JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 305–308 (1988)

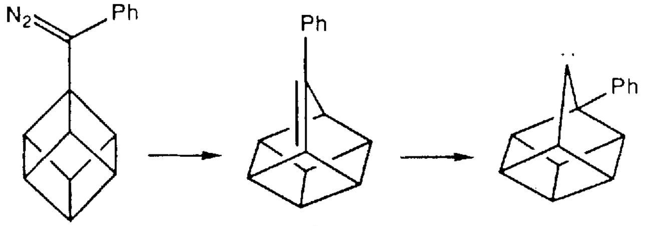
HOMOCUB-1(9)-ENE TRAPPED

NING CHEN AND MAITLAND JONES, JR.*
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

ABSTRACT

Decomposition of the tosylhydrazone salts formed from cubyl carboxaldehyde and homocubanone, potential precursors of cubylcarbene (**5**) and homocubanylidene (**6**), leads in each case to products derived from **6**. It is suggested that homocub-1(9)-ene (**7**) is the active ingredient in the formation of **6** from both precursors. The hydrazones formed from *N*-aziridylamines are useful photochemical sources of **6**, and presumably other carbenes. Flash vacuum pyrolysis of the tosyl hydrazone salts and hydrazones at 600 °C leads to indene.

The use of diazo compounds or their immediate precursors in the synthesis of bicyclo-1-alkenes was described by us many years ago,[1] and has now been used several times.[2] Recently, Eaton and Hoffmann have supplied a spectacular example in which they use cubylphenyl diazomethane (**1**) to generate the homocubene **2**.[3]† Even more exciting was their discovery of the rearrangement of **2** to the carbene **3**, as judged by the isolation of cyclopropanes formed by addition of **3** to alkenes. The conversion of **2** to **3** is a reversal of the more usual carbene-to-alkene rearrangement, and takes place at the quite extraordinary temperature of −78 °C! Rearrangements of alkenes to carbenes are common in the high temperature chemistry of cyclopropenes[4] and there are scattered suggestions of the reaction elsewhere,[5] but this rearrangement must surely be the most spectacular example of the genre.



1 **2** **3**

In this paper we report some observations on the parent cubyl and homocubyl systems which complement the work of Eaton and Hoffmann. In addition, we describe a new photochemical source of carbenes, and comment upon the active ingredient in these potential carbene reactions.

---

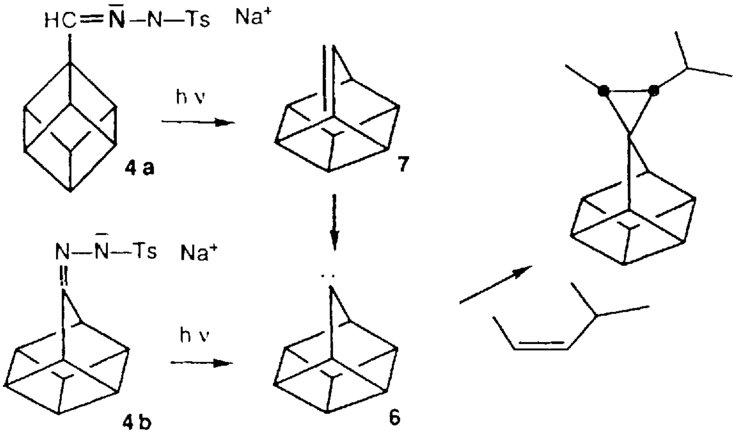
*Author for correspondence

†As recognized by Eaton and Hoffmann it is not required that the cubylcarbene be involved in this reaction. The cubyl system is prone to rearrangement, and a direct ring expansion of cubyl phenyl diazomethane to the bridgehead olefin is possible.

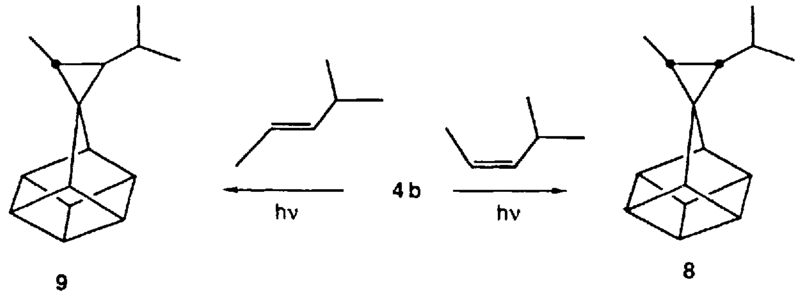
0894–3230/88/050305–04$05.00

Received 29 February 1988
Revised 15 June 1988

We find that decomposition of tosyl hydrazone salts **4a** or **4b**, potential sources of cubylcarbene (**5**), and homocubanylidene (**6**), leads to products derived from **6** in each case. The most logical source of **6** in the photolysis of **4a** is 1(9)-homocubene, **7**.



The photolysis of a heterogeneous mixture of the sodium salt of **4a** or **4b** in *cis*- or *trans*-4-methyl-2-pentene, leads to a single cyclopropane (**8** or **9**) isolated in *ca.* 30% yield. In both **8** and **9** the cage hydrogens appear between δ 3·4 and 2·5, with the *cis* compound **8** showing a considerably less symmetrical group of cage signals. Decoupling experiments using the isopropyl methyne proton and the cyclopropyl hydrogens allowed us to measure the coupling constants for the cyclopropyl hydrogens in the two compounds (**8**, J = 8·4 Hz, **9**, J = 5·3 Hz). By way of comparison, the *cis* and *trans* coupling constants in cyclopropane itself are 9·0 and 5·6 Hz, respectively.[6] Thus we feel our stereochemical assignments are on firm ground. Carbene **6** adds to 4-methyl-2-pentene in stereospecific fashion; there is no detectable amount of the 'wrong' stereoisomer. This agrees with Eaton and Hoffmann's results,[3] and with the report by Moss and Dolling that 7-norbornanylidene added stereospecifically to the same alkene.[7]

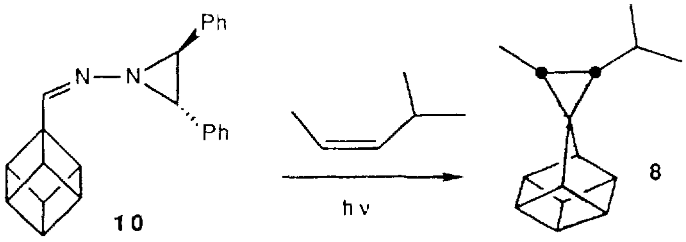


The photolysis of the tosyl hydrazone salt is bedeviled by the formation of a sulfur containing product, and we therefore sought a carbene source less prone to diversion.* Many years ago Eschenmoser and his co-workers described the formation of hydrazones from

---

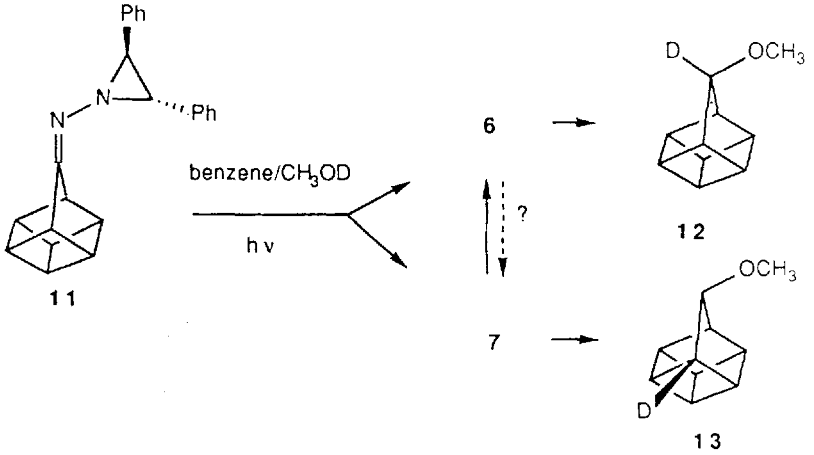
*This product clearly results from the readdition of a fragment of the tosyl hydrazone. Its structure is not certain yet, but it is probably merely the sulfone formed by simple attack of toluene sulfinate on the reactive intermediate.

N-aziridylamines.[8]* Thermal decomposition of such hydrazones induces a fragmentation which apparently generates a carbene. We have found that photolysis also produces carbenes from these compounds. In particular, photolysis in *cis*-4-methyl-2-pentene of the hydrazone **10**, formed from cubyl carboxaldehyde, leads to **8**, the same cyclopropane as is formed from **4a** or **4b**.



Although these results do not require cubylcarbene **5** as intermediate, they do strongly implicate the bridgehead alkene **7** and its rearrangement to **6**. They also show that the phenyl group in **1**, **2** and **3** is not required for the rearrangement. It might have been thought that the ease of migration of phenyl or the increased polarization induced in the bridgehead alkene **2** was responsible for the alkene-to-carbene rearrangement, but such is not the case; the parent compound also rearranges.

A key question involves the reversibility of the conversion of bridgehead alkene **7** to carbene **6**. Irradiation of **11** in a mixture of benzene and CH_3OD did lead to both **12** (formed from **6**) and **13** (formed from **7**), but this result does not identify the first formed intermediate. The lack of other deuterated isomers of 9-methoxyhomocubane does make the intervention of the degenerate 9-homocubyl cation unlikely, however.[9] Authentic **13** was made in a sequence starting from the ethylene ketal of 1-bromohomocuban-9-one, and the ^{2}H-NMR spectra were used for quantitative analysis (**12**, δ = 3·94; **13**, δ = 3·28).



If the carbene **6** is formed first from **11**, then the isolation of **13** shows that it does rearrange to **7**. However, **11** might produce **7** directly, in a Wolff rearrangement-like process, without the intervention of **6**. In this scenario the known conversion of **7** to **6** would account for the formation of both products. The change in the relative amounts of **12** and **13** with methanol

---

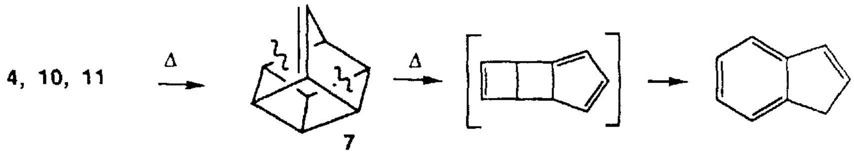
*We send special thanks to Professor A. Dreiding for alerting us to the possibilities of this precursor for carbenes, Fefor, Norway, September 1987.

Table. Relative amount of **12** and **13** as a function of [CH_3OD]

% methanol	100	50	25	9	3	2	1
12/13	1·8	1·8	1·9	2·4	2·9	7·3	9·5

concentration suggests that it is the latter situation that obtains, as it is **13** that increases as the methanol concentration increases (Table).*

Flash vacuum pyrolysis at 400 °C of tosyl hydrazone salts **4a** or **4b** leads to substantial amounts of the sulfur containing material, of uncertain structure, mentioned earlier. Pyrolysis of **4a** and **4b** or **10** and **11** at 600 °C leads cleanly to indene. Although several mechanisms can be envisioned, to us this result seems most easily rationalized if **7** is an intermediate in each case.



ACKNOWLEDGMENTS

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grants CHE 83-18345 and 86-17590) for generous support of this work.

REFERENCES

1. A. D. Wolf and M. Jones, Jr. *J. Am. Chem. Soc.* **95**, 8209 (1973).
2. D. J. Martella, M. Jones, Jr. and P. v. R. Schleyer, *J. Am. Chem. Soc.* **100**, 2896 (1978); D. J. Martella, M. Jones, Jr., P. v. R. Schleyer and W. F. Maier, *J. Am. Chem. Soc.* **101**, 7634 (1979); S. F. Sellers, T. C. Klebach, F. Hollowood, M. Jones, Jr. and P. v. R. Schleyer, *J. Am. Chem. Soc.* **104**, 5492 (1982).
3. P. E. Eaton and K.-L. Hoffmann, *J. Am. Chem. Soc.* **109**, 5285 (1987).
4. J. J. Gajewski, *Hydrocarbon Thermal Rearrangements*, Academic, New York, (1981), pp. 22–25.
5. T. H. Chan and D. Massuda, *J. Am. Chem. Soc.* **99**, 936 (1977); R. T. Conlin, H. B. Huffaker and Y.-W. Kwak, *J. Am. Chem. Soc.* **107**, 731 (1985); T. J. Barton and M.-H. Yeh, *Tetrahedron Lett.* **28**, 6421 (1987).
6. J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks and G. H. Stout, *Organic Structural Analysis*, Macmillan, New York, (1976), p. 66.
7. R. A. Moss and U.-H. Dolling, *Tetrahedron Lett.* 5117 (1972).
8. D. Felix, C. Wintner and A. Eschenmoser, *Org. Syn.* **55**, 52 (1976); R. K. Müller, R. Joos, D. Felix, J. Schreiber, C. Wintner and A. Eschenmoser, *Org. Syn.* **55**, 114 (1976); D. Felix, R. K. Müller, U. Horn, R. Joos, J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **55**, 1276 (1972).
9. R. E. Leone, J. C. Barborak and P. v. R. Schleyer, 'Degenerate Carbonium Ions', in *Carbonium Ions, Vol. IV*, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, (1973), pp. 1863–1868.

---

*We thank Professor P. E. Eaton for urging this point upon us. The issue is not quite settled by this result, as a rapid equilibrium between **6** and **7** could produce ratios of **12/13** that depended upon solvent polarity. An unequivocal source of carbene **6** is needed.