

similar to that observed in the most polar medium, pure methanol. The slight decrease in singlet to triplet product ratio in going from pure methanol to methanol-hexane may be indicative of a very small dilution effect.⁷

The results listed in Table I provide convincing evidence that the precursor of **2** in the solvolysis of **1** is a triplet nitrenium ion. In order to form a triplet nitre-

Table I. Product Yields^a in the Solvolysis of 4,7,7-Trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane (**3**)

Solvent	% yield			Total % yield	% yield of singlet products	
	4	5	6		(4 + 5)	triplet products
CH ₃ OH-C ₆ H ₁₄ ^b	56	10	8	74	66	8.2
CH ₃ OH-CCl ₄ ^b	13	<1	59	73	13	0.22
CH ₃ OH- <i>p</i> -Br ₂ C ₆ H ₄ ^c	33	10	25	68	43	1.7
CH ₃ OH-CHCl ₃ ^b	4	<1	63	68	4	0.064
CH ₃ OH-CHBr ₃ ^b	1	<<1	45	46	1	0.022
CH ₃ OH-CH ₃ OH	59	20	7	86	79	11.3

^a Yields were determined by vpc using *N,N*-dimethylaniline as an internal standard. Yields were reproducible within the limits of analysis by vpc ($\pm 2\%$) with the exception of the CH₃OH-CHBr₃ runs in which the per cent of **6** varied by $\pm 3\%$. ^b Solvent mixtures were 1:1 by volume. ^c The solvent was prepared by mixing methanol and *p*-dibromobenzene on a 1 ml to 1 g basis.

nium ion from **1**, a heterolytic cleavage of the N-Cl bond of **1** must have occurred to produce a singlet nitrenium ion, which was then converted into the triplet nitrenium ion by spin inversion.⁸ Thus, the heavy atom effects discussed in this communication provide the first attestation of the discrete existence of two new ions, the singlet nitrenium ion and the triplet nitrenium ion.

We are currently investigating the spectroscopic and chemical properties of both singlet and triplet nitrenium ions.

Acknowledgment. We wish to thank the National Cancer Institute of the Public Health Service for Grant CA-07110 which supported this research.

(7) Upon dilution, collision with an inert solvent can result in collisional deactivation of the higher energy species to a less energetic state. For examples of such dilution effects see W. Lwowski and J. S. McConaghy, Jr., *J. Am. Chem. Soc.*, **87**, 5490 (1965); E. Ciganek, *ibid.*, **88**, 1979 (1966); M. Jones, Jr., and K. R. Rettig, *ibid.*, **87**, 4013 (1965).

(8) A casual evaluation of our data might tempt one to suggest that the results discussed in this communication could be explained by the homolytic cleavage of **3** to give a chlorine radical and a nitrogen radical. In the presence of chloroform and bromoform the nitrogen radical could be postulated to abstract a hydrogen atom to give **6**, and a radical chain reaction could then ensue. However, the fact that we observe the same qualitative results in carbon tetrachloride, which cannot serve as a hydrogen source, as we do in chloroform and bromoform rules out any explanation involving initial homolytic cleavage of the N-Cl bond of **3**. An alternate explanation would involve initial homolytic cleavage of the heavy atom solvent followed by abstraction of the chlorine from **3**. Since it is inconceivable that dibromobenzene could undergo such spontaneous homolytic cleavage under the reaction conditions, this possibility is also eliminated.

(9) Alfred P. Sloan Foundation Research Fellow, 1967-1969.

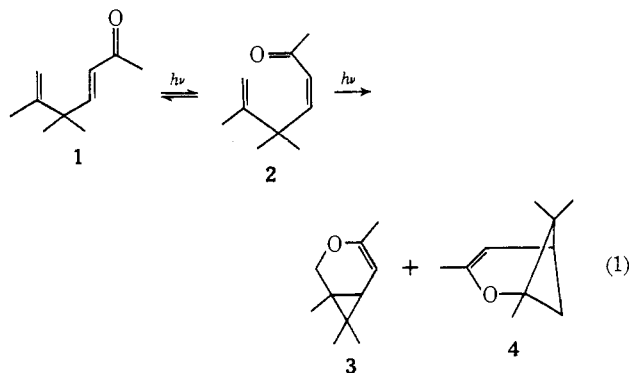
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Received June 6, 1969

Competing Pathways in the Photochemistry of a 2,5-Pentadienone¹

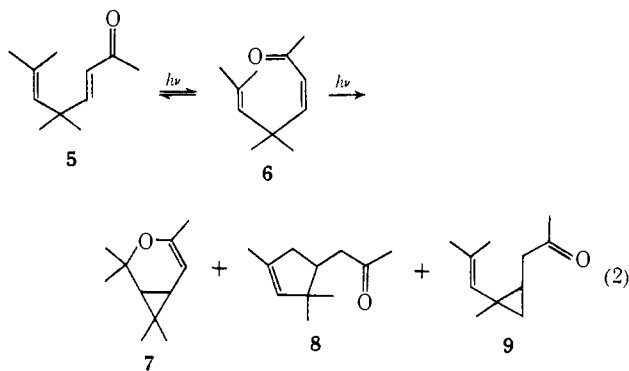
Sir:

We recently reported a novel photochemical 4 + 2 cycloaddition reaction in which the acyclic dienone **1** was transformed, *via* its *cis* isomer **2**, into the dihydropyrans **3** and **4** (eq 1).² We have now found that this



is a rather general reaction of 2,5-dienones, and the details of this work will be reported elsewhere.³ An especially interesting example, however, is provided by 5,5,7-trimethylocta-3,6-dien-2-one (**5**) which, after conversion to its *cis* isomer **6**, shows both the photochemical cycloaddition characteristic of **2** and a pair of hydrogen-abstraction reactions, one of which we have demonstrated to involve a nine-membered-ring transition state.

trans-Dienone **5**⁴ is readily prepared by condensation of 2,2,4-trimethylpent-3-enal⁵ with acetone in the presence of sodium methoxide. Its stereochemistry is clear from its nmr spectrum, which shows a 16.5-cps coupling constant between the α - and β -olefinic protons.⁶ Irradiation of a 1% solution of **5** in 30-50° petroleum ether using a 450-W Hanovia lamp through a Pyrex filter results in relatively rapid equilibration (0.5 hr) with the *cis* isomer **6**.⁴ Further irradiation (*ca.*



(1) The partial support of this research by National Institutes of Health Grants GM-00834 and GM-14662 is acknowledged with pleasure.

(2) R. A. Scheider and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 2023 (1967).

(3) See J. Meinwald, Abstracts, 21st National Symposium on Organic Chemistry, Salt Lake City, Utah, June 15-19, 1969, pp 61-70.

(4) Each new compound described gave satisfactory elemental analyses, as well as infrared and nmr spectra compatible with the assigned structures.

(5) R. H. Hasek, R. C. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961).

(6) I. Fleming and D. H. Williams, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill Publishing Co. Ltd., London, 1966, p 106.

30 hr) leads to the formation of three new photoisomers, shown to be **7** (60%), **8** (15%), and **9** (25%) (eq 2).

The structure of the major product (**7**), analogous to the major dihydropyran produced photochemically from **1**, is apparent from its infrared and nmr spectral characteristics.^{2,3} The second component showed saturated carbonyl absorption in its infrared spectrum at 5.83 μ ; its nmr spectrum showed a single olefinic proton absorption (τ 5.00) and four methyl groups (τ 9.22, 9.00, 8.38, and 7.95), in accord with structure **8**. This product has a prominent peak at m/e 108 in its mass spectrum,⁷ corresponding to loss of acetone in a McLafferty rearrangement. This becomes the base peak at an ionizing voltage of 10 eV. The final component showed upfield absorption in its nmr spectrum at τ 10.00–9.77 (1 H) and 9.44–8.75 (2 H), in addition to other characteristic absorptions compatible with structure **9**.⁸

In benzene, **7** and **8** remain the major products, but **9** is not formed to a significant extent. Using di-*t*-butylnitroxide as a quencher⁹ in a benzene solution of **5**, the dihydropyran **7** continues to form normally, but the cyclopentene **8** almost completely disappears. In methanol, where the formation of **9** assumes major importance, the rate of formation of **9** is not appreciably changed by addition of di-*t*-butylnitroxide. Attempts to sensitize these reactions with benzophenone and acetophenone were frustrated by rapid reactions involving the sensitizers.

The formation of **7** from **6** is analogous to the previously described cyclization of **2** to **3** (which is largely insensitive to quenching by di-*t*-butylnitroxide and piperylene, as well as to sensitization by benzophenone or acetophenone); both reactions appear on this basis to utilize singlet pathways. Both **8** and **9** clearly result from hydrogen-abstraction reactions. The formation of **9** finds close analogy in the work of Jorgenson and Yang on *t*-butyl-substituted α,β -unsaturated ketones.⁸

Two rationalizations may be offered to explain the production of **8**. One involves abstraction of an allylic hydrogen atom from a terminal methyl group by the carbonyl oxygen atom, *via* a nine-membered-ring transition state, followed by radical coupling and ketonization of the resultant enol (eq 3). Alternatively, one can envisage a hydrogen atom abstraction by the α -carbon atom of the enone system, *via* a seven-membered ring, followed by radical coupling to give **8** directly, without intervention of an enol. Evidence in favor of process 3 was provided by irradiation of a solution of **5** in D₂O-dioxane. The **8** thus produced acquires one deuterium atom in the α -methylene group, as determined by nmr and mass spectral evidence.

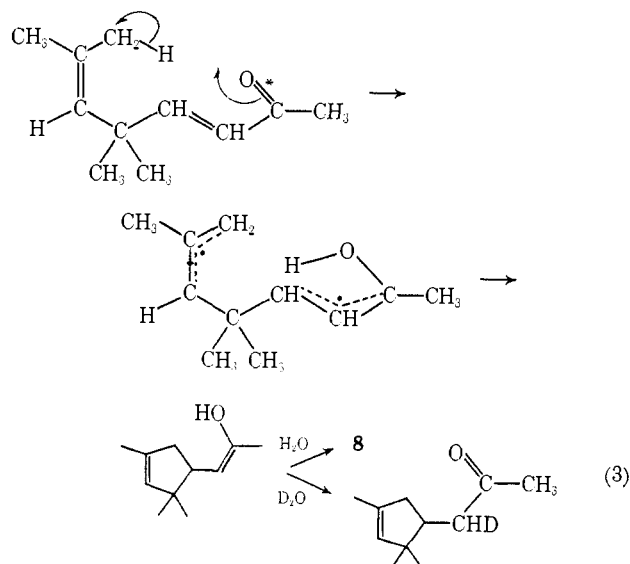
Intramolecular hydrogen-abstraction reactions have generally been considered to occur only when six- or seven-membered-ring transition states were available. Very recently, however, Breslow and Winnik have described intramolecular hydrogen atom abstractions by triplet benzophenones proceeding *via* a large ring.¹⁰ The present results provide the first example of an ex-

(7) Mass spectra were obtained through the good offices of the Cornell High Resolution Mass Spectrometer Facility, sponsored by National Institutes of Health Grant FR-00355.

(8) See, for a leading reference, N. C. Yang in "Reactivity of the Photoexcited Molecule" (Solvay Institute 13th Chemistry Conference), Interscience Publishers, London, 1967, p 145.

(9) See, for example, O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968).

(10) R. Breslow and M. A. Winnik, *ibid.*, **91**, 3083 (1969).



cited acyclic carbonyl compound following a similar pathway *via* a medium-sized-ring transition state. Since this reaction is competitive with two other facile intramolecular processes, it appears that similar reactions may have general importance in favorable cases.

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Received June 9, 1969

Alkoxide-Induced Transformations of Epoxy-N-nitrosocarbamates

Sir:

As a continuation of our investigations on small-membered heterocyclic rings, we sought to define the reactivity of a carbenoid center adjacent to a three-membered oxirane ring.¹ We felt that this would be a particularly interesting species since its chemical properties would probably be different from the related carbocyclic system^{2,3} by virtue of the interaction of the carbenoid center with the electron pair on the adjacent heteroatom. Of the variety of methods that have been developed to generate carbenes,⁴ the thermal decomposition of a α -diazo epoxide seemed most appropriate. In this communication we wish to report the synthesis of two potential epoxycarbene progenitors and the novel reactions they undergo upon treatment with base.

Methyl *trans*-N-(1,3-diphenyl-2,3-epoxypropyl)carbamate was synthesized from *trans*-2,4-diphenyl-3-butenic acid⁵ *via* the acid chloride, the acid azide, the isocyanate, and peracid epoxidation of the N-alkenylcarbamate. The N-nitrosocarbamate **I**, mp 95–96°, was prepared by nitrosation of the corresponding carbamate with dinitrogen tetroxide by established procedures.^{6,7} Methyl *trans*-N-nitroso-N-(3-phenyl-2,3-

(1) For an alternate approach to the preparation of an epoxycarbene, see A. Padwa, *J. Org. Chem.*, **30**, 1274 (1965).

(2) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 365 (1966).

(3) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

(4) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(5) T. L. Jacobs and M. H. Goodrow, *J. Org. Chem.*, **23**, 1653 (1958).

(6) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).

(7) All new compounds were properly characterized, and acceptable chemical analyses were obtained.