution was obtained; the ether layer was decanted and further ether (2 ml) was added to the residue at −40 to −50 °C, and the procedure repeated. The solvent was removed from the combined ether layers at −40 °C and 0.3 mm/Hg to give crude (6,

X = OMe) (0.5 gm, 77.9%) which showed δ_H 3.28 (2H, s), 3.17 (3H, s), 1.25 (3H, s). The compound could not be separated from ca 5 % of (7).

2-Chloro-1,3-dimethyl-3-methoxymethylcyclopropene

(a) Methyl lithium (2.6 ml, 1.6 M) was added over 2 m to a stirred solution of (5, X = OMe) (0.5 g) and isobutene (2 ml) in ether (15 ml) at O °C. After 30 m, the products were allowed to reach 20 °C for 30 m and were then quenched with water (5 ml) and worked up as before. Removal of the solvent at 14 mm Hg and distillation at 20 °C and 0.5 mm Hg gave *2-chloro-1,3-dimethyl-3-methoxymethylcyclopropene* (7) (0.12 g, 40%) (Found M^+: 146.0514. $C_7H_{11}ClO$ requires: 146.0498) which showed δ_H 3.39 (2H, s), 3.31 (3H, s), 2.02 (3H, s), 1.17 (3H, s); δ_C 117.6s, 115.9s, 79.4t, 58.5q, 33.3s, 19.4q, 8.3q; ν_{max} 1450m, 1108vs, 734m cm^{-1}.

(b) The above reaction was repeated in the absence of isobutene, but using 1.5 mol equiv. of methyl lithium; the same product was obtained (44%).

Dimerisation of 1,2-dichloro-3-methyl-3-methoxymethylcycloprop-1-ene

(a) Methyl lithium (3.1 ml, 1.5 M) was added to a stirred solution of (5, X = OMe) (1.0 g) in ether (10 ml) at 0 °C. After 30m the products were quenched with water and worked up as before; the solvent was removed at −20 °C and 14 mmHg and the residual brown oil was dissolved in chloroform (15 ml). After 2 days at 20 °C, the solvent was removed at 14 mmHg and a minor volatile component (9) was removed at 1 mmHg. Chromatography[c] of the residue gave *1,3,4-trichloro-2-(2-chloro-3-methoxyprop-2-yl)-6-methoxy-5-methylcyclohexa-1,4-diene* (9) (0.85 g, 61 %) (Found M^+: 331.9937. $C_{12}H_{16}Cl_4O_2$ requires: 331.9904) which showed δ_H 5.44 (1H, s), 4.82 (1H, s), 3.52 (2H, s), 3.4 (3H, s), 3.3 (3H, s), 2.02 (3H, s), 1.17 (3H, s); δ_C 137.6s, 135.1s, 134.5s, 127.5s, 80.1d, 76.2q, 63.7, 59.35, 58.3, 53.1, 21.2, 18.2; ν_{max} 2989, 1453, 1110 cm^{-1}.

(b) Lithium (200 mg) was stirred with the diene (0.35 g) in t-butanol (2.0 g) and tetrahydrofuran (10 ml). After 3 m, an exothermic reaction occurred which was controlled at a steady reflux for 1 h by periodic cooling. After 2 h at 20 °C, the products were poured into ice-water (20 ml) and extracted with ether (5 x 20 ml). The organic layer was washed with water (3 x 20 ml) and then with sat. brine (20 ml). The solvent was removed at 14 mmHg to give an oil; chromatography[c] gave 5-isopropyl-2-methylanisole (9) (0.12g, 69 %)[10] which showed δ_H 7.04 (1H, d, J 7.5 Hz), 6. (1H, d, J 7.5 Hz), 6.7 (1H, s), 3.83 (3H, s), 2.83 (1H, septet, J 6.9 Hz), 2.18 (3H, s), 1.24 (6H, d, J 6.9 Hz); ν_{max} 2959s, 1612m, 1585m, 1254s, 1133m, 1043m, 851m cm^{-1}.

1-Chloro-1-(1,3-dichloro-2-methyl-2-prop-1-enyl)cyclopropane.

1,2-Dichloro-3-methyl-3-chloromethylcyclopropene (5 g) in ether (5 ml) was mixed with excess ethylene (condensed in high pressure vessel at −90 °C). After 3 days at room temperature, the solvent was removed at 14 mm Hg to leave a brown oil; chromatography[a] gave *1-chloro-1-(1,3-dichloro-2-prop-1-enyl)cyclopropane* (13g) (0.87 g, 15%) (Found M^+: 197.9787. Required for $C_7H_9Cl_3$: 197.9770.) which showed δH 4.2 (2H, s), 1.85 (3H, s), 1.38 (4H, s); ν_{max} 3097, 3012, 2958, 2921, 1641, 1447, 1263, 1179, 1154, 1041, 989, 705, 683 cm^{-1}.

3-Chloro-2-(1,3-dichloro-2-methylprop-1-enyl)-1,1-dimethylcyclopropane

Methyl lithium (15.1 ml, 1.5 M) was added over 2 m to (5, X = Cl) (5.0 g) in ether (15 ml) and isobutene (6 ml) at 0 °C. After 12 h at 20 °C in a sealed tube, work up as above gave

2-chloro-2-(1,3-dichloro-2-methylprop-1-enyl)-1,1-dimethylcyclopropane (13b) (3.26 g, 70 %), b.p. 50 °C and 0.2 mmHg, which gave one peak on glc (Found M^+: 226.0059. $C_9H_{13}Cl_3$ requires: 226.0082) and showed δ_H (rotamer 1): 4.69 (1H, d, J 11.2 Hz), 3.96 (1H, d, J 11.2 Hz), 1.95 (3H, s), 1.56 (1H, d, J 6 Hz), 1.36 (3H, s), 1.26 (1H, d, J 6 Hz), 1.18 (3H, s), (rotamer 2) 4.29 (1H, d, J 11.6 Hz), 4.22 (1H, d, J 11.6 Hz), 1.99 (3H, s), 1.43 (3H, s), 1.24 (1H, d, J 6.5 Hz) 1.11 (3H, s), 1.09 (1H, d J 6.5 Hz) (ratio of rotamers ca 8:7); ν_{max} 1637m, 704s cm^{-1}.

1-Acetoxy-1,2,4-trichloro-3-methylbut-2-ene

1,2-Dichloro-3-chloromethyl-3-methylcyclopropene (0.5g) was stirred in acetic acid (5 ml) for 4 h at 20 °C. The products were treated with sat.aq. sodium bicarbonate (50 ml) and extracted with ether (5 x 10 ml). Removal of the ether at 14 mmHg gave an oil which was one major spot by t.l.c.; chromatography[b] gave *3-acetoxy-1,2,4-trichloro-3-methyl- but-1-ene* (12) (0.45 g, 67 %) (Found M^+: 229.9660. $C_7H_9Cl_3O_2$ requires: 229.9668) which showed δ_H 7.3 (1H, s), 4.2 (2H, s), 2.18 (3H, s), 2.1 (3H, s); ν_{max} 1770s, 1373m, 1204s, 1032s, 708m cm^{-1}.

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

Methyl lithium (15.1 ml, 1.5 M) was added over 2 min. to a stirred solution of (5, X = Cl) (5 g) in ether (15 ml) at 0 °C. After 30 min, the products were quenched with water (2 x 5 ml) at -40 °C and decanted from remaining ice. 2,3-Dimethylbut-2-ene (3.4 g) was added and the mixture was allowed to stand for 12h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one peak by glc. Kugelrohr distillation at 0.3 mmHg (oven temperature 70 °C) gave *3-chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane* (13a) (4.03 g, 77 %) (Found M^+: 254.0432. $C_{11}H_{17}Cl_3$ requires: 254.0396) which showed δ_H(200 MHz, $CDCl_3$) 4.19 (1H, d, J 11.6 Hz), 4.1 (1H, d, J 11.6 Hz), 1.97, (3H, s), 1.28 (3H, s), 1.2 (3H, s), 1.17 (3H, s), 1.15 (3H, s); δ_H ($C_6D_5NO_2$) 4.4 (2H, s), 2.05 (3H, s), 1.35 (3H, s), 1.25 (3H, s), 1.2 (3H, s), 1.15 (3H, s) (unchanged on heating to 400 K); ν_{max} 3005, 1452, 1379, 1264, 1132, 780, 710 cm^{-1}.

3-Chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-Z-1,2-dimethylcyclopropane

The above procedure was repeated using Z-but-2-ene in place of 2,3-dimethylbut-2-ene; work up as above and bulb to bulb distillation at 80 °C and 0.2 mmHg gave *3-chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-Z-1,2-dimethylcyclopropanes* (13c) and (13d) in ratio 5:1 by g.l.c. and n.m.r. (76 %) (Found M^+: 226.0027. $C_9H_{13}Cl_3$ requires: 226.0083) which showed δ_H (major isomer) 4.2 (2H, s), 1.93 (3H, s), 1.51 (2H, m), 1.12 - 1.15 (6H, m); (minor isomer) 2.00 (3H, s), 1.10 (3H, s), 1.08 (3H, s).

Methyl 2-chloro-2-(1,3-dichloro-2-methylprop-1-en-1-yl)cyclopropane carboxylate

The above procedure was repeated using methyl lithium (1.6 ml, 1.5 M) and (5, X = Cl) (0.5 g) in ether (10 ml), except that methyl acrylate (5 ml) was added after quenching with water. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; chromatography[c] gave *methyl 2-chloro- 2-(1,3-dichloro-2-methylprop-1-en-1-yl)cyclopropane carboxylate* (16a) (0.4g, 75 %) (Found M^+: 255.9803. $C_9H_{11}Cl_3O$ requires: 255.9825) which showed δ_H (300 MHz, 230 K) (rotamer 1) 4.62 (1H, d, J 11.2 Hz), 4.11 (1H, d, J 11.2 Hz), 3.76 (3H, s), 2.4 (2H, m), 2.09 (1H, dd, J 5.1, 8.1 Hz), 2.0 (3H, s), (rotamer 2) 4.51 (1H, d, J 11.2 Hz), 4.2 (1H, d, J 11.2 Hz), 3.74 (3H, s), 2.76 (1H, br.t), 1.97 (3H, s), 1.85 (2H, br. t) (ratio ca 5:1); δ_H (60 MHz, 300

K) 4.4 (1H, d J 12 Hz), 4.05 (1H, d J 12 Hz), 3.55 (3H, s), 1.9 - 2.6 (2H, m), 1.8 (3H, s); ν_{max} 2954, 1738, 1440, 1374, 1207, 698 cm^{-1}.

Methyl 2-chloro-2-(1,3-dichloro-2-methylprop-1-en-1-yl)-1-methylcyclopropane carboxylate

The above procedure was repeated except that methyl methacrylate (5 ml) was added after quenching with water. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; chromatography[d] gave *methyl 2-chloro-2-(1,3-dichloro-2-methylprop-1-en-1-yl)-1-methylcyclopropane carboxylate* (0.46g, 82 %) (Found M^+: 269.9968. $C_9H_{11}Cl_3O$ requires: 269.9981) which showed δ_H (300 MHz, 230 K) (rotamer 1) 4.63 (1H, d, J 11.1 Hz), 4.09 (1H, d J 11.1 Hz), 3.71 (3H, s), 2.67 (1H, d, J 6.2 Hz), 1.96 (3H, s), 1.62 (1H, d, J 6.5 Hz), 1.58 (3H, s), (rotamer 2) 3.83 (1H, d, J 10 Hz), 3.67 (3H, s), 2.29 (1H, d, J 6.8 Hz), 2.02 (1H, d, J 8.2 Hz), 1.66 (3H, s); the remaining signals were obscured by those for the major rotamer (ratio of rotamers 2:1); (60 MHz, 300 K) 4.3 (1H, br.d, J 11 Hz), 4.0 (1H, d, J 11 Hz), 3.6 (3H, s), 2.5 (1H, br.d, J 6 Hz), 1.9 (3H, s), 1.46 (1H, d, J 6 Hz); δ_C (230 K) 171.2, 170.9, 135.1, 134.4, 132.6, 131.9, 53.5, 53.0, 52.4, 44.9, 44.7, 36.6, 31.5, 31.2, 29.6, 18.6, 17.4, 17.3; ν_{max} 2952, 1732, 1300, 1165, 704 cm^{-1}.

1-Chloro-1-(1-chloro-3-methoxy-2-methylprop-1-enyl)-E-2,3-dimethylcyclopropane

Methyl lithium (1.6 ml, 1.5 m) was added over 1 m to (5, X = OMe) (0.5 g, 2.1 mM) stirred in ether (12 ml) at 0 °C. After 0.5 h the products were quenched with water and worked up as before; *trans*-but-2-ene (1.8 g) was added and after 12 h at 20 °C the solvent was removed at 14 mm Hg. Flash distillation at 50 °C and 0.1 mm Hg gave *1-chloro-1-(1-chloro-3-methoxy-2-methylprop-1-enyl)-E-2,3-dimethylcyclopropane* (15e) (0.25 g, 54%) which showed a single peak by glc (Found M^+: 222.0582. $C_{10}H_{16}Cl_2O$ requires: 222.0578) which showed δ_H (300 MHz, 220 K) (rotamer 1) 4.18 (1H, d, J 10.6 Hz), 3.81 (1H, d, J 10.6 Hz), 3.33 (3H, s), 1.88 (3H, s), 1.35 (3H, d, J 5.9 Hz) and (rotamer 2) 4.20 (1H, d, J 10.6 Hz), 4.07 (1H, d, J 10.6 Hz), 3.38 (3H, s), 1.88 (3H, s), 1.25 (3H, d J 6.1 Hz), 1.02 (3H, d, J 6.1 Hz) in ratio 2.5:1, together with a broad multiplet at *ca* δ 1.2 integrating to 5H-total. At 303K, the 200 MHz spectrum showed sharp singlets at 3.35 and 5.40 for the two methyl signals, together with a broad three hydrogen doublet at δ 1.33 and a very broad five hydrogen singlet at 1.11; in addition one half of the AB pattern was visible at δ 4.15, the other half apparently appearing as an extremely broad signal centred at 3.9; the coalescence temperatures for the signals at δ 4.18 and 4.20 (ca 280 K) and 3.35 and 3.25 (ca 270 K) corresponded to a $\Delta G^{\#}$ of 13.2 or 13.5 kcal/mol respectively; ν_{max} 1104, 752 cm^{-1}.

1-Chloro-1-(1-chloro-3-methoxy-2-methylprop-1-enyl)-2,2-dimethylcyclopropane

(i) The above procedure was repeated except that isobutene was added after quenching with water. Work up as above gave *1-chloro-1-(1-chloro-3-methoxy-2-methylprop-1-enyl)-2,2-dimethylcyclopropane* (15b), b.p. 50 °C and 0.2 mm Hg (0.29 g, 62%) (Found M^+: 222.0578) which gave one peak one g.l.c. and showed δ_H (rotamer 1): 4.39 (1H, d, J 11.0 Hz), 3.88 (1H, d, J 11.0 Hz), 3.37 (3H, s), 1.9 (3H, s), 1.4 (3H, s), 1.05 (3H, s); (rotamer 2): 4.05 (1H, d J 11.5 Hz), 3.98 (1H, d J 11.5 Hz), 3.34 (3H, s), 1.8 (3H, s), 1.3 (3H, s), 1.2 (2H, m), 1.19 (3H, s); two pairs of doublets were also seen at δ 1.34 (J 6.1 Hz), 1.25 (J 6.1 Hz) and 1.20 (J 6.3 Hz) and 1.05 (J 6.3 Hz), but these were not definitely assigned to a particular rotamer (ratio of rotamers 6:5); ν_{max} 1103vs, 944m, 719m cm^{-1}.

(ii) Compound (13b) (0.5 g) was refluxed for 1.5 h with sodium methoxide (0.54 g) in

methanol (6 ml). The products were treated with water (10 ml) and extracted with ether (2 x 10 ml). Work up as above and chromatography[c] gave (15b) (0.35 g, 71 %) identical by n.m.r. and i.r. to that obtained above.

Methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylprop-1-enyl)cyclopropanecarboxylate

The above procedure was repeated except that methyl acrylate (5 ml) was added after quenching with water. Work up as above gave *methyl 2-chloro-2-(1-chloro- 4-methoxy-2-methylprop-1-enyl)cyclopropane carboxylate* (17a) (0.28 g, 54%), b.p. 65 °C at 0.1 mm Hg (Found: 252.0303. $C_{10}H_{14}Cl_2O_3$ requires: 252.0320) which showed δ_H (200 MHz, 303 K) 4.07 - 4.3 (2H, complex), 3.65 (3H, s), 3.3 (3H, s), 2.5 (1H, br.dd, J 6.9 Hz), 2.2-1.8 (5H, m), including 1.85 (3H, s); δ_H (300 MHz, 230K): (rotamer 1) 4.35 (1H, d, J 11.8 Hz), 4.15 (1H, d, J 11.8 Hz), 3.75 (3H, s), 3.37 (3H, s), 2.43 (1H, dd, J 9.2, 6.9 Hz), 2.16 (1H, t, J 6.9 Hz), 2.09 (1H, dd, J 9.2, 6.9 Hz); (rotamer 2) 4.17 (1H, d, J *ca* 11.6 Hz), 3.97 (1H, d, J 11.6 Hz), 3.71 (3H, s), 3.35 (3H, s), 2.70 (1H, dd, J 9.3, 7 Hz), 1.96 (1H, t, J *ca* 7 Hz), 1.89 (3H, s), 1.79 (1H, dd, J 6.7, 9.3 Hz) (ratio of rotamers *ca* 7:3); δ_C (230 K) 169.4, 169.2, 130.6, 130.2, 129.3, 127.6, 71.4, 71.3, 50.3, 50.1, 53.0, 48.0, 47.3, 35.5, 30.3, 27.0, 24.3, 17.7, together with a number of minor signals; ν_{max} 1739vs, 702w cm^{-1}. An analysis of the ^1H spectra at the two temperatures indicated a barrier between the two rotamers of ca 14.4 kcal/mol.[18]

Methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylpropenyl)-1-methylcyclopropane carboxylate

(a) The above procedure was repeated except that methyl methacrylate was added after quenching with water. Work up as above led to *methyl 2-chloro-2-(1-chloro-3-methoxy- 2-methylprop-1-enyl)-1-methylcyclopropane carboxylate* (17b), b.p. 70 °C at 0.1 mmHg which was single component by glc (0.29 g, 52%) (Found M^+: 266.0470. Calculated for $C_{11}H_{16}Cl_2O_3$ 266.0476) which showed δ_H (60 MHz): 4.01 (2H, br. s), 3.25 (3H, s), 2.3 (1H, d, J 6 Hz), 1.82 (3H, s), 1.58 (3H, s), 1.4 (1H, d, J 6 Hz); (300 MHz, 230 K) (rotamer 1) 4.35 (1H, d, J 11.8 Hz), 4.13 (1H, d, J 11.8 Hz), 3.72 (3H, s), 3.37 (3H, s); (rotamer 2) 3.91 (1H, d, J 11.6 Hz), 3.89 (1H, d, J 11.6 Hz), 3.65 (3H, s), 3.34 (3H, s) in ratio *ca* 6:5, together with 2.40 (1H, d, J 6.3 Hz), 2.26 (1H, d, J 6.7 Hz), 1.34 (1H, d, J 6.7 Hz) [the exact integrals of these final signals could not be determined; the fourth doublet required for the two rotamers was apparently partly obscured by the signal at 1.64, but was centred at 1.63]; the n.m.r. at ambient temperature included a very broad signal at δ 3.6 - 4.2 (ca 2H), a broad singlet at 3.65 (3H), a singlet at 3.33 (3H), two broad peaks at 2.04 and 2.17 (1H total) a singlet at 1.86 (3H) and a broad singlet at 1.6 (ca 4H); δ_C (50.3 MHz, 300 K) 171.0, 137.3 br, 130.7br, 71.9, 58.3, 53.8, 52.5, *ca.* 32 (very broad), 29.6 (very broad), 17.55, 17.5; δ_C (75.5 MHz, 230 K) 171.5, 171.1, 137.3, 136.7, 130.9, 130.0, 71.8, 71.3, 50.6, 50.3, 53.9, 53.1, 52.9, 52.7, 37.7, 36.6, 32.8, 31.1, 29.2, 17.5, 17.4; ν_{max} 1733 vs, 718 m cm^{-1}. Application of the Gunther approximation[18] to the ^1H and ^{13}C spectra at different temperatures showed a barrier between the two rotamers of ca. 14.8 kcal/mol.

(b) The ester (16b) (0.5 g) in methanol (0.5 ml) was refluxed for 1.5 h with sodium methoxide (0.5 g) in methanol (6 ml). The products were treated with water (10 ml) and extracted with ether (2 x 10 ml). Removal of the solvent from the organic layer at 14 mmHg gave an oil; chromatography[d] gave (17b) (0.32 g, 65 %), identical by n.m.r. and i.r. to that above.

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

The above procedure was repeated except that 2-methylbut-2-ene (1.8 g) was added after quenching with water. Work up as above gave *1-chloro-1-(1-chloro-3-methoxy-2-methylprop-1-enyl)-2,2,3-trimethylcyclopropane* (0.33 gm, 68%), b.p. 60 °C and 0.1 mm/Hg (Found M^+: 236.0726. $C_{11}H_{18}OCl_2$ requires 236.0735) which showed ν_{max} 1455m, 1379m, 1103s, 760m. The n.m.r. (200 MHz) was complex but included signals in the regions 3.7 - 4.2, 3.33 - 3.37, 1.88 - 1.89, and 1.0 - 1.5 in the ratio 2:3:3:10. There were two singlets in ratio 1:1 at 1.88 and 1.89, and four in the ratio 6:2:3:8 at δ 3.37, 3.36, 3.35, and 3.33, and at least three AB patterns in the low field region, at δ 4.18 and 3.81 (J 11.0 Hz), 4.00 and 3.96 (J 11.5 Hz), and 4.02 and 3.87 (J 11.4 Hz). The high field region included a large number of signals. The ^{13}C spectrum included eight signals in the alkene region at δ 138.3, 138.0, 137.0, 136.1, 135.1, 132.6, 131.7, and 131.4 as well as groups of signals at 72 - 73, 55 - 58, and 10 - 36.

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

The above procedure was repeated except that 2,3-dimethylbut-2-ene (1.8 g) was added after quenching with water. After 3 h, work up as above and flash distillation at 0.1 mmHg and 70 °C gave *1-chloro-1-(1-chloro-3-methoxy-2-methylprop-1-enyl)-2,2,3-trimethylcyclopropane* (15a) (0.36 gm 69%) (Found M^+: 250.0867. $C_{12}H_{20}OCl_2$ requires 250.0891) which showed δ_H (200 MHz) 4.01 (1H, d, J 11.4), 3.84 (1H, d, J 11.4), 3.35 (3H, s), 1.88 (3H, s), 1.27 (3H, s), 1.20 (3H, s), 1.16 (3H, s), 1.07 (3H, s); ν_{max} 3004s, 2925s, 2821m, 1684m, 1452s, 1380s, 1106s, 886m, 782m cm^{-1}. Irradiation at δ 1.07 caused a 6 % n.O.e. enhancement in that at 4.01, 3 % in that at 3.84 and 2 % in that at 1.88; enhancements in these signals on irradiation at 1.27, 1.20 or 1.16 were all below 2 %.A more volatile minor component was 1-chloro-2,3-dimethyl-3-methoxymethyl-1-cyclopropene (85 mg, 14%).

3-Chloro-3-(1-chloro-3-methoxy-2-methylprop-1-enyl)-Z-1,2-dimethylcyclopropane

The above procedure was repeated except that *cis*-but-2-ene (1.8 g) was added after quenching with water. After 12 h at 20 °C, work up as above gave an oil which showed two peaks close together by glc (ratio *ca* 6:1); the major component was characterised as *3-chloro-3-(1-chloro-3-methoxy-2-methylprop-1- enyl)-Z-1,2-dimethylcyclopropane* (15c), b.p. 55 °C at 0.1 mm Hg (0.26 g, 56%) (Found M^+:222.0571. Calculated for $C_{10}H_{16}OCl_2$: 227.0578) which showed δ_H (200 MHz) 4.05 (2H, s), 3.34 (3H, s), 1.81 (3H, s), 1.36 (2H, m), 1.13 (6H complex); in addition small signals were seen at 3.36(s), 1.91(s), and 1.0-1.2, presumably caused by the minor isomer (15d); ν_{max} 1102s, 738s cm^{-1}. No *trans*-isomer (15e) was seen by glc.

1,2-Dichloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropene

Methyl lithium (1.26 ml, 1.5 M) was added over 1 m to a stirred solution of (5, X = NPr^i_2) (0.52g) in ether (10 ml) at 0 °C. After 30 m the products were quenched with water at -40 °C, decanted from the ice and evaporated at that temperature and 1 mmHg to give *1,2-dichloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropene* (6, X = NPr^i_2) (0.33 g, 83%) which was very unstable even at 20 °C, giving a very thick brown oil in a period of minutes. However the n.m.r. at 230 K showed δ_H 2.87 (2H, septet, J 6.7 Hz), 2.57 (2H, s), 1.24 (3H, s), 0.94 (12H, d, J 6.7 Hz); δ_C 114s, 50.4t, 46.9d, 43.8s, 22.5q, 20.6q.

2,2-Dimethyl-1-cyclopropyl ethyl ketone

Potassium hydroxide (1 g) in water (10 ml) was refluxed with (13b) (0.5 g) for 22h. The products were treated with water (10 ml) and extracted with ether (3 x 5 ml). The organic layer was dried and the solvent was removed at 14 mm Hg to give an oil which was one spot by t.l.c.; flash distillation gave *2,2-dimethyl-1-cyclopropyl ethyl ketone* (24) (0.17 g, 61.4 %), b.p. 20°C at 0.3 mmHg (Found M^+: 126.1055. Required for $C_8H_{14}O$: 126.1045) which showed δ_H (200 MHz): 2.5 (2H, q, J 7.3 Hz), 1.83 (1H, dd, J 5.6, 7.53 Hz), 1.23 (1H, dd, J 3.9, 5.6 Hz), 1.19 (3H, s), 1.07 (3H, t, J 7.3 Hz), 1.06 (3H, s), 0.8 (1H, dd, J 3.9 7.6 Hz); ν_{max} 2973, 2947, 2876, 1697, 1395, 1131, 1026, 918, 733 cm^{-1}.

2-Propan-1-oyl-1-methylcyclopropanecarboxylic acid

Potassium hydroxide (1 g) in water (10 ml) was refluxed with (16b) (0.5 g) for 3h. The products were treated water (10 ml) and extracted with ether (2 x 10 ml). The organic layer was dried; removal of the solvent at 14 mm Hg gave no product. The aqueous layer was acidified with 2M hydrochloric acid, extracted with ether (4 x 10 ml) and the solvent was removed at 14 mm Hg. Chromatography[c] of the remaining yellow oil gave *2-(propan-1-oyl)-1-methyl-cyclopropanecarboxyic acid* (25) (0.26 g, 90.3%) (Found M^+: 156.0775. Required for $C_8H_{12}O_3$: 156.0786) which showed δ_H (200 MHz): 2.68 (1H, dd, J 8.35, 6.7 Hz), 2.6 (2H, m), 1.56 (1H, dd, J 4.0, 8.35 Hz), 1.50 (1H, dd, J 4.0, 6.7 Hz), 1.27 (3H, s), 1.09 (3H, t); δ_C 206, 180, 38, 34, 29, 21, 12, 8; ν_{max} 3086 (v.br), 2978, 2679, 1694, 1385, 1300, 1198, 1124, 887 cm^{-1}.

1-(1,3-dichloro-2-methylprop-2-en-1-ylidene)-2,2,3,3-tetramethylcyclopropane

Potassium t-butoxide (2.07 g, 18.5 mmole) was added over 5 min. to a stirred solution of (13a) (1.35 g, 5.28 mmol) in dry ether (30 ml) at 0 °C. After 15 min. at 20 °C, the solution was diluted with water (20 ml) and petrol (30 ml). Work up as above and flash distillation at 35 °C and 0.4 mm Hg gave *1-(1,3-dichloro-2-methylprop-2-en-1-ylidene)-2,2,3,3-tetramethyl-cyclopropane* (21) (1.03 g, 89%) (Found M^+: 218.0609. Required for $C_{11}H_{16}Cl_2$: 218.0629) which showed δH (200 MHz): 6.6 (1H, q, J 1.2 Hz), 1.97 (3H, d, J 1.2 Hz), 1.23 (6H, s), 1.22 (6H, s); ν_{max} 3099, 2989, 2950, 2920, 2867, 1709, 1606, 1448, 1111, 926, 787 cm^{-1}.

1-(1-chloro-2-methoxymethylprop-2-en-1-ylidene)-2,2,3,3-tetramethylcyclopropane

Potassium t-butoxide (2.34 g, 20 mmole) was added over 5 min. to a stirred solution of (17b) (1.5 g, 6 mmole) in dry ether (30 ml) at 0 °C. After 15 min. at 20 °C, work up as above gave an oil which was one spot by t.l.c.; flash distillation at 30 °C and 0.5 mm Hg gave *1-(1-chloro-2-methoxymethylprop-2-en-1-ylidene)-2,2,3,3-tetramethylcyclopropane* (23) (1.1 g, 85.8%) (Found M^+: 214.1130. $C_{12}H_{19}OCl$ requires: 214.1124) which showed δH (60 MHz): 5.58 (1H, br.s), 5.28 (1H, br.s), 3.8 (2H, s), 3.3 (3H, s), 1.2 (12H, s); ν_{max} 2988, 1714, 1451, 1373, 1111, 909, 734 cm^{-1}.

***E- and Z*-1-(1,3-dichloro-2-methyl-1-prop-1-ylidene)-2,2-dimethylcyclopropane**

a) Potassium t-butoxide (4.34 g, 38.4 mmole) was added over 5 min. to a stirred solution of (13b) (2.5 g, 11 mmole) in ether (30 ml) at 0 °C. After 15 min. at 20 °C, work up as above gave an oil which was one spot by t.l.c.; chromatography[a] gave E and *Z* 1-(1,3-dichloro-2-methyl-1-prop-1-ylidene)-2,2-dimethylcyclopropanes (22) (ratio 1:1) (1.5 g, 74%) (Found M^+: 190.0316. Required for $C_9H_{12}Cl_2$: 190.0316) which showed δH (200 MHz): (1 st isomer) 6.7 (1H, br.s), 2.06 (3H, d, J 1.2 Hz), 1.47 (2H, s), 1.27 (6H, s); (2 nd isomer): 6.7 (1H, br.s), 2.01 (3H, d, J 1.2),

1.25 (6H, s), 1.21 (2H, s); ν_{max} 3098, 2962, 1786, 1730, 1606, 1450, 1373, 1122, 933, 786 cm^{-1}.

b) The mixture of cyclopropanes from (a) (0.16 g, 0.84 mmole) in dichloromethane (5 ml) was stirred with tetracyanoethene (0.11 g, 0.88 mmole) for 72h at room temperature. Removal of the solvent at 14 mm Hg gave a solid which was recrystallised from ether and petrol to give cis- and trans-4,6-dichloro-5-methyl-7,7,8,8-tetracyano-1,1-dimethylspiro[2.5]oct-2-ene in the ratio 1:1 (0.094g, 35%) (Found M^+: 318.0418. Required for $C_{15}H_{12}N_4Cl_2$: 318.0439) which showed δH (200 MHz): 1st isomer: 5.15 (1H, d, J 1 Hz), 2.22 (1H, d, J 7 Hz), 2.21 (3H, d, J 1 Hz), 1.83 (3H, s), 1.75 (3H, s), 1.5 (1H, d, J 7 Hz); 2nd isomer: 4.96 (1H, d, J 0.93), 2.16 (3H, d, J 0.93 Hz), 2.07 (1H, d, J 7.25 Hz), 1.66 (1H, d, J 7.25 Hz), 1.4 (3H, s), 1.3 (3H, s); ν_{max} (KBr) 3094, 3038, 2984, 2937, 2250, 1619, 1465, 1382, 1232, 1110, 971, 761 cm^{-1}.

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\+ Only the syn- form of the carbene relative to rotation about the 1,2-bond is shown.

$$ During our work we became aware of a report that (14, X = Y = Me) is converted to the corresponding allylidenecyclopropane by reaction with potassium t-butoxide (W.Gothling, Dissertation, University of Hamburg, 1985).

* Although the cyclopropenes could be isolated, this was not generally necessary and yields are based on starting cyclopropane.

** It should be noted however that (2,3,3-trimethylcylopropen-1-yl)ethanol does not react with acetic acid at 20 °C, though a rapid reaction does occur on addition of a catalytic amount of p-toluene sulphonic acid (J.R.AlDulaymmi and M.S.Baird, unpublished results).

\# A preliminary account of some of these results has already appeared.[7a,9b]