

알릴아조알칸의 광화학적 분해반응

Christopher J. Nalepa · Paul S. Engel · 蔡禹基*

미국 Rice 대학교 화학과

*충북대학교 자연과학대학 화학과

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Photochemical Decomposition of Allylic Azoalkanes

Christopher J. Nalepa, Paul S. Engel and Woo Ki Chae*

Department of Chemistry, Rice University, Houston, Tx. 77001, U.S.A

*Department of Chemistry, Chungbuk National University,

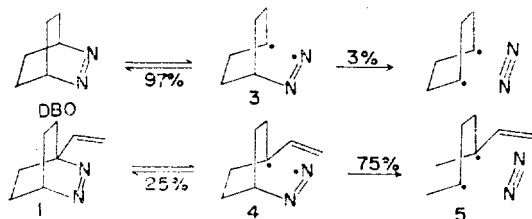
Cheongju 310, Korea

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Photochemical decomposition of azoalkanes is a clean and general method for producing biradicals¹⁻³ and a few azo compounds⁴⁻⁶ lose nitrogen with particular difficulty. We recently^{7,8} studied the mechanism for the decomposition of bicyclic azoalkanes **1** and **2** which are derivatives of 2,3-diazabicyclo[2.2.2]-oct-2-ene (DBO). In this paper, we will discuss on the products from the photodecomposition of compound **1** and **2**.

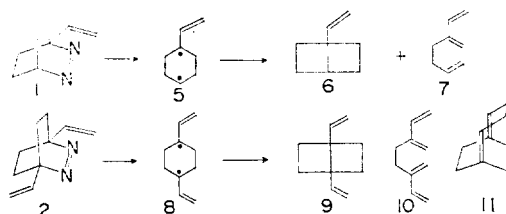
RESULTS AND DISCUSSION

Since triplet DBO undergoes very little decomposition and does not phosphoresce, its major fate must be radiationless decay. One suggested mechanism for this decay⁹ is reversible cleavage to a diazenyl radical as shown below.



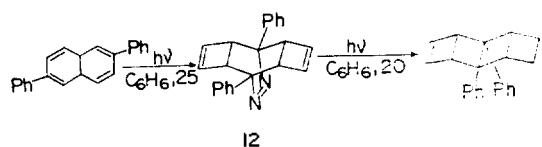
If **1** and **2** behaved like DBO, their photochemical products would be derived by ring clo-

sure and opening of the expected diradicals **5** and **8**. These species are of interest as possible intermediates in the Cope rearrangement¹⁰. The ultimate products from **2** might be bicyclohexane **9**, which we calculated to be thermodynamically less stable than **8**¹¹, tetraene **10**, whose thermal reactions are under investigation¹², and finally the recently synthesized *anti*-Bredt compound **11**. We have found that irradiation of **2** at 25 °C produces only tetraene **10**, as judged by nmr comparison with an authentic sample. Although a considerable number of compounds similar to **9** are known¹⁴⁻¹⁶, it seemed possible that **9** might be a thermally labile intermediate between **2** and **10**. We therefore irradiated **2** at -78 °C and ran the nmr spectrum of the product at low temperatures but only **10** was observed.



Martin¹⁷ reported recently that irradiation of **12** in frozen benzene caused ring clo-

sure but that the product in fluid solution arose by ring cleavage. Unfortunately, irradiation of **2** in frozen benzene led only to tetraene **10**. Chapman and Hayes monitored the photolysis of **2** at 26 °K by matrix isolation infrared spectroscopy; however, the observed spectrum of the product still corresponded to that of **10**.



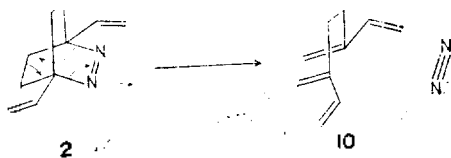
Irradiation of **1** at -78 °C in CD₃COCD₃ with 366 nm light also gave only ring opening, judging by comparison with an authentic sample of **7**. These low temperature results, coupled with our eventual synthesis of **6** are convincing evidence that neither **6** nor **9** are intermediates on the pathway to **7** and **10**. The reason we don't observe ring closure products from **1** and **2** when DBO and compound **13** give both a 1,5-hexadiene and bicyclo[2.2.0]hexane is questioned.



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Stabilization of the diradical by allylic resonance does not seem to be the answer because the ratio of cleavage to closure in the Norrish Type II 18 reaction¹⁸ or in six-membered monocyclic azoalkanes¹ shows no particular dependence on resonance stabilization of the biradical. Conformational effects¹⁹ are not likely either, in view of the similar product distribution from DBO and **13**. Triplet diradicals undergo more cleavage than singlet diradicals from DBO⁹ and a six-membered azoalkane²⁰; however, even the pure triplet reaction gives 25 % ring closure. Spin multiplicity differences are therefore not the answer. A more appealing explanation

is that diradicals **5** and **8** do not lie on the decomposition pathway but that the unstabilized cyclohexane-1,4-diyl does. Thus concerted cycloreversion might be facilitated in **1** and **2**, in the same way that radical stabilizing groups accelerate the Cope rearrangement²¹.



We have earlier postulated diazenyl radical **4** as the key intermediate and this species might fragment to give the most stable products. It follows that either DBO does not give a similar diazenyl radical **3** or that if it does, **3** behaves differently from **4**. An esr study of the photolysis of **1** and **2** at low temperature might be of help in sorting out these possibilities.

Although photolysis of **1** and **2** did not produce any bicyclo[2.2.0]hexanes, these compounds are sufficiently interesting to warrant independent synthesis. Our attempts to prepare **9** from the known 1,4-bis(hydroxymethylene) bicyclo[2.2.0]hexane²² using selenium chemistry²³ or the Wittig reaction²⁴, were not fruitful. We did succeed, however, in synthesizing **6** by the Wittig route. This compound underwent thermal rearrangement at 33.5 °C with a half life of 8 hours, demonstrating that it would have been detected in the photolysis of **1**. Using literature data, one calculates that **9** should have a half life at 78 °C of 3.7 min and would be exceedingly stable at 26 °K.

The relevant data are summarized in Table 1. Each added vinyl group in the monocyclic series lowers ΔG^* by about 11 kcal · mol⁻¹, corresponding to one allyl resonance energy. Since a similar decrease in ΔG^* occurs on adding a vinyl group to bicyclo[2.2.0]hexane, it seems reasonable to expect another decrease of this

Table 1. Activation parameters for cyclobutane thermolysis.

Compound	ΔH^* kcal · mol ⁻¹	ΔS^* , eu	ΔG^* (100 °C)	Ref
Cyclobutane	61.1	9.1	57.7	24
Vinylcyclobutane	48.6	5.4	46.6	25
<i>trans</i> Divinylcyclobutane	33.7	-2	34.4	26, 27
<i>cis</i> Divinylcyclobutane	23.1	-11.7	27.5	27
Bicyclo(2.2.0)hexane	36.0	1.5	35.4	28
1-Vinyl bicyclo(2.2.0)hexane (1)			24.5*	This work
1,4-Divinylbicyclo(2.2.0)hexane (2)			(13.5)	Estimated

* Based on one determination only.

magnitude in **9**. Even if the geometry of **9** were favorable for Cope rearrangement as that of *cis* divinylcyclobutane, the half life of **9** would still be several years at 26 °K. To summarize the above discussion, the only photoproducts found, to date are triene **7** and tetraene **10**, and these do not seem to arise *via* vinylbicyclohexanes **6** and **9**.

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REFERENCES

- P. S. Engel, *Chem. Rev.*, **80**, 99 (1980).
- J. A. Berson, *Acc. Chem. Res.*, **11**, 446 (1978).
- M. Schneider, *Angew. Chem. Int. ED. Engl.*, **14**, 707 (1975).
- N. J. Turro, K. C. Liu, W. Cherrly, J. M. Liu and B. Jacobson, *Tetrahedron Lett.*, 555 (1978).
- J. P. Snyder, *Diss. Abstr.*, **26**, 5728 (1966).
- N. J. Turro, J. M. Liu, H. D. Martin and M. Kunze, *Tetrahedron Lett.*, 1299 (1980).
- P. S. Engel, R. L. Allgren, W. K. Chae, R. A. Reckonby and N. A. Marron, *J. Org. Chem.*, **44**, 4233 (1979).
- P. S. Engel, C. J. Nalepa, R. A. Leckonby and W. K. Chae, *J. Amer. Chem. Soc.*, **101**, 6435 (1979).
- W. D. K. Clark and C. Steel, *J. Amer. Chem. Soc.*, **93**, 6347 (1971).
- M. F. Mirbach, M. J. Mirbach, K. C. Liu and N. J. Turro, *J. Photochem.*, **8**, 299 (1978).
- M. Rule, M. G. Lazzara and J. A. Berson, *J. Amer. Chem. Soc.*, **101**, 7091 (1979).
- K. Shea and S. Wise, *J. Amer. Chem. Soc.*, **100**, 6519 (1978); *Tetrahedron Lett.*, 2283 (1978).
- J. R. Wiseman and J. J. Vanderbilt, *J. Amer. Chem. Soc.*, **100**, 7730 (1978).
- K. B. Wiberg and M. E. Jason, *J. Amer. Chem. Soc.*, **98**, 3393 (1976); E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **95**, 7884 (1973); D. Bellus and G. Rist, *Helv. Chim. Acta.*, **57**, 194 (1974).
- C. S. Chang and N. L. Bauld, *J. Amer. Chem. Soc.*, **94**, 7593 (1972).
- W. R. Roth and G. Erker, *Angew. Chem.*, **85**, 510 (1973).
- H. D. Martin and M. Hekman, *Tetrahedron Lett.*, 1183 (1978).
- P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
- P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7506 (1972).
- P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).
- M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, **99**, 4417 (1977).

22. L. Lantos and D. Ginsburg, *Tetrahedron*, **28**, 2507 (1972).
23. H. J. Reich, F. Chow and S. K. Shah, *J. Amer. Chem. Soc.*, **101**, 6638, 6648 (1979).
24. Calculated from data in R. W. Carr and W. D. Walters, *J. Phys. Chem.* **67**, 1370 (1963).
25. H. M. Frey and R. Pottinger, *J. Chem. Soc. Far. I.*, **74**, 1827 (1978).
26. W. Brachwitz, R. Hübner and W. Pritzkow, *J. Prakt. Chem.*, **317**, 479 (1975).
27. G. S. Hammond and C. D. Deboer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).
28. M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 5119 (1972).