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THE BARRIER FOR 1,2 HYDROGEN SHIFT IN DIALKYL CARBENES

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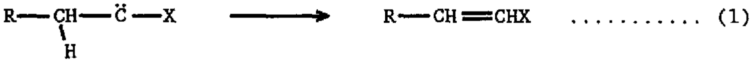
Summary The products from the thermolysis of 4-diazirinopentanoic acid (**2**) allow the estimate of an experimental value for the E_a - 1.1 ± 1 $kcal.mol^{-1}$ for the barrier height for 1,2 H shift in dialkyl carbenes.

The most common reaction of alkyl substituted carbenes is the migration of a hydrogen 1,2 to *afford* an alkene, equation (1), and much work has been *expended on* delineating the mechanism.[1]



$$R{-}\underset{H}{CH}{-}\ddot{C}{-}X \longrightarrow R{-}CH{=}CHX \quad \ldots\ldots\ldots\ldots (1)$$

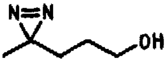
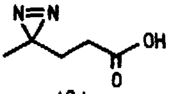
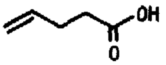
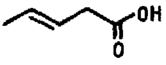
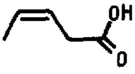
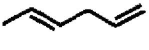
The reaction is generally acknowledged to be of the 'pull-push' type, with the migrating hydrogen suffering an electrophilic 'pull' from the vacant p orbital of the carbene centre, followed by a 'push' from the carbene lone pair with consequent rehybridisation to alkene.[1,2] Theoretical calculations have confirmed this pathway and have deduced barriers to rearrangement ranging from zero to 27 $kcal.mol^{-1}$.[3-7] The original zero value,[3] obtained using the semi-empirical MINDO method, was considered unreliable due to the known deficiency of MINDO in favouring cyclic structures. Ab initio methods initially gave large values,[2,5] but more sophisticated calculations involving polarisation functions and correlation effects reduced this to 2.1 $kcal.mol^{-1}$.[6] Finally the most recent ab initio study of singlet ethylidene ($CH_3\ddot{C}H$) indicates that it is not a local minimum on the C_2H_4 potential energy surface and that rearrangement to ethylene occurs without activation.[7]

Despite these theoretical conclusions, experimental work on 1-aryl-2-diazopropanes has produced evidence in favour of a definite barrier to 1,2 H shift in dialkyl carbenes even though no value could be assigned.[8] The effect of temperature on the E:Z product ratio in the photolysis of $PhCN_2.CHMePh$ and $PhCN_2.CH_2R$ also points to the existence of a finite barrier for reaction (1) in aralkyl carbenes.[9]

By examining the competitive inter- and intra-molecular reactions of the carbenes, Liu and Subramanian have recently obtained experimental values for the barrier in $PhCH_2\ddot{C}C\ell$ and $PhCH_2\ddot{C}Br$ of 6.4 and 4.7 $kcal.mol^{-1}$ respectively.[10] But halogen substitution at the carbene is known markedly to affect its stability and its reactivity enabling intermolecular reactions to compete with reaction (1),[11] and this may be ascribed to an increased barrier for H shift. Tending to confirm this, there have been no reports so far of the successful intermolecular capture of a dialkyl carbene.

It seemed to us that a suitable intramolecular competition might allow an experimental estimate of the size of the barrier in dialkyl carbenes; we have therefore examined the reactions of the diazirines (1) and (2) with the results given in the table.[12,13] For comparison purposes, data on the products from diazirines (3)[14] and (4)[15] are also included.

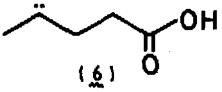
Table: Products from Diazirine Decomposition

Diazirine	Conditions	% Composition[13]			
 (1)					
	Δ^a	2	74	24	< 0.5
	$h\nu^b$	15.0	51.9	23.4	4.7
 (2)					
	Δ	22	52	26	
 (3)					
	Δ	3.3	66.6	23.5	0.5
	$h\nu$	23.2	38.0	34.7	3.7
 (4)					
	Δ	5.0	75.2	18.2	1.0
	$h\nu$	22.8	46.0	27.2	4.0

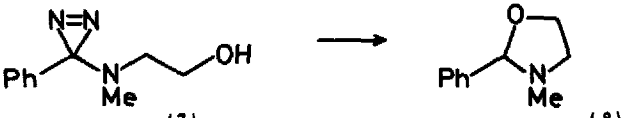
a. Thermolysis at 100°C b. Photolysis

For both (1) and (2) the product composition is similar to that produced from the alkyl - (3) and alkenyl -(4) diazirines, and for the hydroxydiazirine (1) this also holds true for the change in product composition between thermolysis and photolysis. Diazirines are well recognised as decomposing *via* carbenes[16] and the products observed are those expected from rearrangement of the carbenes (5) and (6).


(5)

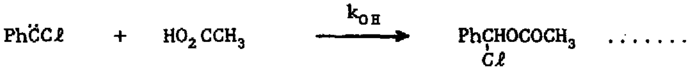

(6)

The surprising feature of the products from both (1) and (2) is the lack of any cyclic compound formed by insertion into the OH group,[17] particularly as diazirine (7) has been shown to give the oxazolidine (8) in high yield.[18]



(7) (8)

Despite the lack of any cyclic product, these results enable us to make a reasonable estimate for the upper bound for the barrier for the 1,2 H shift, by using the previously determined absolute rate data for $Ph\ddot{C}C\ell$ with acetic acid, equation (2).[19]



$$Ph\ddot{C}C\ell \quad + \quad HO_2CCH_3 \quad \xrightarrow{k_{OH}} \quad Ph\underset{C\ell}{C}HOCOCH_3 \quad \ldots\ldots\ldots\ldots \quad (2)$$

We may estimate the effective concentration of the CO_2H group in the carbene (6) at 1.1M,[20] and using the known bimolecular rate constant for reaction (2), 1.78 x 10^9 $M^{-1}s^{-1}$, one arrives at a rate constant (k_{OH} = 2 x $10^9 s^{-1}$) for the rate of the intramolecular OH insertion in (6). The absence of lactone shows that the rate of 1,2 H shift (k_{CH}) is not less than two orders of magnitude greater than this, i.e. $k_{CH} \geq 10^2\ k_{OH} = 2 \times 10^{11}\ s^{-1}$. At 100°C, the A factor for a unimolecular process with zero entropy change is $10^{13.3}$ and assuming that nearly one degree of rotational freedom is lost during the H transfer, we may estimate A = $10^{12.5}$ and hence calculate Ea = 2.0 $kcal.mol^{-1}$ for the 1,2 C-H insertion process. This is certainly a maximum value, because (i) the rate k_{OH} for (6) is likely to be greater than that of reaction (2), (ii) the ratio alkene : lactone is greater than 10^2, and (iii) the assumed A factor is the largest it could reasonably be.

Previously, A factors of $10^{12.1}$ have been measured for 1,2 H shifts in radicals[21] and Liu[10] obtained values of $10^{12.17}$ and $10^{12.1}$ for $PhCH_2\ddot{C}C\ell$ and $PhCH_2\ddot{C}Br$. The data do not allow a definite minimum value for E_a, but using $k_{CH}:k_{OH}$ = 500 and A = $10^{12.1}$ results in E_a = 0.17 $kcal.mol^{-1}$, and we therefore suggest a probable value of 1.1 ± 1 $kcal.mol^{-1}$ for the barrier height.

It is noteworthy that the three experimental values for the barrier in reaction (1) viz: 6.4 (R = Ph, X = $C\ell$), 4.7 (R = Ph, X = Br) and 1.1 (R = HO_2CCH_2, X = CH_3) lie in the order expected given the influence of X on the reactivity of the carbene and parallel the values calculated using MNDO methods.[4]

Finally we note that, in view of the fact that the rate for reaction (2) is near the diffusion-controlled limit and among the fastest yet measured for intermolecular carbene reactions, the absence of lactone from (6) would indicate that the rate of 1,2 H shift in a dialkyl carbene is about 3 orders of magnitude faster than for any likely intermolecular capture reaction.

Acknowledgements

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References and Footnotes

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13. Product compositions were determined by ^{1}H nmr and/or GC-MS methods and by comparison with authentic materials.
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18. R A Moss, D P Cox and H Tomioka, Tetrahedron Letters, 25, 1023 (1984).
19. D Griller, M T H Liu, C P Montgomery and J C Scaiano, J.Org.Chem., 48, 1359 (1983). Although RCCl are known to have lower reactivities than RC-Alkyl,[11] this model provides a reasonable estimate for k_{OH} because it is close to the diffusion limit.
20. This was done using the distance from the carbene carbon in (6) to the outer limit (van der Waals) of the CO_2H group as the radius of a sphere within which one carboxyl group must lie. This gives a maximum radius of 7A. MM2 calculations on (6) suggest a slightly smaller value for the most favourable conformation. The effective concentration (1.1M) falls at the lower end of the range of values observed experimentally for similar 5 membered ring closures/proton transfers. See N S Isaacs 'Physical Organic Chemistry'. Longman, Harlow (1987) p 602 and references therein.
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