Interception of Alkylchlorocarbenes

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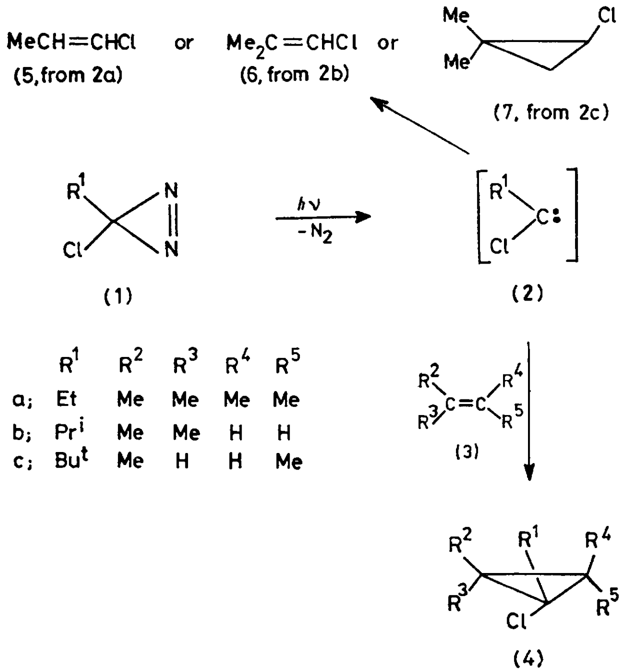
Summary Ethylchloro-, isopropylchloro-, and t-butylchloro-carbenes have been generated by photolysis of the corresponding 3-alkyl-3-chlorodiazirines and added to several alkenes; the partition between intermolecular interception and intramolecular liquidation of the carbenes was mainly dependent on the structure of the carbenic alkyl groups.

Coincidental to the determination of activation parameters for the thermal decompositions of 3-alkyl-3-chlorodiazirines (**1a**—**c**) to alkylchlorocarbenes (**2a**—**c**),[1,2] it was reported that (**2a**) did not add to cyclohexene,[2] and that (**2c**) was not intercepted by (gaseous) ethene.[1] Indeed, it is generally accepted that if a singlet carbene has an internal insertion or cycloaddition available, it will not be possible to trap it efficiently with an external reagent.[3] However, our recent successful capture[4] of the elusive[5] cyclopropylchlorocarbene, together with our previous finding of easy olefinic interception of methylchlorocarbene,[6] encouraged us to survey the potential addition reactions of (**2a**—**c**); *cf.*, Scheme. Contrary to expectations,[1–3] two of these carbenes could be efficiently intercepted by simple alkenes.

The diazirines (**1a**—**c**) were generated[7] from the corresponding alkylamidinium chlorides,[8] and condensed into alkenes at −78 or −120 °C. Olefinic solutions of (**1**) (*ca.* 1 M) were photolysed in Pyrex vessels at −20 °C with a focused Osram 200 W XE mercury lamp; decompositions of 2—13 mmol of (**1**), monitored by nitrogen evolution, required 2—8 h. Careful removal of excess of alkene, followed by n.m.r. scrutiny and g.l.c. analysis and purification (SF-96), revealed the products indicated in the Scheme, with the absolute yields reported in the Table.



Ethylchlorocarbene (**2a**) added readily to the alkenes (**3a**—**c**), affording the appropriate 1-ethyl-1-chlorocyclopropanes (**4a**—**c**),[†] in each case accompanied by the intramolecular hydride-shift products, *cis*- and *trans*-1-chloropropene (**5**).[1,2] Intermolecular addition was more efficient than intramolecular rearrangement (Table), except with (**3a**), where steric effects appear to be important (see below).

Table. Inter- and intra-molecular reactions of alkylchlorocarbenes.[a]

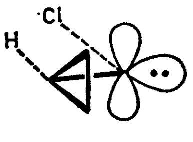
		Intermol. reaction		Intramol. reaction	
Carbene (**2**)	Substrate (**3**)	Product (**4**)	Yield (%)[b]	Product	Yield (%)[b]
a	**a**	**a**(R^1=Et)	30	(**5**)	54
,,	**b**	**b** ,,	35	,,	10
,,	**c**	**c** ,,	42	,,	8
,,	None[c]	—	—	,,	78
b	**a**	**a**(R^1=Pr^i)	d	(**6**)	96
,,	**b**	**b** ,,	8	,,	70
,,	**c**	**c** ,,	7	,,	47
,,	None[c]	—	—	,,	84
c	**a**	**a**(R=Bu^t)	d	(**7**)	e
,,	**b**	**b** ,,	37	,,	2[f]
,,	**c**	**c** ,,	79	,,	<1

[a] Photolyses (λ >300 nm) of *ca.* 1 M solutions of the diazirines (**1a**—**c**) were carried out at −20 °C. [b] Yields are based on mmol of products, as determined by n.m.r. analyses of crude reaction residues against internal $CHCl_3$ standards, relative to the mmol of N_2 evolved during the photolyses. Yields calculated relative to the amidinium salt precursors of (**1a**—**c**) were generally 25—33% of the tabulated values. Azine formation (**2** + **1**) accounts for a substantial part of the material loss. [c] The diazirine was photolysed in pentane. [d] Product (**4a**) could not be detected. [e] See text. [f] This product was analysed by quantitative g.l.c.

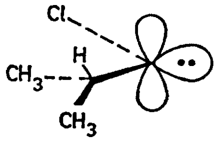
[†] Structures were established by consistent i.r. and n.m.r. spectra, as well as acceptable C, H, and Cl microanalyses or exact (±0·002 m.u.) mass spectroscopic determinations of M^+. Preliminary experiments indicated that photolytically or thermally (83 °C) generated (**2a**) also added to cyclohexene.

An opposite picture emerged for isopropylchlorocarbene (**2b**). No adduct could be obtained from the olefin (**3a**) and, although addition of the carbene did occur with the substrates (**3b**) and (**3c**),‡ formation of the intramolecular hydride-shift product, 1-chloro-2-methylpropene (**6**),[9] was strongly dominant.

Finally, although t-butylchlorocarbene was too hindered to add to (**3a**), it was readily intercepted by the olefins (**3b**) and (**3c**). Here, the addition was far more efficient than intramolecular γ-insertion leading to 1,1-dimethyl-2-chlorocyclopropane (**7**),§ although (**2c**) generated by photolytic (as opposed to gas phase thermal[1]) decomposition of (**1c**) appears reluctant to form (**7**). The by-product which accompanied the cyclopropanes [and which was formed overwhelmingly upon photolysis of (**1c**) in n-pentane or neopentane solutions] appears to be either the azine derived from (**2c**) + (**1c**), or a decomposition product of that azine.



(8)



(9)

Excepting the case $R^1 = Pr^i$, our survey of $R\ddot{C}Cl$ shows that the other simple structural types are sufficiently long-lived to resist dominant intramolecular liquidation by 1,2-hydride shifts (R^1 = Me[6] or Et),¶ 1,2-methide shift, or γ-insertion ($R^1 = Bu^t$; the former process is slow even with $R\ddot{C}H$[3]), or ring expansion (R^1 = cyclopropyl[4]). In the latter examples, intermolecular cycloaddition is preferred unless it is opposed by heavy alkylation of the substrate *e.g.* (**3a**). It is tempting to attribute successful intermolecular interceptions of $R\ddot{C}Cl$ to resonance stabilization of the carbenes by Cl,[10] because alkyl carbenes are considerably more difficult to capture.[3]

In conclusion, two comparisons seem instructive. That 1,2-hydrogen migration in ethylchlorocarbene competes poorly against intermolecular addition, but is dominant in comparable situations for isopropylchlorocarbene, appears consistent with substantial hydride character for the migrant hydrogen, and concomitant positive charge development at the migration origin.[11] Stabilization of positive charge is needed for a competitively efficient 1,2-shift, and is more adequately available to (**2b**) than to (**2a**) ($Me_2C^{\delta+}$ *vs.* $MeCH^{\delta+}$). Moreover, the efficient intermolecular capture of cyclopropylchlorocarbene,[4] again relative to the difficulty of intercepting isopropylchlorocarbene, suggests that, whereas the former species probably adopts the 'bisected' conformation (**8**), in which stabilizing factors include the dual interactions of a chlorine lone pair and of the 'bent' σ-bonds of the cyclopropyl group with the vacant p orbital at the carbenic centre,[4] isopropylchlorocarbene, at relatively low energy cost, can adopt conformations such as (**9**), making possible a ready hydride shift.[12]

We thank the National Science Foundation, and the U.S. Public Health Service (National Cancer Institute) for financial support, and Professor J. Rosen for g.l.c.-m.s. experiments.

(*Received*, 1*st June* 1978; *Com.* 564.)

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‡ Pure (**4b**) and (**4c**) ($R = Pr^i$) were not isolated, but the presence of cyclopropyl protons in the n.m.r. spectra, and g.l.c.–m.s. parent ions at *m/e* 146 and 148 (ratio 3 : 1) leave little doubt as to the identity of these minor products.

§ Identified by n.m.r. and g.l.c. comparisons with an authentic sample prepared by addition of chlorocarbenoid to isobutene (G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1960, **82**, 5723).

¶ n-Propylchlorocarbene, presumably as a carbenoid, has been added to trimethylethylene, but in only 15% yield (S. Arora and P. Binger, *Synthesis*, 1974, 801).

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