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Hot Radical Effects in Carbene Reactions

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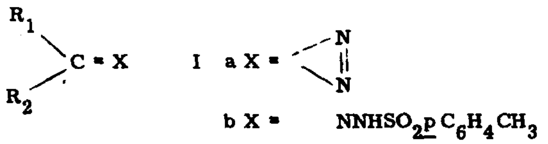
It has been shown that carbenes may be produced by the thermal or the photolytic decomposition of diazirines (1,2,3). In the few cases where both methods have been used to generate them, a marked difference in the product composition has been found. The direction of these differences has led to the postulate that the photolytic process produces an excited carbene (3,4,5).

We now wish to report our results on the photolysis and pyrolysis of a number of acyclic diazirines (Ia).



These results are summarised in the table (columns 1 and 2).

Table

R_1 and R_2 in I	Products	1[a]	2[b]	3[c]
II CH_3, CH_3CH_2	Butene-1	23.2	3.3	5[d]
	trans Butene-2	38.0	66.6	67
	cis Butene-2	34.7	29.5	28
	Methylcyclopropane	3.7	0.5	0.5
	iso Butene	0.3	0.0	-
III $(CH_3)_2CH, H$	*iso* Butene	53.6	53.6	63.1(63)[d]
	Methylcyclopropane	29.4	45.5	36.9(37)
	trans Butene-2	9.3	0.5	
	cis Butene-2	7.7	0.3	
IV CH_3CH_2, CH_3CH_2	trans Pentene-2	57.0	67.5	69.1
	cis Pentene-2	38.4	30.6	28.2
	Ethylcyclopropane	4.0	1.3	2.2
	2-Methylbutene-1	0.6	-	
	2-Methylbutene-2	-	0.3	0.5
V $CH_3, (CH_3)_2CH$	3-Methylbutene-1	20.5	3.0	5.1
	2-Methylbutene-2	70.3	93.2	89.7
	1,2-Dimethylcyclopropane	9.1	3.7	5.2
VI $CH_3(CH_2)_4-, H$	Pentene-1	86.0	90.6	
	Ethylcyclopropane	14.0	9.4	

Table (cont.)

R_1 and R_2 in I	Product	1[a]	2[b]	3[c]
VII $(CH_3)_3$	1,1 Dimethylcyclopropane	51[e]	92[e]	92[d]
	2-Methylbutene-2	49	8	7
	3-Methylbutene-1	0	0	1
VIII $(CH_3)_3C$, CH_3	3,3 Dimethylbutene-1	55.1	51.4	52[d]
	1,1,2 Trimethylcyclopropane	34.5	48.2	47
	2,3 Dimethylbutene-2	10.4	0.3	trace

a. Diazirine photolysis (3130Å)

b. Diazirine pyrolysis at 160°

c. Tosylhydrazone decomposition

d. Results of Friedman and Schechter ref. 6

e. Results of Frey and Stevens ref. 5

The pyrolyses were carried out in the gas phase at ~160° and the results are very similar to those obtained by the pyrolyses of the sodium salts of the corresponding tosylhydrazones (Ib, see table column 3), except for the case of isobutyraldehyde tosylhydrazone III. While we have no direct evidence on the reason for this difference, it may be due to some incursion of an ionic mechanism into the tosylhydrazone decomposition.

The photolyses were conducted in the gas phase in the presence of added nitrogen at total pressures up to 850 mm. using an unfiltered medium pressure mercury arc and Pyrex vessels. The absorbtion spectra of the diazirines are such that light of 3130Å would be the principal activating wavelength. In most cases the pressure in the system was sufficiently high to avoid secondary isomerisation of the initially formed excited products; but where this was not possible, the product ratios were extrapolated to infinite pressure.

In all cases the difference between the results of photolysis and pyrolysis is quite striking and can in each case be most readily explained on the basis of a hot-radical effect in the intramolecular insertion reactions. With increasing size of the excited molecule, the magnitude of this effect diminishes as might be expected. Thus the 'hot' isopropyl carbene gives 17% of carbon-carbon insertion products, whereas the corresponding 'hot' methyl isopropyl carbene gives less than 0.1%. Also in the 1:3 hydrogen insertion reaction to form cyclopropanes, the difference between the thermal and the 'hot' ethyl methyl carbene is sevenfold and only two and a half fold for the corresponding methyl isopropyl carbene.

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References

1. H.M. Frey and I.D.R. Stevens, Proc. Chem. Soc., 79 (1962).
2a. H.M. Frey and I.D.R. Stevens, J. Chem. Soc., 3865 (1962).
b. " " " 3514 (1963).
3. " " J. Amer. Chem. Soc., **84**, 2647 (1962).
4. " " " , 4700 (1964).
5. " " " , 3101 (1965).
6. L. Friedman and H. Shechter, J. Amer. Chem. Soc., **81**, 5512 (1959).