Tetrahedron Letters,Vol.24,No.51,pp 5713-5714,1983
Printed in Great Britain

0040-4039/83 $3.00 + .00

"ELECTRONIC EFFECT ON 1,2-HYDROGEN SHIFT IN CHLOROCARBENES"

Michael T.H. Liu* and Michal Tencer

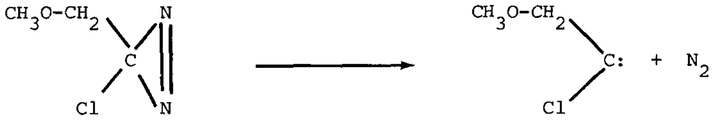
Department of Chemistry, University of Prince Edward Island

Charlottetown, Prince Edward Island Canada C1A 4P3

Summary. 1,2-hydrogen shift in chlorocarbene is accelerated by a methoxy substituent and is decelerated by a phenyl substituent at the migration origin.

Carbenes are recognized as important intermediates in a variety of thermal and photochemical processes. A characteristic for a singlet carbene is the intramolecular migration of a hydrogen atom to produce an alkene.[1] Recently it was discovered that chlorocarbenes bearing an α-hydrogen (or atoms) can nevertheless be intercepted with sufficiently nucleophilic alkenes presumably due to a stabilizing effect by the chlorine atom adjacent to the electron-deficient center.[2] It has been also implied that the H-shift occurs easier when the α-carbon carries an alkyl group. However, it is not known whether the effect is due to an inductive factor or a steric one. Su and Thornton have shown that electron releasing parasubstituents in aryl carbenes enhance H-shift.[3] Kirmse and Buschoff[4] also reported that alkoxy substituents accelerated 1,2-hydrogen rearrangement. In this communication, we use a competition technique (H shift vs intermolecular trapping by alkene and acetic acid) to demonstrate the importance of the inductive effect on 1,2-H migration in the chlorocarbene, $R_1R_2CH - \ddot{C} - Cl$.

By introducing more alkyl (R_1 and R_2 = alkyl) substituents, Moss and co-workers[2b] observed a large increase in the proportion of the intramolecular reaction. However, this increase is due to two effects acting at the same time and in the same direction. In the first place, the electron donating properties of alkyls and secondly, the steric factor which makes cyclopropanation less favorable. In order to separate these two effects, 3-chloro-3-methoxymethyldiazirine, **1**, was synthesized[5] and methoxymethylchlorocarbene, **2**, was generated thermally from **1**.



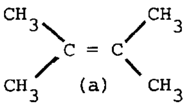
1 **2**

Values for the hydrogen shift vs intramolecular trapping by tetramethylethylene and by CH_3COOH for various chlorocarbenes are given in Table. It is observed that in the reaction of **2** with tetramethylethylene, 83% of the carbene reacted intramolecularly compared with 64% in the case of ethylchlorocarbene. The increase in carbene reaction may not be that significant, nevertheless, this demonstrates that the methoxy group promotes a better stabilization

($CH_3O>CH_3>H$) of the $\delta+$ charge developed in the transition state of the 1,2 H-shift. However, it should be borne in mind that since the methoxy group bears no α-hydrogen atoms on the oxygen, it is capable of adopting the least strained conformation[6] and is, therefore, much less sterically hindered than a methyl substituent. Hence, the electronic effect in the methoxy substituent is even more pronounced. With benzychlorocarbene, $\underset{\sim}{3}$, which was thermally generated from 3-chloro-3-benzyldiazirine[5], the reverse effect is observed: the carbene was quantitatively intercepted by the alkene. As the steric requirements of the phenyl group are large, it was also found that the trapping of chlorocarbene by acetic acid can successfully compete with the 1,2-hydrogen migration. In the reaction of carbene with acetic acid, the steric effect should play a negligible role. Thus, carbene $\underset{\sim}{3}$ is mostly intercepted by acetic acid and only ~10% of the rearrangement product is observed. On the other hand, $\underset{\sim}{2}$ rearranges completely to olefin and no acetate is observed which provides additional evidence for the importance of electronic effect in the case of the methoxy group.

The strong effect of the electron-donating group confirms the hydride-like character of the 1,2-H shift to the carbenic centre. This is in keeping with intramolecular competition of Kirmse and Buschoff[4] and the Hammett analysis of Su and Thornton[3]. It also adds support to Thornton's view that the 1,2-H shift proceeds with a definite activation barrier.

Table: Relative yields of intramolecular vs intramolecular reactions [olefin/olefin + adduct] of $R_1R_2CH\text{-}\ddot{C}\text{-}Cl$

Substituents R_1	 R_2	Substrate	 (a)	$CH_3COOH^{(b)}$	Ref.
CH_3O	H		0.83	1	This work.
Ph	H		<0.05	$0.10^{(c)}$	This work.
H	H		$0.5^{(d)}$	-	2a
CH_3	H		0.64	-	2b
CH_3	CH_3		1	-	2b

(a) Tetramethylethylene used as a solvent.
(b) Molar ratio of acetic acid to diazirine 2:1
(c) Interpolated.
(d) An approximate value pointing out to comparable yields of products.

References

(1) (a) Kirmse, Carbene Chemistry, Academic Press, New York, 1971.
(b) W.M. Jones in Rearrangements in Ground and Excited States, vol. 1 Academic Press, 1980.
(c) H.F. Schaefer 111, Acc. Chem. Res., 12, 288 (1979).
(2) (a) R.A. Moss and A. Mamantov, J. Am. Chem. Soc. 92, 6951, (1970).
(b) R.A. Moss and R.C. Munjal, J.C.S. Chem. Comm. 775 (1978).
(3) D.T.T. Su and E.R. Thornton, J. Am. Chem. Soc. 100, 1972 (1978).
(4) W. Kirmse and M. Buschoff, Chem. Ber., 100, 1972 (1978).
(5) (a) G.F. Bradley, Thesis, Univ. of Southampton, 1967. (b) W.H. Graham, J. Am. Chem. Soc. 87, 4396 (1965). Polymerization occurs when $\underset{\sim}{1}$ is photolyzed in solution.
(6) E.L. Eliel, N.L. Allinger, S.J. Angyal and G.A. Morrison, Conformational Analysis, Interscience 1966.

Acknowledgement. M.T.H.L. thanks the Natural Sciences and Engineering Research Council of Canada and the University of Prince Edward Island for financial support.

(Received in USA 8 August 1983)