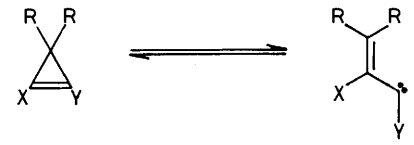
A Highly Stereoselective Generation and Trapping of 1,2-Dichloro-3-methyl-4-phenylbut-2-enylidene†

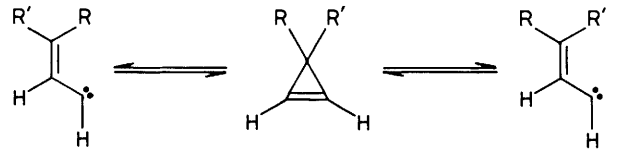
Juma'a R. Al-Dulayymi, Mark S. Baird,* and William Clegg
Department of Chemistry, Bedson Building, The University of Newcastle upon Tyne, NE1 7RU

3-Benzyl-1,2-dichloro-3-methylcyclopropene undergoes an apparent cyclopropene to vinylcarbene rearrangement at 20 °C; one stereoisomer of the derived vinylcarbene is trapped selectively in either intra- or inter-molecular processes, and in the latter case trapping by addition to the alkene bond of methyl methacrylate leads to a cyclopropane with vinyl and ester groups *cis*-related. The stereochemistries of the products of both inter- and intra-molecular processes have been established by *X*-ray crystallography.

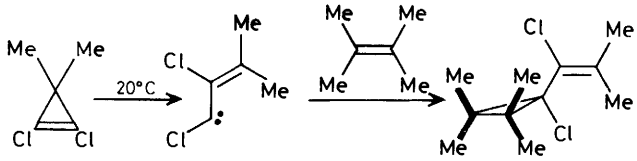
A number of cyclopropenes have been reported to rearrange on heating,[1] in some cases reversibly,[2] to give products apparently derived from a vinylcarbene (see Scheme 1), and the effects of different groups, X and Y, on the selectivity of the reaction has been examined.[3] However, when the two 3-substituents are different, there is the additional possibility of two stereoisomeric carbenes (see Scheme 2). There are a number of cases in which intramolecular trapping leads to products apparently derived from only one of the two possible stereoisomeric carbenes;[4] this may suggest that only one of the carbenes is produced, but could also reflect selective trapping of that isomer, caused by the effect of an activating substituent. 1,2-Dichloro-3,3-dimethylcyclopropene is known to rearrange to the corresponding vinylcarbene at 0—20 °C, and to be trapped by alkenes[5] (see Scheme 3).



Scheme 1.



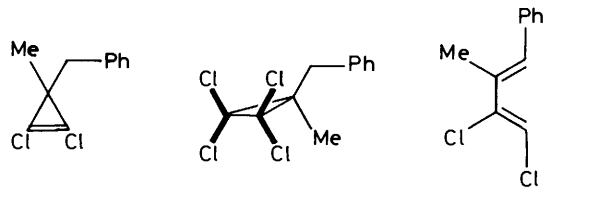
Scheme 2.



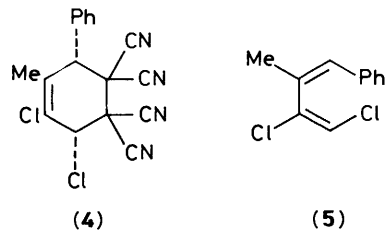
Scheme 3.

The corresponding phenyl-substituted cyclopropene (**1**) is available by reaction of (**2**) with methyl-lithium at 20 °C for 30 min.[6] When allowed to stand for 36 h in deuteriochloroform solution, compound (**1**) rearranged to a diene characterised as (**3**), although only in moderate yield (35%). This compound showed the expected two vinyl hydrogen signals in its ^{1}H n.m.r. spectrum at δ 7.11 and 6.58, one of which showed allylic coupling to the methyl group. However, it could not be distinguished with certainty from the three other possible stereoisomeric dienes.

However, compound (**3**) reacted readily with TCNE to give an adduct (**4**), the structure of which was proved by *X*-ray crystallographic examination, the result of which is shown in Figure 1. On the basis of a concerted $4\pi_s + 2\pi_s$ cycloaddition, the diene must, therefore, be either (**3**) or (**5**), but the latter would appear very unlikely on steric grounds, and would be difficult to explain mechanistically. Compound (**3**) is formally derived by a 1,4-shift of hydrogen in the carbene (**6**) (see Scheme 4), a process which has been reported to occur for a number of other vinylcarbenes.[7] Such a rearrangement would necessarily produce a (*Z*)-1,2-dichloroalkene as in (**3**); the *E*-arrangement about the 3,4-double bond would presumably result from steric control in the transition state. An alternative mechanism would involve insertion of the carbene into the vinylic C–H bond to give a *trans*-cyclobutene (**7**) which could undergo conrotatory ring-opening, again leading to the observed stereochemistry of the diene; the fact that the rearrangement of (**1**) to (**3**) occurs at ambient temperature, would suggest that the cyclobutene may not be an intermediate,



(**1**) (**2**) (**3**)



(**4**) (**5**)

although phenyl substituents are known to reduce the barrier to ring-opening.[8] The formation of (**3**) may be interpreted in terms of selective ring-opening of (**1**) to (**6**) rather than to the isomeric carbene (**8**); however, the benzylic C–H bond *cis* to the carbene

† A preliminary account of these results has already appeared: J. R. Al Dulayymi, M. S. Baird, and W. Clegg, *Tetrahedron Lett.*, 1988, 6149.

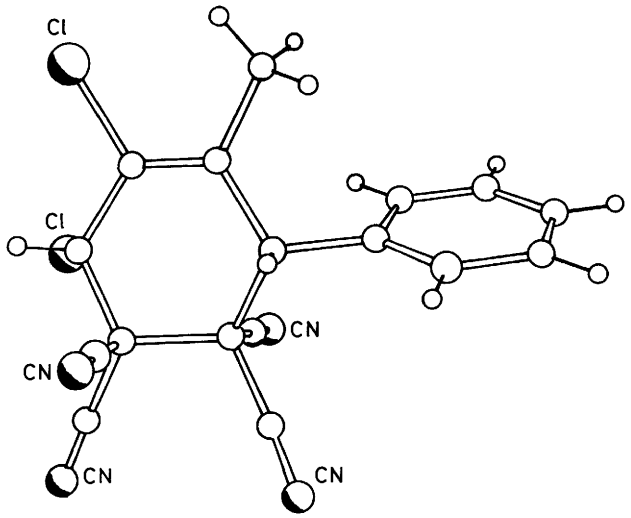
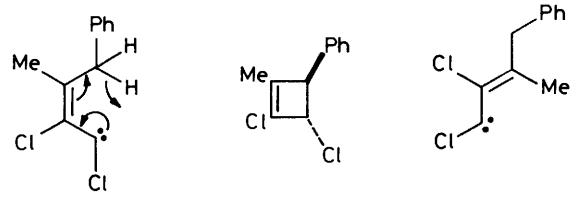


Figure 1. Molecular structure of compound (**4**)

Table 1. Atomic co-ordinates (10^4) for compound (**4**)

Atom	*x*	*y*	*z*
C(1)	2 562(2)	6 234(2)	6 079(2)
C(2)	2 149(2)	5 505(2)	5 108(2)
C(3)	2 292(2)	4 360(2)	4 996(2)
C(4)	2 921(2)	3 637(2)	5 900(2)
C(5)	3 035(2)	4 258(2)	7 037(2)
C(6)	3 408(2)	5 569(2)	6 907(2)
Cl(1)	1 366(1)	6 802(1)	6 723(1)
Cl(2)	1 504(1)	6 337(1)	4 031(1)
C(31)	1 946(2)	3 745(2)	3 937(2)
C(41)	2 453(2)	2 411(2)	5 964(2)
C(42)	1 289(2)	2 202(2)	5 985(2)
C(43)	867(3)	1 099(3)	6 014(2)
C(44)	1 568(4)	182(3)	6 029(3)
C(45)	2 730(4)	332(3)	6 014(3)
C(46)	3 188(3)	1 465(2)	5 982(2)
C(51)	1 959(2)	4 211(2)	7 569(2)
N(51)	1 140(2)	4 145(2)	7 991(2)
C(52)	3 923(2)	3 665(2)	7 775(2)
N(52)	4 692(3)	3 245(2)	8 292(2)
C(61)	3 555(2)	6 156(2)	7 983(3)
N(61)	3 684(3)	6 589(3)	8 835(3)
C(62)	4 530(2)	5 550(2)	6 469(2)
N(62)	5 396(2)	5 503(3)	6 141(2)



Scheme 4.

centre in (**6**) would be expected to be more reactive than the C–H bonds of the methyl group which are *cis* to the carbene centre in (**8**), and selective trapping of one carbene in an equilibrium between (**1**), (**6**), and (**8**) is an alternative explanation.

When an ethereal solution of (**1**) was treated with an excess of methyl methacrylate, complete reaction occurred over a period of *ca.* 2 h; the n.m.r. spectrum of the crude product at 300 K was rather complicated because of restricted rotation in the products but it showed the presence of one major component

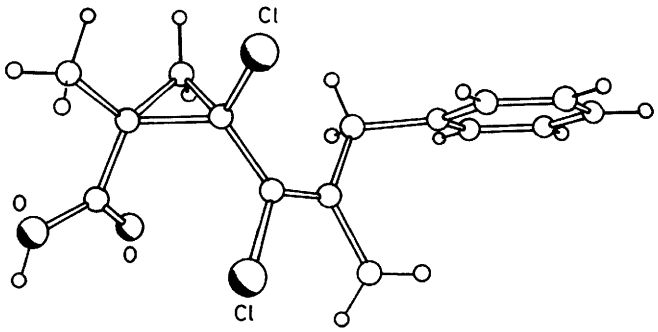


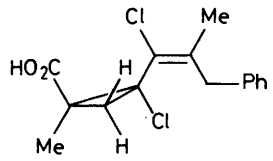
Figure 2. Molecular structure of compound (**9**)

Table 2. Atomic co-ordinates (10^4) for compound (**9**)

Atom	*x*	*y*	*z*
C(1)	3 276(2)	9 665(1)	3 879(2)
C(2)	1 962(2)	9 369(1)	2 937(2)
C(3)	1 136(2)	10 244(2)	2 175(2)
C(4)	1 347(2)	8 447(1)	3 316(2)
C(5)	1 891(2)	8 313(1)	2 303(2)
C(6)	3 075(2)	7 702(1)	2 489(2)
C(7)	3 331(2)	6 759(1)	2 954(2)
C(8)	4 620(2)	6 242(2)	3 225(3)
C(9)	2 334(2)	6 133(2)	3 265(2)
C(10)	2 214(2)	5 050(1)	2 728(2)
C(11)	1 793(3)	4 882(2)	1 428(3)
C(12)	1 738(4)	3 891(3)	945(4)
C(13)	2 102(3)	3 067(2)	1 747(4)
C(14)	2 492(3)	3 214(2)	3 028(4)
C(15)	2 547(2)	4 203(2)	3 533(3)
O(1)	3 666(1)	10 572(1)	3 750(2)
H(1)	4 458(30)	10 714(24)	4 327(29)
O(2)	3 913(1)	9 045(1)	4 727(1)
Cl(1)	747(1)	8 217(1)	695(1)
Cl(2)	4 178(1)	8 371(1)	1 992(1)

and one minor one, in ratio *ca.* 5:1; an analysis of the spectrum is given later. The two components could not be separated by column chromatography or by g.l.c. However, hydrolysis with KOH–MeOH–H_2O led to a mixture of acids, the major component of which could be purified by recrystallisation. The structure of the product was established by an *X*-ray crystallographic study as (**9**) (see Figure 2). As is normally the case for vinylcyclopropanes, the vinyl group is aligned almost parallel to the opposite cyclopropane bond.[9] The 200 MHz n.m.r. of this acid at 295 K was broad, but again showed the presence of two rotamers in ratio *ca.* 3:2. The major rotamer showed an **AB** pattern centred at δ 3.86 and 3.70 (*J* 15.1 Hz) for the benzylic methylene hydrogens; one half of a second **AB** pattern was also visible at δ 2.45 (*J* 6.2 Hz). The minor rotamer showed an **AB** pattern at δ 3.93 and 3.09 (*J* 13.8 Hz), partly obscured by the signals for the major rotamer at δ 3.86, and two broad one-hydrogen signals at δ 2.34 and 1.40. In addition, there was a large signal for the methyl groups in both rotamers at δ 1.62—1.72.

Re-esterification of (**9**) using diazomethane gave (**10**); the n.m.r. spectrum of this at 300 K was rather broad. At 330 K, the spectrum simplified considerably, though some of the peaks were still broad. The C-methyls now appeared as two relatively sharp signals, although the methoxy group was broad. The two **AB** patterns for the benzylic hydrogens of the rotamers had collapsed to one, although one half of the pattern was obscured by the methoxy signal. At 240 K, the spectrum showed two rotamers in ratio 3:1. The spectrum of the major one included an **AB** double doublet at δ 3.98 and 3.63 for the benzylic hydrogens, and a second one at δ 2.42 and 1.55 for the cyclo-



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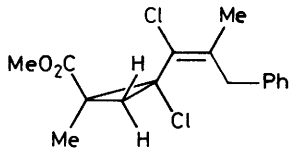
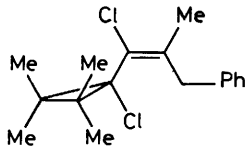
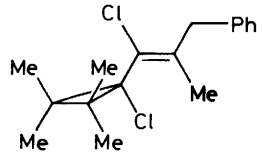


(10)



(11)

propane hydrogens. The minor rotamer showed corresponding AB patterns at δ 3.93 and 2.94, and 2.32 and 1.38. On warming to 280 K, the signals at δ 3.98 and 3.93 coalesced; those at δ 3.63 and 2.94, 2.42 and 2.32, and 1.55 and 1.38 coalesced at 300 K, and others at 300—330 K. These coalescence temperatures correspond to a $\Delta G^{\dagger}$ of *ca.* 15 kcal mol^{-1} for the rotation about the exocyclic bond(s).[10]



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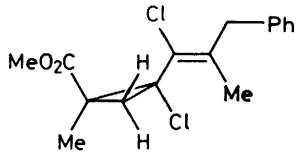
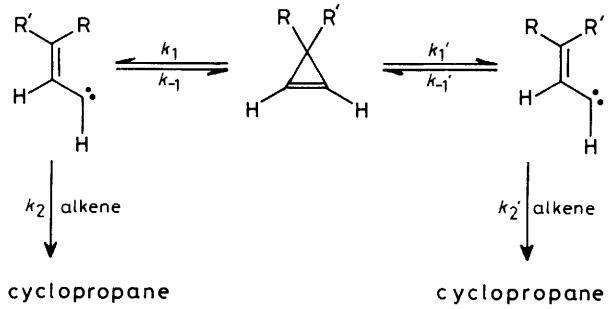


(13)

A comparison of the spectrum of (**10**) at 240 K with that for the mixture of isomers obtained from the reaction of (**1**) with methyl methacrylate confirmed that the major component of this was (**10**). However, some minor additional signals were present, corresponding to *ca.* 17% of other products. Because the spectrum was complicated by the presence of two rotamers of (**10**), not all the signals could be clearly seen. The additional signals included two doublets of approximately equal area centred at δ 2.35 and 2.30 (coupling constants 6.3 and 6.8 Hz respectively); in addition a doublet (*J* 6.8 Hz) appeared at δ 1.33, while there were four singlets at δ 1.91, 1.68, 3.34, and 3.70, each integrating to three times the area of each of the doublets. A fourth doublet (*J* 16 Hz), integrating for one hydrogen, was also present at δ 3.30. When the temperature was increased to 300—330 K the two doublets coalesced to a single doublet; other signals also changed, but became hidden in the signals for the major isomer. Nonetheless, these results are best explained in terms of the presence of two rotamers of the minor isomer, with a similar rotation barrier to that for the major isomer. This could be isomeric with (**10**), either in the geometry of the cyclopropane or of the vinyl group, or indeed of both; it is, however, characterised as (**13**) on the basis of the following. Treatment of (**1**) with 2,3-dimethylbut-2-ene for 2 h at 20 °C also led to one major and one minor isomer, again in ratio 5:1. Each of these gave ^{1}H n.m.r. spectra consistent with restricted rotation about the exocyclic bond and a preferred geometry with the vinyl group not bisecting the cyclopropane.[9] The major isomer, characterised as (**11**) by comparison with (**10**) showed five distinct methyl-groups, a phenyl group and a widely separated pair of doublets for the methylene group at δ 3.89 and 3.18 (*J* 14.4 Hz). The minor isomer showed a similar spectrum, though in this case the doublets were much closer in chemical shift, at δ 3.67 and 3.54 (*J* 14.3 Hz). This isomer is characterised as (**12**); irradiation at δ 1.18 showed an n.O.e. enhancement in the benzylic hydrogens of the major isomer, and a smaller increase in the signal for the olefinic methyl group at δ 1.67; the methyl group at δ 1.18 is the highest field signal for this isomer, in agreement with a position in the shielding zone of the alkene and close to the benzylic methylene. In contrast, irradiation of a methyl signal at δ 1.09 arising from the minor isomer caused an enhancement in the olefinic methyl (δ 1.76) but caused no effect on the benzylic hydrogen signals of this isomer; again the methyl at δ 1.09 represents the highest field signal of this isomer. Thus both carbene isomers, (**6**) and (**8**), are trapped by reaction of (**1**) with the alkene, in ratio 5:1. Since the reaction of (**1**) with methyl methacrylate also led to a major isomer (**10**) and a minor one, again in ratio 5:1, the minor isomer is characterised as (**13**).

The increase in the rate of reaction of (**1**) in the presence of an alkene compared to its decomposition to (**3**) in the absence of the alkene supports the reversibility of the ring-opening.



The selective trapping of one of the two carbenes may reflect differences in any one of the pairs of rates k_1/k_1', k_{-1}/k_{-1}', or k_2/k_2', or indeed in more than one of the rates. It is not clear why there should be a marked increase in k_2 relative to k_2'; the proximity of the phenyl group to the carbene centre in (**6**) may lead to a stabilizing interaction reducing k_{-1} relative to k_{-1}', but this same effect might be expected to reduce k_2 relative to k_2'. An alternative explanation would involve substituent control of k_1 and k_1'; the formation of planar carbenes (**6**) and (**8**) from (**1**) involves a formal monorotation with close similarity to the cyclopropyl–allyl cation electrocyclic rearrangement. Although many analyses of electrocyclic reactions assume stereocontrol of the process, recent calculations have suggested that electronic factors are more important.[11]

The addition of vinylcarbenes to α,β-unsaturated esters has been shown in certain cases to lead to products with alkene and ester groups *cis*-related,[12] although the reaction appears to be highly dependent on substituents and in other cases leads predominantly to *trans*-products.[13] Nonetheless, the reaction leading to (**9**) does represent a highly stereocontrolled trapping of a carbene.

Experimental

All new compounds were homogeneous by t.l.c. and/or g.l.c., unless otherwise stated. Column chromatography was carried out using Merck Kieselgel 60 7736 eluting with light petroleum (b.p. 40—60 °C). N.m.r. spectra were run in solution in $CDCl_3$ and recorded at 200 or 300 MHz for ^{1}H and the corresponding frequencies for carbon on Bruker Spectrospin instruments. I.r. spectra were obtained on a Nicolet 20SX Fourier transform spectrometer, while mass spectra were recorded on an AEI MS9 or Kratos MS80 instrument, using the E.I. method. Melting points are uncorrected.

1,1-*Dichloro*-2-*methyl*-3-*phenylprop*-1-*ene*.—1,1,3-Trichloro-2-methylprop-1-ene (15.0 g) was added carefully to phenylmagnesium bromide prepared from bromobenzene (17.7 g) and magnesium (3.0 g) in dry tetrahydrofuran (15 ml). The products were refluxed for 2 h and then stirred for 18 h at 20 °C. The

products were quenched with water, 15% hydrochloric acid was added to dissolve the precipitate, and the aqueous layer was saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (2 × 40 ml). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (30 ml) and brine (30 ml), and dried; the solvent was removed at 14 mmHg to give an oil which was distilled to give the *title compound* (13.2 g, 70%), b.p. 66 °C at 0.4 mmHg (Found: M^+, 200.0140. $C_{10}H_{10}Cl_2$ requires M, 200.0159) which showed δ_H 7.02 (5 H, s), 3.55 (2 H, s), and 1.8 (3 H, s); $\nu_{max.}$ 3 062, 3 030, 2 918, 1 624, 1 599, 1 481, 737, and 698 cm^{-1}.

3-*Benzyl*-1,1,2,2-*tetrachloro*-3-*methylcyclopropane*.—Sodium hydroxide (20 g) in water (20 ml) was stirred vigorously with 1,1-dichloro-2-methyl-3-phenylprop-1-ene (10 g) and cetrimide (1 g) in chloroform (75 ml). After 48 h at 20 °C the products were extracted with water (3 × 50 ml); the aqueous layer was washed with dichloromethane (3 × 100 ml). The combined organic layers were washed with brine (100 ml), dried, and the solvent was removed at 14 mmHg. The residue was purified by column chromatography over silica, eluting with light petroleum, and characterised as the *title compound*, m.p. 45—47 °C (7.6 g, 54%) (Found: M^+, 281.9525; C, 46.45, H 3.4. $C_{11}H_{10}Cl_4$ requires M, 281.9537; C, 46.51; H, 3.54%) which showed δ_H 7.15 (5 H, br s), 2.9 (2 H, s), and 1.18 (3 H, s); $\nu_{max.}$ 1 453, 1 200, 863, 725, and 698 cm^{-1}.

3-*Benzyl*-1,2-*dichloro*-3-*methylcyclopropene*.—Methyl-lithium (1.5M; 1.3 ml) was added over 1 min to a stirred solution of 3-benzyl-1,1,2,2-tetrachloro-3-methylcyclopropane (0.5 g, 1.76 mmol) in ether (5 ml) under nitrogen at 0 °C. After 0.5 h the reaction mixture was quenched with water (1 ml) at −40 °C; the organic layer was washed with water (1 ml) at that temperature, and the solvent was removed carefully at 14 mmHg to give the *title compound* (0.29 g, 77%) (Found: M^+, 212.0139. $C_{11}H_{10}Cl_2$ requires M, 212.0160) which showed δ_H 7.1 (5 H, br s), 2.89 (2 H, s), and 1.23 (3 H, s); $\nu_{max.}$ 2 917, 2 856, 1 494, 1 451, 1 375, 918, 737, 699 cm^{-1}.

(*Z*,*E*)-1,2-*Dichloro*-3-*methyl*-4-*phenylbuta*-1,3-*diene*.—3-Benzyl-1,2-dichloro-3-methylcyclopropene (1.0 g) was allowed to stand at 20 °C in deuteriochloroform (5 ml) for 36 h; no starting material then remained. The solvent was removed at 14 mmHg to leave an oil which was purified by column chromatography over silica, eluting with light petroleum to give a colourless oil characterised as the *title compound* (0.35 g, 35%) (Found M^+, 212.0170. $C_{11}H_{10}Cl_2$ requires M, 212.0159) which showed δ_H 7.29 (5 H, s), 7.11 (1 H, s), 6.58 (1 H, s), and 2.07 (3 H, s); δ_C 138.8, 136.9, 131.8, 130.9, 129.5, 128.4, 127.5, 116.4, and 15.8; $\nu_{max.}$ 1 694, 1 494, 1 026, 868, 749, and 699 cm^{-1}. A second fraction (*ca.* 0.2 g) showed a very complex n.m.r. spectrum.

1,6-*Dichloro*-2-*methyl*-3-*phenylcyclohexene*-4,4,5,5-*tetracarbonitrile*.—1,2-Dichloro-3-methyl-4-phenylbuta-1,3-diene (0.18 g) in dichloromethane (5 ml) was allowed to stand with tetracyanoethene (0.12 g) at 20 °C for 48 h. Removal of the solvent at 14 mmHg gave a solid which was recrystallised from ether and light petroleum to give the *title compound* (0.12 g, 39%), m.p. 159—161 °C (Found: M^+, 340.0250. $C_{17}H_{10}Cl_2N_4$ requires 340.0282) which showed δ_H 7.4 (5 H, br s), 5.1 (1 H, br s), 4.3 (1 H, br s), and 1.8 (3 H, s); $\nu_{max.}$ 2 257, 1 649, 1 457, 1 253, 1 088, 789, 736, 719, and 700 cm^{-1}. The structure of this compound was established by *X*-ray crystallography (see below).

3-*Chloro*-3-(1-*chloro*-2-*methyl*-3-*phenylprop*-1-*enyl*)*tetramethylcyclopropane*.—Methyl-lithium (1.5M; 1.09 ml) was added over 1 min to a stirred solution of 3-benzyl-1,1,2,2-tetrachloro-3-methylcyclopropane (0.41 g) in ether (5 ml) at 0 °C. After 30 min the reaction mixture was quenched with water (1 ml) at −40 °C and decanted from the ice which remained. 2,3-Dimethylbut-2-ene (2 g) was added and the mixture was allowed to stand at 20 °C for 2 h; n.m.r. spectroscopy then showed essentially complete reaction of (**1**). After 12 h, removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with light petroleum to give the *title compound* (0.36 g, 84%) (Found: M^+, 296.1098. $C_{17}H_{22}Cl_2$ requires M, 296.1098) which showed δ_H(60 MHz) 7.18 (5 H, br s), 3.85 (1 H, d, *J* 12 Hz), 3.12 (1 H, d, *J* 12 Hz), 1.65 (3 H, s), and 1.2 (12 H, s); δ_H(200 MHz) 7.15—7.4 (5 H, m), 3.89 (1 H, d, *J* 14.4 Hz), 3.18 (1 H, dd, *J* 0.7, 14.4 Hz), 1.67 (3 H, d, *J* 0.7 Hz), 1.29 (3 H, s), 1.25 (3 H, s), 1.23 (3 H, s), and 1.18 (3 H, s); in addition, there were signals for a minor isomer at δ 3.67 (1 H, d, *J* 14.3 Hz), 3.54 (1 H, d, *J* 14.3 Hz), 1.76 (3 H, s), and 1.09 (3 H, s), the remaining signals being obscured by those for the major isomer (ratio 1:5); $\nu_{max.}$ 2 922, 1 602, 1 452, 1 378, 1 191, 751, 731, and 700 cm^{-1}.

Methyl 2-*Chloro*-2-(1-*chloro*-2-*methyl*-3-*phenylprop*-1-*enyl*)-1-*methylcyclopropanecarboxylate*.—(a) Methyl-lithium (1.5M; 0.94 ml) was added over 1 min to a stirred solution of 3-benzyl-1,1,2,2-tetrachloro-3-methylcyclopropane (0.35 g) in ether (5 ml) at 0 °C. After 30 min the reaction mixture was quenched with water (1 ml) at −40 °C and decanted from the ice which remained. Methyl methacrylate (5 ml) was added and the mixture was allowed to stand at 20 °C for 12 h. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with light petroleum–ether (10:2) to give the *title compound* (0.31 g, 80%) (Found: M^+, 312.0700. $C_{16}H_{18}Cl_2O_2$ requires M, 312.0684) which $\nu_{max.}$ 2 949, 1 730, 1 454, 1 300, 1 199, and 1 164 cm^{-1}. The ^1H n.m.r. spectrum of this (300 MHz; 230 K) included all the signals present in the spectrum of the pure ester described in (b), together with some additional minor signals corresponding to the presence of *ca.* 17% of two rotamers (ratio *ca.* 1:1) of a second component: δ_H 2.35 (d, *J* 6.3 Hz), 2.30 (d, *J* 6.8 Hz), 1.33 (d, *J* 6.8 Hz), 1.91 (s), 1.68 (s), 3.34 (s), 3.70 (s), and 3.30 (d, *J* 16 Hz) in ratio 1:1:1:3:3:3:1. Other signals were presumably hidden by those of the major isomer. Increasing the temperature to 300—333 K caused the doublets at δ 2.35 and 2.30 to coalesce to a single doublet.

(b) The free acid (described below) was converted into the methyl ester by reaction with a slight excess of diazomethane in ether, followed by removal of the solvent at 14 mmHg. The ester showed δ_H(300 MHz; 330 K) 7.2—7.4 (5 H, complex), 3.9 (1 H, d, *J* 16 Hz), 3.7 (4 H, v br), 2.4 (1 H, v br), 1.7 (3 H, s), 1.6 (3 H, s), and 1.5 (2 H, br m); δ_H(300 MHz; 240 K) (rotamer 1) 7.1—7.4 (5 H, complex), 3.98 (1 H, d, *J* 15.7 Hz), 3.79 (3 H, s), 3.63 (1 H, d, *J* 15.7 Hz), 2.42 (1 H, d, *J* 6.3 Hz), 1.73 (3 H, s), 1.60 (3 H, s), 1.55 (1 H, d, *J* 6.3 Hz); (rotamer 2) 7.1—7.4 (5 H, complex), 3.93 (1 H, d, *J* 14.9 Hz), 3.68 (3 H, s), 2.94 (1 H, d, *J* 14.9 Hz), 2.32 (1 H, d, *J* 6.7 Hz), 1.64 (6 H, s), 1.38 (1 H, d, *J* 6.7 Hz) (the ratio of the rotamers was 3.3:1). The signals at 3.98 and 3.93 coalesced at 280 K; those at 3.63 and 2.94, 2.42 and 2.32, and 1.55 and 1.38 at 300 K, and others at 300—330 K.

2-*Chloro*-2-(1-*chloro*-2-*methyl*-3-*phenylprop*-1-*enyl*)-1-*methylcyclopropanecarboxylic Acid*.—The ester (1.0 g) was refluxed for 15 min with sodium methoxide [prepared from sodium (1 g)] in methanol (10 ml) and water (0.5 ml). The products were neutralised with dilute hydrochloric acid and extracted with ether (3 × 30 ml). The organic layer was dried and the solvent was removed at 14 mmHg; the residue was recrystallised from ether and light petroleum to give the *title*

compound (0.54 g, 54%), m.p. 59—61 °C (Found: M^+, 298.0525. $C_{15}H_{16}Cl_2O_2$ requires M, 298.0527) which showed δ_H(200 MHz; 293 K) 7.21—7.37 (5 H, complex), 2.34 (1 H, br), 1.71—1.58 (complex), 1.40 (1 H, v br) and (rotamer 1) 3.93 (1 H, partly hidden), 3.09 (1 H, br d, J 13.8 Hz); (rotamer 2) 3.86 (1 H, br d, J 15.1 Hz), 3.70 (1 H, br d, J 15.1 Hz), 2.45 (1 H, d, J 6.2 Hz) (ratio of rotamers 1:2); $\nu_{max.}$ 3 000—2 500 v br and 1 698s cm^{-1}. The structure of this product was determined by *X*-ray crystallography and is shown in Figure 2; atomic co-ordinates are given in Tables 1 and 2.

X-Ray Crystallography.—Crystal Data for (**4**). $C_{17}H_{10}N_4Cl_2$, M_r = 341.2. Monoclinic, $P2_1/c$, a = 11.757(2), b = 11.470(2), c = 12.233(2) Å, β = 96.05(2)°, V = 1 640.5 Å^3, Z = 4, D_c = 1.381 g cm^{-3}, $F(000)$ = 696, μ = 3.65 mm^{-1} for Cu-K_α radiation (λ = 1.54184 Å).

Crystal data for (**9**). $C_{15}H_{16}Cl_2O_2$, M_r = 299.2. Monoclinic, $P2_1/c$, a = 11.113(2), b = 12.969(3), c = 11.247(2) Å, β = 112.04(1)°, V = 1 502.5 Å^3, Z = 4, D_c = 1.322 g cm^{-3}, $F(000)$ = 624, μ = 3.92 mm^{-1} for Cu-K_α radiation.

Data collection and processing. All *X*-ray data were measured at 293 K with a Stoe–Siemens diffractometer. For compound (**4**) [for (**9**) in square brackets where different]: crystal size 0.3 × 0.5 × 0.5 [0.4 × 0.5 × 0.5] mm, cell parameters from 2θ values for 32 reflections measured at ±ω, with 2θ 30—40° [20—30°]. Intensity measurements in ω/θ scan mode with variable measuring time and width on-line profile fitting,[14] $2\theta_{max.}$ = 130°, index ranges h −13→13, k 0→13, l 0→14 [h −13→13, k 0→15, l 0→13, together with Friedel opposites, h 8→13 only]; no significant variation in three standard reflection intensities, no absorption correction. 2 764 [2 847] Reflections measured, 2 629 [2 507] unique reflections R_{int} = 0.01 [0.04], 2 167 [2 357] with $F > 4\sigma_c(F)$ for structure determination and refinement; $\sigma_c(F)$ based on counting statistics only.

Structure determination and refinement.[15] Direct methods, blocked-cascade least-squares refinement to minimise $\Sigma w\Delta^2.\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 34 - 169\ G + 269\ G^2 - 91\ S + 57\ S^2 + 238GS[\sigma_c^2(F) + 2 - 8\ G + 21\ G^2 - 3\ S + S^2 - 10\ GS]$ ($G = F_o/F_{max.}$, $S = \sin\theta/\sin\theta_{max.}$).[16] Anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atoms included with constraints: C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring angle external bisectors, O–H freely refined, $U(H) = 1.2U_{eq}(C)$ or $1.2U_{eq}(O)$. Parameters refined 212 [182], extinction $x = 9(4) \times 10^{-6}$ [$1.5(1) \times 10^{-5}$] to give $F'_c = F_c/(1 + xF_c^2/\sin 2\theta)^{0.25}$, R = 0.075 [0.039], wR = 0.081 [0.048], slope of normal probability plot = 1.34 [0.93], max. shift/e.s.d. = 0.12 [0.04], mean = 0.02 [0.01], no significant features in a final difference synthesis, scattering factors from ref. 17. Atomic co-ordinates are given in Tables 1 and 2; bond lengths and angles have been deposited as supplementary data.

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Perkins Trans. 1*, 1989, Issue 1, secton 5.

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