The Rearrangement of Cyclopropylcarbenes

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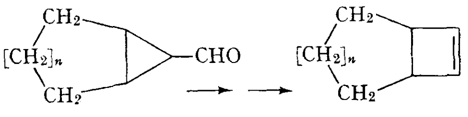
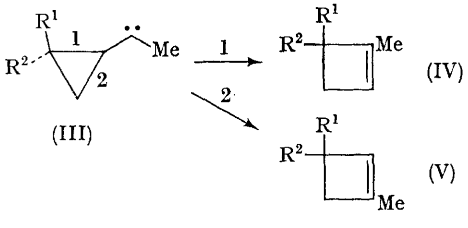
THE decomposition of the tosylhydrazones derived from cyclopropyl aldehydes and ketones in aprotic solvents gives rise predominantly to cyclobutenes in high yields. In the case of cyclopropanecarboxaldehyde, cyclobutene itself is formed.[1] Alkyl substituents on the cyclopropane ring give rise to cyclobutenes substituted in the 3 and, or, 4 positions of the cyclobutene ring; thus 2,2′-dimethylcyclopropanecarboxaldehyde yields 3,3′-dimethylcyclobutene.[2] It has recently been shown[3] that the decomposition of the tosylhydrazones of bicyclic aldehydes of the type (I) yields predominantly the bicyclic cyclobutenes (II) together with some cycloalkene plus acetylene.



(I) n=1, 2, 3 (II)

Among ketones, methylcyclopropyl ketone gives a good yield of 1-methylcyclobutene[1] and dicyclopropyl ketone affords 1-cyclopropylcyclobutene.[2] All these reactions almost certainly involve the rearrangement of the carbenes of the type R^1–$\ddot{C}$–R^2, where R^1 = cyclopropyl, and R^2 = H, alkyl, aryl, or cycloalkyl.[4]

To date, no work has appeared on this rearrangement with an unsymmetrical cyclopropyl ketone where the direction of ring opening can be determined. We report here work on the decomposition of the tosylhydrazones of 2,2′-dimethyl- (IIIa), *cis*-2-methyl- (IIIb), and *trans*-2-methyl-cyclopropyl methyl ketone (IIIc). Depending on which bond in the cyclopropane ring is broken either a 1, 3, (3′) (V) or a 1, 4,(4′) (IV) substituted cyclobutene should be formed:



(III) (IV) (V)

Decomposition of the respective tosylhydrazones in diglyme in the presence of three equiv. of sodium methoxide at 135—140° gave the hydrocarbon products shown in the Table.

TABLE†

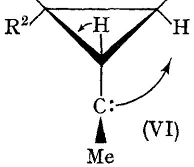
Carbene (III)	Cyclobutenes‡ (IV)	(V)
(a) $R^1 = R^2$ = Me	2·5	97·5
(*b*) R^1 = Me, R^2 = H (*cis*)	4·4	95·6
(c) R^1 = H, R^2 = Me (*trans*)	27·9	72·1

† Alkaline decomposition of tosylhydrazones in diglyme.

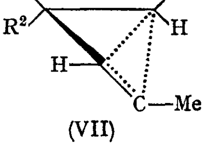
‡ Normalized to 100. In each case small (1—2%) amounts of fragmentation products were formed and somewhat larger amounts (10—15%) of the dienes derived by pyrolysis of the cyclobutenes. The dienes were formed in the same ratios as the cyclobutenes.

The cyclobutenes were identified by ^1H n.m.r. spectrometry, by comparison with authentic materials (IVb, Vb) and by pyrolysis to the corresponding substituted butadienes which were synthesized independently.

In all three cases the predominant product is that formed by migration of the less substituted bond of the cyclopropane ring. This result is surprising on two counts. Firstly, for (IIIa) and (IIIb) the selectivity is very marked, a most unusual feature in carbene reactions. Secondly the reaction involves the cleavage of the stronger carbon–carbon bond of the cyclopropane ring. We can only attribute this to a steric effect. Two possible explanations may be advanced. The first is that the reaction is not truly a carbene one; but involves a synchronous loss of nitrogen and migration of the ring bond in the intermediate diazo-compound (but see ref. 4). Assuming a '*trans*' migration, this would favour movement of the less substituted bond, for migration of the more substituted one results in strong steric



(VI)



(VII)

interaction between the 'ring' methyl and the 'carbene' methyl. The second possibility is that because the rearrangement must involve rotation of the 'carbene group' into the plane of the cyclopropane ring, this will be easier if the rotation occurs away from the ring-substituted carbon atom, *viz.*, (VI) → (VII). Experiments to test these hypotheses are in progress.

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[1] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, 1960, **82**, 1002.

[2] H. M. Frey and I. D. R. Stevens, unpublished observations.

[3] W. Kirmse and K.-H. Pook, *Chem. Ber.*, 1965, **98**, 4022.

[4] Pyrolysis of 3-cyclopropyl-3-methyldiazirine also gives 1-methylcyclobutene as the major product lending support to the hypothesis of a carbene intermediate: G. F. Bradley, Ph.D. Thesis, Southampton, 1967.