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METHOXYCHLOROCARBENE

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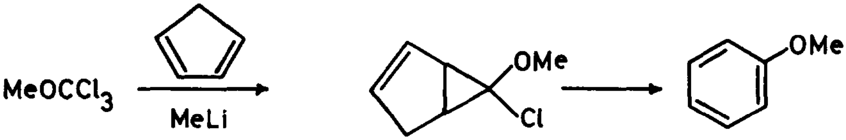
Carbenes have been classified as falling into two general categories, being either electrophilic (the great majority) or nucleophilic (e.g. $(MeO)_2C:$);[1] but there are almost no examples of carbenes showing the ambiphilic character to be expected from the singlet structure expressed as $R_2C^{\pm}$. It seemed to us that methyoxychlorocarbene (1) should possess the right combination of substituents to fall into this category.

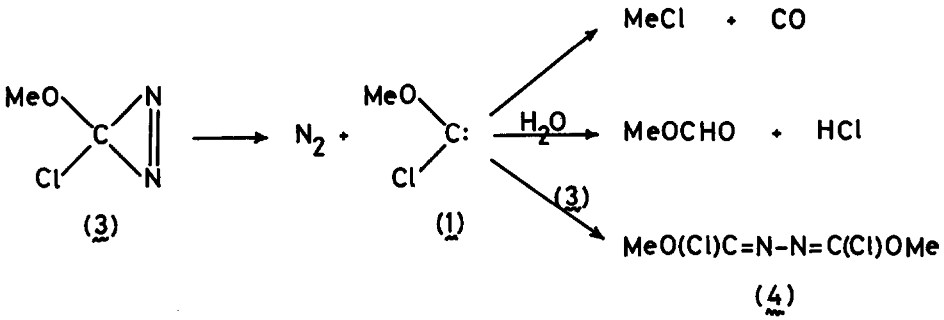
Although alkoxyhalocarbenes have been postulated as intermediates in the alkaline hydrolysis of haloforms since the pioneering work of Hine[2] and Skell,[3] only one report of their capture by an alkene has been made,[4] despite the many thousands of dihalocyclopropanations that have been carried out. Schöllkopf and Paust[4] generated (1) by the action of methyllithium on trichloromethyl methyl ether and in the presence of cyclopentadiene obtained anisole, presumably via (2). Their route is inconvenient, involving strongly basic media, and is not readily adapted to a variety of alkyl groups. We find that



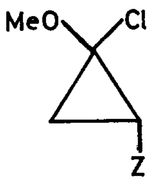
(2)

3-chloro-3-methoxydiazirine (3) can be easily prepared from O-methyl isourea toluene-p-sulphonate using Graham's method for 3-alkyl-3-chlorodiazirines.[5] Although (3) can decompose explosively at 20° when condensed as a pure liquid, it can be safely handled in solution or the gas phase. Like all diazirines, it is chemically very inert,[6] permitting its use under a wide variety of conditions. In solution, (3) decomposes smoothly at temperatures between 20 and 50° in a first order manner at rates from 6×10^{-5} to 8×10^{-4} sec^{-1}, with formation of N_2, CO, MeCl and MeOCHO and the cis and trans azines (4).[7] The products indicate the formation of methoxychlorocarbene (Scheme 1) which either decomposes unimolecularly or is intercepted by water or by (3).

SCHEME 1

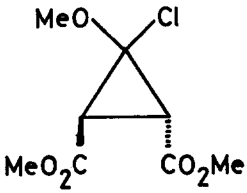


In the presence of electrophilic olefins such as ethyl acrylate and acrylonitrile, (1) is trapped in 25 and 40% yield respectively, as a mixture of the *syn* and *anti* 2-chloro-2-methyoxycylopropanes (5 *a*,*b*).[8,9] Trapping with dimethyl fumarate gave (6) as the sole cyclic product,[10] suggesting a stereospecific reaction; although we were unable to form an adduct with dimethyl maleate to confirm this. These reactions clearly show the nucleophilic properties to be expected from the contribution of canonical form (7) to the singlet state resonance hybrid of MeOCCl (cf $(MeO)_2C:$).[11]

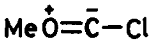


(5) *a* Z = CO_2Et

b Z = CN



(6)

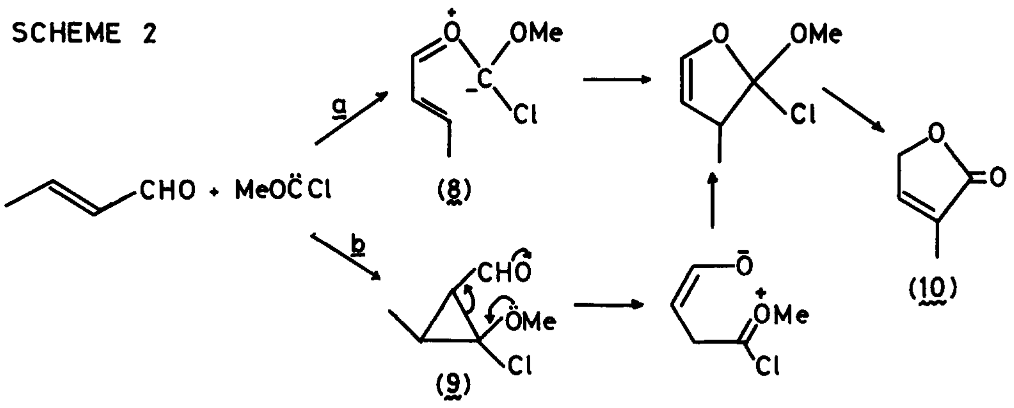


$Me\overset{+}{O}{=}\overset{-}{C}{-}Cl$

(7)

On the other hand, (1) also reacts as an electrophile, adding to diphenylacetylene to afford 1,2-diphenylcyclopropanone, and with alcohols to give the corresponding formates. The major product from reaction with crotonaldehyde is the butenolide (10), which may arise by initial attack at oxygen to give the carbonyl ylid (8) followed by the electrocyclic closure shown on Scheme 2 (route *a*). Alternatively, (10) may be formed by initial cyclopropanation (9), followed by a vinylcyclopropane type rearrangement (route *b*). In view of the thermal stability of (5*a*,*b*) and of (6), as well as the known [3,2] sigmatropic reactions of α-carbena allyl thioethers,[12] and of the ylids derived from allyl methyl ether with carbomethoxycarbene,[13] and from allyl thioethers with allenylidene,[14] we favour route *a*. Assuming that this path is correct, it would appear to show that (1) is somewhat more electrophilic than nucleophilic.

SCHEME 2



These results clearly establish methoxychlorocarbene as a potentially ambiphilic carbene of great importance. The ambiphilic character may be anticipated from the recent m_{CXY} treatment of Moss and his colleagues,[15] where the predicted value for MeOCCl (1.59) lies between those of the electrophilic CF_2 (1.48) and the nucleophilic $(MeO)_2C$ (2.22).[16]

Finally, we would report that neither in the gas phase (20 torr), nor in solution did we observe any products which would have arisen from intramolecular migration or insertion in MeOCCl.[17] This is surprising in view of the reports that such products have been found in cases where alkoxyhalocarbenes have been proposed as intermediates,[18] and would cast some doubt on the paths suggested for their formation.

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References and Notes

1. W. Kirmse, "Carbene Chemistry", 1st Edition, Academic Press, London, 1964; R.A. Moss in "Carbenes", Vol 1, M. Jones, Jr., and R.A. Moss, Ed., Wiley-Interscience, New York and London, 1973, p 153.
2. J. Hine, E.L. Politzer and H. Wagner, J. Amer. Chem. Soc., 1953, **75**, 5607.
3. P.S. Skell and I. Starer, J. Amer. Chem. Soc., 1959, **81**, 4117.
4. U. Schöllkopf and J. Paust, Chem. Ber., 1965, **98**, 2221.
5. W.H. Graham, J. Amer. Chem. Soc., 1965, **87**, 4396.
6. See inter alia, G.L. Bradley, W.B.L. Evans and I.D.R. Stevens, J.C.S. Perkin II, 1977, 1214; R.F.R. Church and M.J. Weiss, J. Org. Chem., 1970, **35**, 2465.
7. In the gas phase at 30°, $\Delta H^{\neq} = 99.1 \pm 3.3$ k J mol^{-1}, $\Delta S^{\neq} = 3.5$ J K^{-1} mol^{-1}; see also N.P. Smith and I.D.R. Stevens, J.C.S. Perkin II, (in press).
8. The diazirine was condensed into ether at -78° and then added to a solution of the alkene in ether. Yields are isolated yields of adducts. All new compounds gave satisfactory analytical and spectroscopic data.
9. (**5a**) was a 3:1 mixture of isomers and showed cyclopropyl protons form 7.50 to 8.50 τ two superimposed ABC systems. (**5b**) was a 1.3:1 mixture of isomers, separable by g.l.c. Each isomer had cyclopropyl protons at 7.70 to 8.40 τ analysed as an ABC system.

10. (**6**) had ^{1}H nmr signals (100 MHz, CCl$_4$) at τ 6.31 (s, 3H, CO$_2$Me), 6.32 (s, 3H, CO$_2$Me) 6.50 (s, 3H, OMe), 7.18 (s, 2H, cyclopropyl CH$_2$).

11. R.W. Hoffmann, E. Lilienblum and B. Dittrich, *Chem. Ber.*, 1974, **107**, 3395;
R.W. Hoffmann and M. Reiffen, *ibid*, 1976, **109**, 2565.

12. D.A. Evans and C.L. Sims, *Tetrahedron Letters*, 1973, 4691.

13. W. Ando, Y. Saiki, and T. Migita, *Tetrahedron*, 1973, **29**, 3511.

14. D. Michelot, G. Linstrumelle and S. Julia, *Chem. Comm.*, 1974, 10.

15. R.A. Moss, C.B. Mallon and C. -T. Ho, *J. Amer. Chem. Soc.*, 1977, **99**, 4105.

16. See accompanying Communication.

17. Expected products would be acetyl chlroide and 2-chloro-oxiran or their transformation products.

18. C.W. Martin and J.A. Landgrebe, *Chem. Comm.*, 1971, 15;
C.W. Martin, J.A. Landgrebe and E. Rapp, *ibid*, 1971, 1483.