

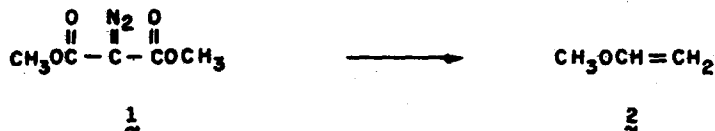
METHOXYL GROUP MIGRATION TO CARBENOID CENTERS

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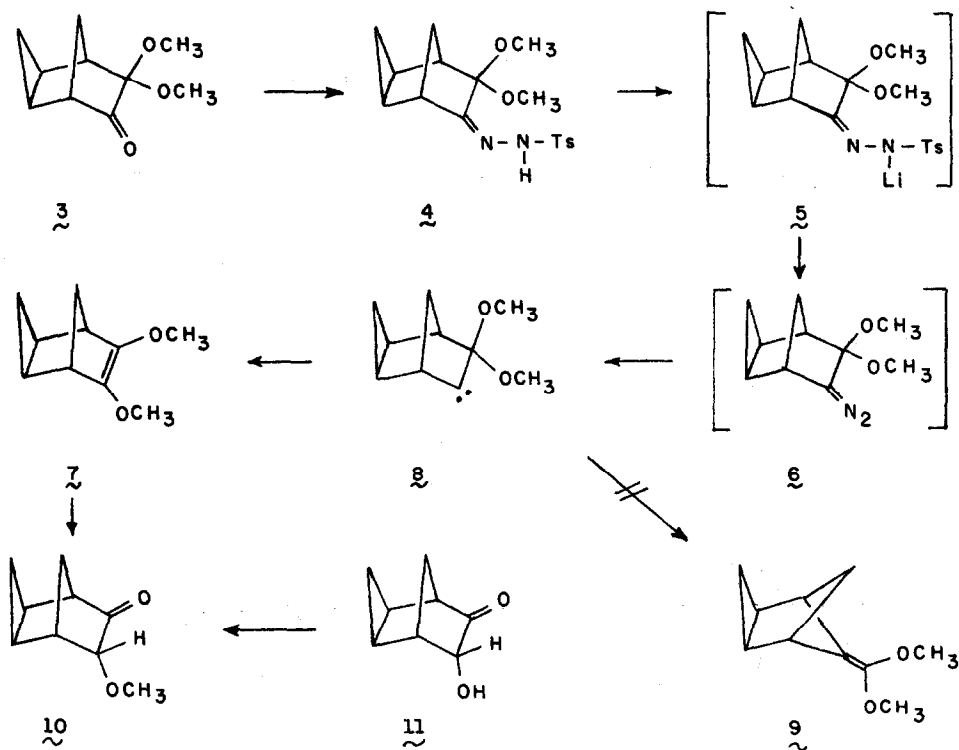
(Received in USA 11 August 1972; received in UK for publication 22 September 1972)

Although numerous examples of alkoxy group migration to photochemically generated carbenoid centers have been reported, instances of similar behavior with thermally generated carbenes appear rare.^{1,2} A survey of the literature reveals that such alkoxy shifts to thermally generated carbenoid centers occur only when alkoxy is the sole group capable of migrating. For instance, 1 has been found¹ to yield 35-40% of 2 at 350-550°. This has been interpreted in terms of carbenoid intermediates. The lack of alkoxy group migration, when



other groups are in a position to migrate, has been discussed for the pyrolysis of salts of tosylhydrazones.² Even in the case of photolytic generation of carbenes from diazoalkanes, it has been noted that "the alkoxy group is not particularly prone to migrate but rather that a β -alkoxy group tends to promote migration of other β -substituents".³ We now wish to report an example of alkoxy group migration to a thermally generated carbenoid center in a system where alkyl group migration is feasible.

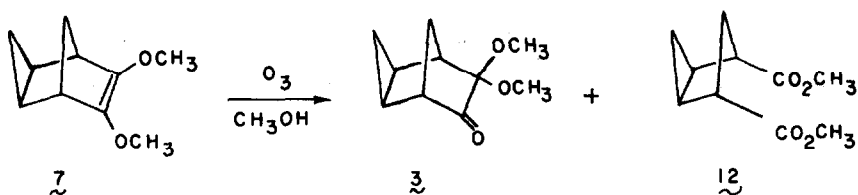
As part of our interest in methods of constructing strained ring systems via ring contractions, we decided to explore the possibility of ring contracting 3.⁴ In view of the prior literature discussed above, ring contraction via alkyl shift might be expected to take precedence over an alkoxy shift in any thermal reaction involving a carbenoid intermediate. Treatment of 3 with *p*-toluenesulfonylhydrazine gave the hydrazone 4, mp 169-170°. *n*-Butyllithium in hexane was added to a solution of 4 in tetrahydrofuran to product the lithio salt 5. Pyrolysis of dry 5 at 110° gave 6, which yielded 7 as the only



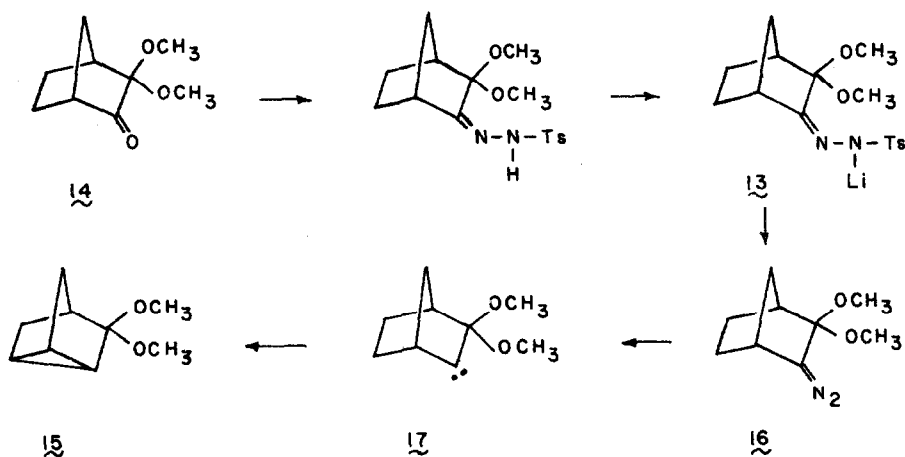
volatile product under the pyrolysis conditions. It was presumed that loss of nitrogen from **6** produced the carbene **8**. Interestingly, no trace of **9**, which would be expected from alkyl migration, was detected, nor were any insertion products found.

The structure of **7** was assigned on the basis of both spectroscopic and chemical evidence. The nmr spectrum of **7** showed absorption at τ 6.33 (6H; s), 7.30 (2H, m), and 8.40-9.30 (6H, m). Treatment of **7** with 0.1N hydrochloric acid in water gave **10** which was identical to an authentic sample of **10** prepared by methylation of **11**⁴ with sodium hydride and methyl iodide. Additional evidence for the structural assignment was obtained from the ozonolysis⁵ of **7** which gave **3** and **12** in the ratio of 52:48. Both **3** and **12**⁴ were identical in all respects to authentic samples.

In contrast to the conversion of **4** into **7** via alkoxy group migration to a thermally generated carbenoid center, was the pattern observed in the pyrolysis of **13**. Formation of



13 from the tosylhydrazone of 14⁴ followed by pyrolysis at 120° gave a 60% yield of 15. Presumably, 16 and 17 were intermediates in the formation of 15, which was identified by comparison with an authentic sample.⁵ This example illustrates that other modes of reaction are generally to be preferred to alkoxy group migration to carbenoid centers. C-H insertion of the carbene 8 apparently does not occur because of the strained nature of the



products which would be formed. Similarly, it would appear that strain was a major factor in the failure of alkyl group migration to occur to the carbenoid center of 8. Thus, it would appear that the energy factors, which separate alkoxy group migration from other well established processes observed in carbene reactions, are small. However, when alternate mechanistic paths involve an increase in strain energy, as in the formation of 9 from 8, alkoxy group migration can become the predominant process.

Acknowledgement. We are indebted to the National Science Foundation for a grant in partial support of this study. We also wish to thank the B.F. Goodrich Corporation for a fellowship to X.C. and Professor H. Shechter for a helpful discussion.

REFERENCES

1. D.C. Richardson, M.E. Hendrick, and M. Jones, Jr., J. Amer. Chem. Soc., 93, 3790 (1971). This reference contains an extensive list of the photochemical studies in this area.
2. J.H. Robson and H. Shechter, ibid., 89, 7112 (1967).
3. W. Kirmse and M. Buschhoff, Angew. Chem. internat. Edit., 4, 692 (1965); W. Kirmse and M. Buschhoff, Chem. Ber., 100, 1491 (1967).
4. The synthesis of this compound will be described elsewhere in a detailed report on this subject.
5. For an in-depth discussion of this ozonolysis see the following communication.
6. We wish to thank Dr. J. MacMillan for providing spectra of authentic 2,2,-dimethoxytricyclo[2.2.1.0^{3,5}]heptane (15).