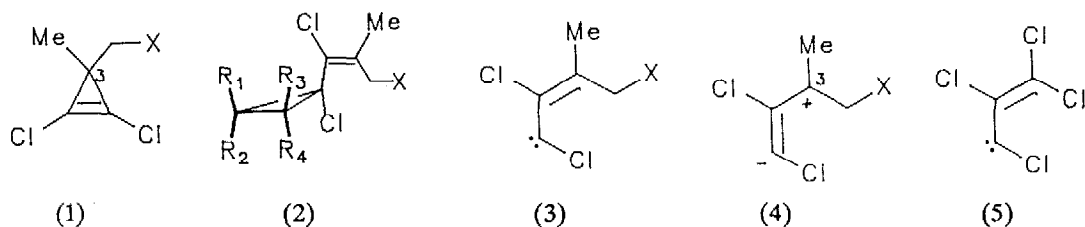


**SUBSTITUENT EFFECTS IN THE GENERATION AND TRAPPING OF
 1,2-DICHLORO-3,3-DIALKYLPROP-2-EN-1-YLIDENES**

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The ring-opening of cyclopropenes (1) to carbenes (3) occurs more readily when X is an electron releasing group, and in the case of (1, X = C₆H₄-4-Y) the rate of cyclopropanation of alkenes correlates with σ_I for Y. The selectivity of carbenes (3, X = H, OMe) towards alkenes correlates well with that for tetrachloroprop-2-en-1-ylidene.

The cyclopropene - vinylcarbene interconversion has been the subject of several theoretical,¹ and experimental studies.² In most cases, eg. 3,3-dimethylcyclopropene³ and tetrachlorocyclopropene,⁴ the ring-opening only occurs at a reasonable rate at 150 - 180 °C. However, a number of 3,3-dialkylcyclopropenes having an electron withdrawing substituent at C-1 open at ambient temperature or below.^{5,6} Thus the chlorides (1, X = H, Cl, OMe, Ph) react with alkenes R₁R₂C=CR₃R₄ at 20 °C or below to produce cyclopropanes (2) apparently derived by addition of the carbenes (3).^{6,7} Although there are a number of possible singlet and triplet structures for vinylcarbenes,¹ one possible explanation for the ease of ring-opening would invoke heterolytic cleavage to a transition state similar to (4), which could be stabilized by electron releasing substituents at C₃ and electron withdrawing ones at C₁, and which, if 90° rotation occurred at C₃, would correspond to the dipolar resonance form of the planar singlet carbene.



We now report the effect of changing the substituent at C-3 on the rate of ring opening of (1) and the selectivity of trapping of derived carbenes. The following conclusions may be drawn:

(i) The selectivity of carbenes (3, X = H, OMe) towards alkenes at 20 °C does not give a good linear correlation with that for dichlorocarbene at 20 °C, but compares better with that observed for 1,2,3,3-tetrachloroprop-2-en-1-ylidene (5) at 180 °C. Etheral solutions of the cyclopropenes (1, X = H, OMe) were allowed to stand for several hours at 20 °C with an excess of a mixture of alkenes, and the ratio of derived cyclopropanes (2, X = H or OMe) was determined by g.l.c., standardizing the responses with known mixtures of the cyclopropanes.^{6,7}

The results are summarised in the Table.

TABLE Relative Reactivities of Carbenes (3) and (5) Towards Alkenes**

	(3, X = H)	(3, X = OMe)	(5)
2,3-dimethylbut-2-ene	1.0 ⁺	1.0	1.0
2-methylbut-2-ene*	1.54	1.1	1.44
2-methylprop-1-ene	0.95	0.75	0.63
trans-but-2-ene	0.10	0.08	0.2
cis-but-2-ene*	0.48	0.34	0.64
methyl acrylate*	0.40	0.06	
methyl methacrylate*	3.22	0.81	

It is apparent that the reactivity patterns of the two carbenes (3, X = H, OMe) with alkylalkenes are very similar; indeed a plot of $\log(k/k_0)$ for one carbene against that for the other gives a straight line with a slope of 1.08, corresponding to carbenes of almost equal selectivity. However, a plot of $\log(k/k_0)$ for either species against the corresponding figures for dichlorocarbene^a does not, unlike many such plots, lead to a good linear correlation (fig. 1a). A similar plot for either of the carbenes (3, X = H, OMe) against carbene (5)^a does lead to a reasonable correlation, eg. (fig. 1b), especially when the difference in the temperatures of reaction (20 and 180 °C respectively) and slight differences in the alkenes used are taken into account;¹⁰ once again the slope corresponds to carbenes of approximately equal selectivity. It is also noteworthy that carbenes (3, X = H, OMe) react readily with electron poor alkenes, but that in the cases examined there is a marked difference in reactivity between the two species.

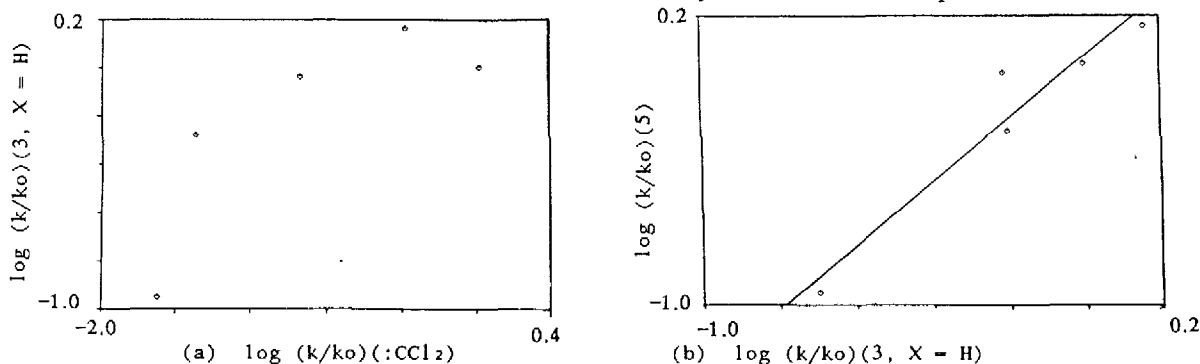
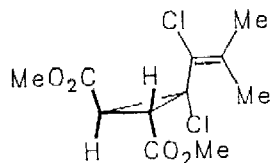
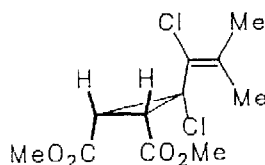


Fig.1 Relative reactivities towards alkylalkenes compared to 2,3-dimethylbut-2-ene (k_0)

(ii) Although the reactions of (1, X = H, OMe) with *cis*- and *trans*-but-2-ene are stereospecific,^{6,7} addition of (1, X = H) to dimethyl maleate is not. Reaction of the cyclopropene (1, X = H) with dimethyl fumarate led to an adduct (6) in low yield (35 %).¹¹ The reaction of dimethyl maleate with the same cyclopropene proceeded in even lower yield (17 %), but an inseparable mixture of the two adducts (6) and (7)¹² was isolated (ca. 3:2). A similar non-stereospecific addition to maleates has been reported for phenylhalocarbenes,^{13a} and for 3,3-dimethoxyvinylcarbene.^{13b}

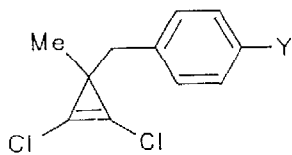


(6)

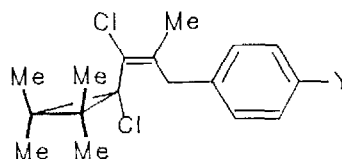


(7)

(iii) The rate of formation of the cyclopropanes (2) is not dramatically affected by the solvent. The cyclopropene (1, X = H) was allowed to stand in *d*-chloroform, *d*₆-benzene or *d*₆-acetone in the presence of excess 2,3-dimethylbut-2-ene, and the reactions were followed by n.m.r. at 283 K.⁺⁺ The disappearance of the cyclopropene in each case followed pseudo-first order kinetics, with a corresponding increase in the signals for (2). The rates of reaction in chloroform and benzene were essentially identical (ca $2 \times 10^{-2} \text{ sec}^{-1}$), while that in acetone was about twice as fast.¹⁴ The cyclopropene (1, X = Cl) is rather more stable and at the same concentrations reacts completely in ca 2h at 310 K in the presence of an alkene. Again, the reaction proceeds about 50 % faster in acetone than in chloroform or benzene ($k = 2 \times 10^{-3} \text{ sec}^{-1}$). The temperature dependence of the rate of reaction of (1, X = Cl) with 2,3-dimethylbut-2-ene in CDCl_3 between 293 and 323 K corresponds to an E_{act} of ca 61 kJ/mol, very much lower than those reported for simple alkylcyclopropanes.¹⁵



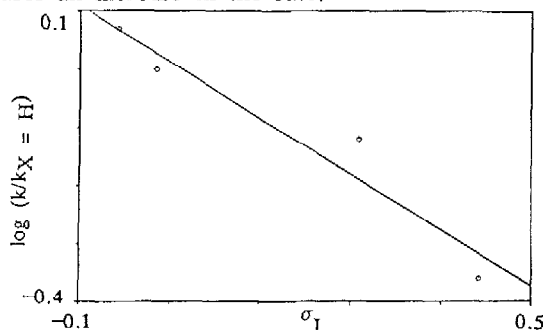
(8)



(9)

(iv) The rate of reaction of cyclopropanes (8) with 2,3-dimethylbut-2-ene to give cyclopropanes (9) can be correlated with the electronic character of the *p*-substituent. Equimolar quantities of pairs of cyclopropanes (8) were allowed to react with excess 2,3-dimethylbut-2-ene in *d*-chloroform at ambient temperature and the reactions were followed by n.m.r. using the signal for the benzylic methylene groups. In each case a plot of $\log(c)$ versus time gave a good linear correlation, the relative rates being in the order $\text{Me} > \text{H} > \text{MeO} > \text{CF}_3$ (ca. 19:16:12:7). A plot of $\log(k_Y/k_{Y=H})$ for the rates compared to that for (8, Y = H) against σ_I for the substituent,¹⁶ gives a reasonable correlation, with a ρ -value of -0.8 (fig.2), corresponding to a reaction in which electron release at C_3 causes an increase in the rate.

Fig. 2
The effect of substituents
on the rate of formation of
cyclopropanes (9) as a
function of σ_I of Y



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1. For a recent study see N.Honjou, J.Pacansky and M.Yoshimine, *J.Amer.Chem.Soc.*, 1984, 106, 5361.
 2. For a recent review see B.Halton and M.G.Banwell, "Cyclopropenes", in *The Chemistry of Functional Groups, Cyclopropanes, Part II*, Ed. Z. Rappoport, Wiley, 1988.
 3. A.deMeijere, S.Untiedt and R.Walsh, personal communication; R.Srinivasan, *J.Chem.Soc., Chem.Comm.*, 1971, 1041.
 4. W.Weber and A.deMeijere, *Angew.Chem.Int.Edn.Engl.*, 1980, 19, 138.
 5. See eg., M.Franck-Neumann and J.J.Lohmann, *Tetrahedron Letters*, 1979, 2397; *Angew.Chem. Int.Edn.Engl.*, 1977, 16, 323.
 6. (a) M.S.Baird, S.R.Buxton and J.S.Whitley, *Tetrahedron Letters*, 1984, 1509; (b) M.S.Baird and H.H.Hussain, unpublished results.
 7. M.S.Baird and J.Al-Dulayymi and W.Clegg, *Tetrahedron Letters*, 1988, 6149.
 8. The values used were the same as those quoted in R.A.Moss, M.A.Joyce and J.K.Huselton, *Tetrahedron Letters*, 1975, 4621.
 9. R.R.Kostikov and A.deMeijere, *J.C.S.Chem.Comm.*, 1984, 1528.
 10. The alkenes quoted in ref.9 are in some cases slightly different from those used in the present work and those in ref.8; the figures quoted for *cis*- and *trans*-hexene and 2-methyl-but-1-ene are assumed to be close to those for *cis*- and *trans*-but-2-ene and isobutene.
 11. This showed δ_{H} (200 MHz, 303K) 3.78 (3H, s), 3.69 (3H, s), 2.99 (1H, d, J 7.3 Hz), 2.90 (1H, d, J 7.3 Hz), 1.96 (3H, s), 1.83 (3H, s).
 12. Although the coupling constant for the ring hydrogens (10.8 Hz) shows them to be *cis*- to each other, it is not clear whether they are *cis*- or *trans*- to the alkene; the fact that the ^{13}C n.m.r. shows restricted rotation at 233 K may support an all *cis*-arrangement.
 13. (a) M.P.Doyle, J.W.Terpstra and C.H.Winter, *Tetrahedron Letters*, 1984, 901; (b) P.Binger and B.Biedenbach, *Chem.Ber.*, 1987, 120, 601.
 14. In each case the cyclopropene reacted even in the absence of an alkene, but at a much lower rate; the products will be described elsewhere. An examination of the rate in methanol was not possible because the cyclopropene (1, X = H) reacts rapidly with this solvent to produce Z-1,2-dichloro-3-methoxy-3-methylbut-1-ene, possibly by proton abstraction from the solvent by (3, X = H) and solvation.
 15. For a summary of these values see M.G.Steinmetz, R.Srinivasan and W.J.Leigh, *Rev.Chem.Intermed.*, 1984, 5, 57.
 16. R.A.Y.Jones, *Physical and Mechanistic Organic Chemistry*, Cambridge, 1979.
- + The ratio of the rate for each alkene compared to 2,3-dimethylbut-2-ene (k/k_0), as determined by the ratio of cyclopropanes produced.
- * The relative reactivity quoted is based on a combination of both stereoisomers of product for the unsymmetrical alkylalkenes; the esters gave a single stereoisomer about the cyclopropane ring, believed to have the vinyl and ester groups *cis*-.^{6b,7}
- ** For simplicity, it is assumed at this stage that the sets of reactions involve trapping of common intermediates.
- ++ Reactions were carried out with standard concentrations of cyclopropane and alkene.

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