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FORMATION OF A DIPOLAR ADDUCT IN THE REACTION OF ARYLCHLOROCARBENES WITH DIETHYL MALEATE

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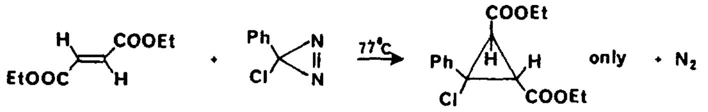
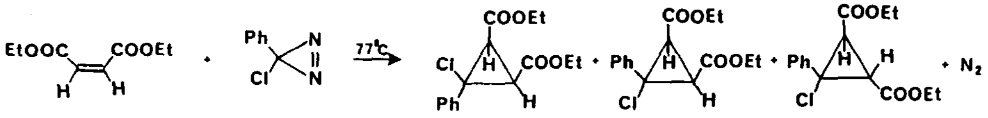
Summary: Non-concerted addition of arylchlorocarbenes to diethyl maleate, accompanied by isomerization of maleate to fumarate, is consistent with an intermediate carbene-alkene dipolar adduct.

Carbene philicity has been defined with reference to relative reactivities for carbene addition to alkenes.[1] Preferential addition to "electron-rich" olefins is consistent with an electrophilic carbene, whereas enhanced reactivity for addition to electrophilic alkenes such as α,β-unsaturated esters and nitriles is associated with nucleophilic carbenes. When relative reactivities for carbene addition display a parabolic dependence on alkene ionization potential, the carbene is regarded as ambiphilic.[2] We were therefore surprised to find that chlorophenylcarbene, generated from the corresponding diazirine and belonging to the classification of electrophilic carbenes,[3] underwent addition with electrophilic alkenes to form the corresponding cyclopropane compounds in high yield.[4] Furthermore, the relative reactivity of this carbene towards a combination of the nucleophilic n-butyl vinyl ether and the electrophilic ethyl acrylate was very close to unity.

Decomposition of 3-chloro-3-phenyldiazirine in the presence of diethyl fumarate and diethyl maleate provided results of special significance.[4] With diethyl fumarate (DEF) only one cyclopropane product was produced, and its structure retained the trans geometry of the carboethoxy groups (eq. 1, Ar = Ph). However, reaction with diethyl maleate (DEM) under the



(1)



2a 2b 1

(2)

same conditions produced three cyclopropane products: two that retained the cis geometry of the reactant olefin and one in which the carboethoxy groups were trans (eq. 2, Ar = Ph). This rearrangement demanded the intervention of a reaction intermediate with sufficient lifetime to allow bond rotation to occur. Since formation of **1** from thermal decomposition of 3-chloro-3-phenyldiazirine could not be attributed to diethyl fumarate in the maleate reactant or to dipolar addition, followed by dinitrogen extrusion, from isomerization of the diazirine to the corresponding diazo compound, we suggested the formation of a ylide intermediate. We have reexamined this reaction system and now report convincing evidence for the reversible production of a σ-complex with sufficient lifetime to cause isomerization of maleate to fumarate as well as to allow formation of both **1** and **2**.

Our first indication that ylides were not causative intermediates in reactions of chlorophenylcarbene with α,β-unsaturated esters was obtained from laser kinetic studies on the reaction of substituted chlorophenylcarbenes with diethyl fumarate.[5] Absolute rate constants for ArCCl addition were 1.0×10^8 $M^{-1}s^{-1}$ (Ar = $\underline{p}$-$NO_2C_6H_4$), 3.8×10^6 $M^{-1}s^{-1}$ (Ar = C_6H_5), and 6.3×10^5 $M^{-1}s^{-1}$ (Ar = $\underline{p}$-$MeOC_6H_4$), and this trend is in agreement with electrophilic carbene addition. Furthermore, we have found that the reactivities of α,β-unsaturated esters towards chlorophenylcarbene[6] relative to nucleophilic alkenes such as styrene and cyclohexene were independent of both the absolute amount of ester and the molar ratio of the two olefinic components. Linear relationships were observed between the mole ratio of cyclopropane products and the mole ratios of olefin reactants with intercepts at the origin; reactivities relative to ethyl acrylate were 4.4 (styrene), 1.5 (diethyl fumarate), 0.8 ($\underline{n}$-butyl vinyl ether), and 0.8 (cyclohexene). If a ylide was the reaction intermediate, a square dependence on the concentration of ester should have been observed. Finally, based on recent developments with hypervalent iodide (iodide ylides) reported by Moriarity,[7] iodobenzene was employed as a potential trap for chlorophenylcarbene, but there was no noticeable influence on relative reactivity even when the molar amount of iodobenzene was 100-times that of 3-chloro-3-phenyldiazirine and 10-times that of the ester.

Reactions of chlorophenylcarbene with diethyl maleate were investigated in detail, and careful examination of all of the reaction products revealed the full extent of the rearrangement process. The diethyl maleate reactant was isomerically pure (DEM/DEF = 330). Thermal and photochemical decomposition of the diazirine in carbon tetrachloride containing 3- to 9-fold excesses of DEM produced the results reported in Table 1. The combined yields of **1** and **2** ranged from 14 to 30 percent, depending on the molar excess of DEM employed. Both dimeric 1,2-dichloro-1,2-diphenylethene and azine products[8] accounted for the residual carbene. Particularly noteworthy is the observation that DEM is isomerized to DEF during the course of the reaction. Control experiments established that isomerization did not occur in the absence of the diazirine under either the photochemical conditions employed for diazirine decomposition or even after heating in carbon tetrachloride under reflux for 3 days. Furthermore, product ratios and the DEM/DEF ratio were not altered with extended reaction times after

Table 1. Decomposition of 3-Chloro-3-aryldiazirines in the Presence of Diethyl Maleate[a]

Diazirine			Rel. Yield, %					
Ar =	Method	DEM/DEF	**1**	**2a**	**2b**	**2/1**	**2a/2b**	DEF/**1**
C_6H_5	thermal, 77°C	68	13	62	25	6.7	2.5	2.0
	hν, 40°C	130	10	70	20	10	3.5	2.1
$\underline{p}$-$NO_2C_6H_4$	thermal, 77°C	21	27	54	19	2.7	2.8	2.1
	hν, 40°C	37	24	62	14	3.2	4.4	2.6
$\underline{m}$-$NO_2C_6H_4$	thermal, 77°C	76	12	68	20	7.3	3.4	3.1

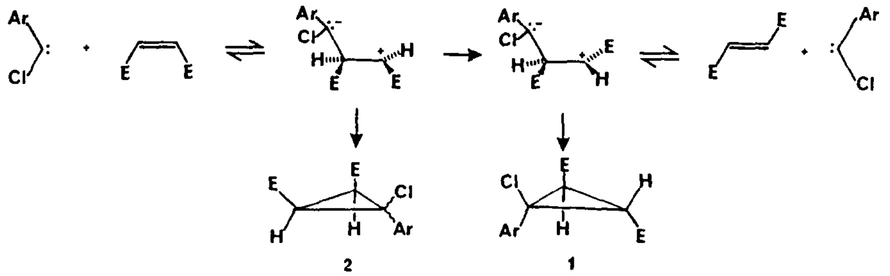
[a] Results reported for reactions performed in CCl_4 with DEM/diazirine of 3.0.

diazirine decomposition was complete. Unreacted DEM and DEF were recovered intact.

Neither of the stereoisomer ratios, **2/1** or **2a/2b**, changed with the reactant ratio (DEM/diazirine), and the DEF/**1** ratio was independent of the molar ratio of reactants, the latter observation indicating that formation of **1** and isomerization of DEM are intimately related. Furthermore, both the formation of **1** and isomerization of DEM are enhanced by the p-nitro substituent (Table I). That the increase in rearrangement/isomerization observed with the p-nitro-substituted diazirine is not the result of a direct interaction of the nitro group with the carbene is seen from the results reported for the corresponding m-nitrophenyldiazirine which closely approximate those obtained from decomposition of 3-chloro-3-phenyldiazirine.

These results are consistent with the formation of a carbene-alkene dipolar adduct whose lifetime is sufficiently long so that bond rotation can occur. Turro and Moss have described weakly interacting carbene-alkene complexes as encounter pairs that are stabilized by weak charge-transfer interactions,[9] but Liu has proposed a similar dipolar carbene-alkene adduct to explain alkene-dependent 1,2-hydrogen migrations of benzylhalocarbenes.[10] Results from the DEM-PhCCl system add a new dimension to these dipolar adducts: bond rotation and carbene-alkene dissociation (Scheme I). Since the molar ratio of DEF to **1** is constant, carbene disso-

Scheme I



ciation after bond rotation has occurred must be competitive with ring closure to form **1**. Furthermore, stabilization of the dipolar adduct by the p-nitro substituent would be expected, and the yields of both **1** and DEF from reactions with chloro-p-nitrophenylcarbene are predicted and observed to increase relative to those from reactions with chlorophenylcarbene. The charge-reversed dipolar adduct, although appearing to be a more suitable representation for the reaction intermediate, is not in accord with the electrophilic character of ArCCl or with the influence of the carbene p-nitro substituent on product ratios (Table 1).

The mechanism proposed in Scheme I explains a growing list of rearrangements that occur during reactions of carbenes with alkenes.[11-13] The recent report of the isomerization of trans-cyclooctene to cis-cyclooctene during addition of CBr_2, but not of CCl_2,[12] compliments our observation of DEM isomerization and suggests that the formation of discrete carbene-alkene dipolar adducts may be a more common occurrence than previously envisioned.

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REFERENCES AND NOTES

1. (a) Moss, R.A.; Jones, M., Jr. In "Reactive Intermediates" Vol. 3; Jones, M., Jr.; Moss, R.A., Eds.; Wiley: New York, 1985. (b) Moss, R.A. Acc. Chem. Res. **1980**, 13, 58.
2. (a) Moss, R.A.; Perez, L.A. Tetrahedron Lett. **1983**, 24, 2719. (b) Moss, R.A.; Fedorynski, M.; Shieh, W-C. J. Am. Chem. Soc. **1979**, 101, 4736.
3. Cox, D.P.; Gould, I.R.; Hacker, N.P.; Moss, R.A.; Turro, N.J. Tetrahedron Lett. **1983**, 24, 5313.
4. Doyle, M.P.; Terpstra, J.W.; Winter, C.H. Tetrahedron Lett. **1984**, 25, 901.
5. Liu, M.T.H.; Subramanian, R. Tetrahedron Lett. **1985**, 26, 3071.
6. Generated from 3-chloro-3-phenyldiazirine in carbon tetrachloride at 77°C.
7. Moriarity, R.M.; Bailey, B.R., III; Prakash, O.; Prakash, I. J. Am. Chem. Soc. **1985**, 107, 1357.
8. Liu, M.T.H.; Ramakrishnan, K. Tetrahedron Lett. **1977**, 3139.
9. Gould, I.R.; Turro, N.J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N.P.; Lehr, G.F.; Moss, R.A.; Cox, D.P.; Guo, W.; Munjal, R.C.; Perez, L.A.; Fedorynski, M. Tetrahedron **1985**, 41, 1587.
10. (a) Liu, M.T.H.; Subramanian, R. J. Phys, Chem. **1986**, 90, 75. (b) Liu, M.T.H. J. Chem. Soc., Chem. Commun. **1985**, 982.
11. Lambert, J.B.; Larson, E.G.; Bosch, R.F. Tetrahedron Lett. **1983**, 24, 3799.
12. Dehmlow, E.V.; Kramer, R. Angew. Chem. Int. Ed. Engl. **1984**, 23, 706.
13. Yang, N.C.; Marolewski, R.A. J. Am. Chem. Soc. **1968**, 90, 5654.

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