

Figure 1. The nmr spectrum of a photomixture of **2b** and **3b** containing a small amount of **1b** in degassed C_6D_6 .

silahexa-1,3,5-trienes ($Me_2Si=CPh-CR=CR-CPh=SiMe_2$, $R = H, Ph$) are the possible intermediates in these photochemical reactions in view of similar behavior of **1a** and **1b** to those of 1,3-cyclohexadiene and 1-sila-2,4-cyclohexadienes.¹

Results of the trapping experiments of these intermediates as well as of kinetic study on the novel vinyl-silacyclopropane-silacyclopentene rearrangement will be reported shortly.

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Hot Molecule Effects in 1,4-Diradicals.¹ The Thermal Generation of a Norrish Type II Intermediate

Sir:

We wish to report the generation of the Norrish type II diradical **1** from cyclobutanol precursors.² Since the behavior of **1** generated by photoreaction of ketone **2** has been documented,³ this represents an ideal opportunity to compare in detail the behavior of diradicals generated by very different means. We find that the pyrolysis route involves a substantially less stereospecific cleavage to the product butenes.⁴ Explanations

(1) The Chemistry of Diradicals, V; for previous work see L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95**, 2849 (1973).

(2) Such pyrolyses have previously been studied by E. D. Feit, *Tetrahedron Lett.*, 1475 (1970).

(3) C. P. Casey and R. A. Boggs, *J. Amer. Chem. Soc.*, **94**, 6457 (1972).

(4) The 1,2,3-trimethylcyclobutanols were prepared as follows. Addition of dichloro ketene (generated *in situ* from dichloroacetyl chloride and triethylamine) to *cis*-2-butene at 0° yielded 2,2-dichloro-*cis*-3,4-dimethylcyclobutanone (48%).⁵ Dechlorination with Zn-HOAc produced *cis*-2,3-dimethylcyclobutanone (38%).⁶ The Grignard addition of CH_3MgI gave the cyclobutanol, **4**. Isomers **7** and **8** were synthesized by CH_3MgI addition to *trans*-2,3-dimethylcyclobutanone, which resulted from the isomerization of the *cis* ketone with NaOMe in MeOH.^{7,8} It is interesting to note that the mass spectra of the three isomers are identical, characteristic of common McLafferty-type intermediates.⁹ Pyrolyses of **4**, **7**, or **8** were conducted in a flash vacuum apparatus at 585° and ~2 Torr for varying lengths of time. The products were analyzed by vapor phase chromatography. The olefins did not isomerize under the reaction conditions. Packing

of this difference based on geometrical or structural features of the system are inadequate, and we suggest that the excess energy associated with the photochemical route is responsible for the result.

The stereochemical characteristics of several diradical reactions are given in Table I. It is clear from this table

Table I. Stereochemical Characteristics of Some Selected 1,4-Diradical Cleavage Reactions

Reactant	Method	Product	Product ratio	Ref
	$h\nu$	2-Butene-2-d	cis/trans = 10	3
	Δ	2-Butene	cis/trans = 1.8	b
	Δ	2-Butene	cis/trans = 2.3	a
	$h\nu$	2-Butene-2-d	trans/cis = 24	3
	Δ	2-Butene	trans/cis = 8.0	b
	Δ	2-Butene	trans/cis = 4.0	a
	Δ	2-Butene	trans/cis = 3.0	a

^a This work. ^b H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 3935, 4884 (1951).

that cyclobutane pyrolyses yield cleavage products with low stereochemical retention in the olefin moieties, while photochemical singlet reactions are apparently more stereospecific. With the exception of the present report, a diradical prepared by these two very different methods has not been described. Earlier, most of the photochemically derived diradicals involved tertiary radical centers, while many of the cyclobutane derived diradicals involved secondary centers. Several workers^{10,11} have ascribed the higher stereospecificity in the photoreactions to ponderal rotor effects caused by increasing alkyl substitution at the radical site but neglected differences in mode of generation. The present report demonstrates the importance of the latter.

the reaction vessel with quartz wool did not influence the results. Vpc analysis showed that cleavage proceeded eight-ten times faster than isomerization or back-abstraction to ketones, and the results in Table I are olefin ratios for low per cent conversion runs (<5%).

(5) W. T. Brady and J. P. Hieble, *J. Org. Chem.*, **36**, 2033 (1971).

(6) N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970).

(7) Nmr and microanalytical data are in agreement with these structures.

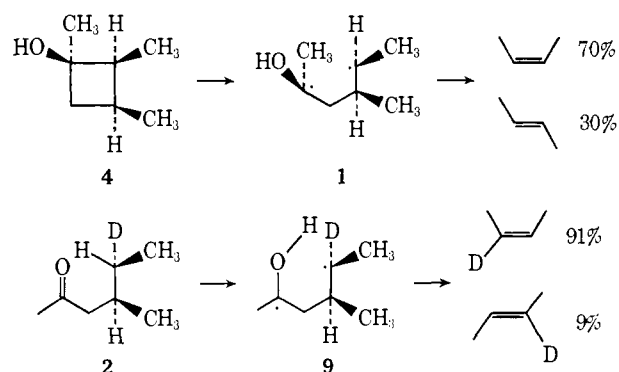
(8) (a) M. Julia, Y. Noël, and R. Guégan, *Bull. Soc. Chim. Fr.*, **35**, 3742 (1968); (b) E. D. Feit, private communication.

(9) (a) P. Ausloos and R. E. Ribbert, *J. Amer. Chem. Soc.*, **83**, 4897 (1961); (b) G. Eadon, *ibid.*, **94**, 8938 (1972).

(10) J. A. Berson, D. C. Tompkins, and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 5799 (1970).

(11) G. Jones, II, *J. Chem. Educ.*, **51**, 175 (1974).

A detailed comparison of two of the reactions in Table I illustrates this point. Photoreaction of ketone 2 will produce diradical 9 which in turn gives the 2-butenes



in the ratio cis/trans = 10. Pyrolysis of cyclobutanol 4 leads to the structurally identical diradical 1 which in turn gives the 2-butenes in the ratio cis/trans = 2.3. Obviously the photoreaction is more stereospecific. Curiously, this is true despite the fact that the orbital alignment in 9 must be initially less favorable than that in 1 for the subsequent cleavage reaction to 2-butene and acetone enol.¹² We would expect an even greater contrast in stereospecificity if both species were to be generated in identical configurations.

This greater stereospecificity can be rationalized by noting that diradicals produced in photochemical steps possess substantial excess energy (40–60 kcal/mole above the estimated diradical ground state, calculated by taking the n, π^* singlet energy, 100 kcal/mol, and then making adjustments for the bonds which have been broken and formed). Thus, in accord with simple chemical activation concepts and RRKM theory¹³ those reactions with high preexponential factors (A factors) such as bond cleavage and/or closure ($\sim 10^{13}$) would begin to dominate those with lower preexponential terms such as rotation ($\sim 10^{11}$). The result would be that all reaction rates would increase, but cleavage and closure rates would increase faster. Thus greater stereospecificity for the "hot" molecule reactions would be expected. This hypothesis as it applies to both 1,3- and 1,4-diradicals derived from both photochemical reactions and from relatively high energy azo compounds has been discussed in a previous paper.¹⁴

We feel that if the photoreaction were to be carried out in the gas phase, this hot molecule effect would be even more pronounced. In general such effects become more important at low pressure¹⁵ and we would expect a comparison of the reactions of diradicals 1 and 9, for example, would be even more dramatic under identical conditions than is the case here.

A scheme (Scheme I) capable of rationalizing many of the important aspects of 1,4-diradical chemistry is presented below. This picture still leaves several important questions unanswered. For example, details of the competition between hot, singlet diradical de-

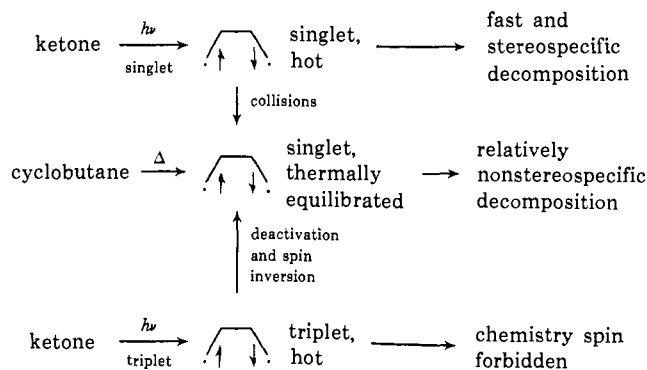
(12) (a) N. J. Turro and D. S. Weiss, *J. Amer. Chem. Soc.*, **90**, 2185 (1968); (b) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Bartrop, and J. D. Coyle, *ibid.*, **93**, 7213 (1971).

(13) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley Interscience, New York, N. Y., 1973.

(14) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

(15) For an example of this behavior and an example of a chemical activation effect which persists even in solution see J. I. Brauman, W. E. Farneth, and M. B. D'Amore, *J. Amer. Chem. Soc.*, **95**, 5043 (1973).

Scheme I



activation and decomposition are unknown. Data of Rabinovitch¹⁶ indicate that as much as 5 kcal/mol excess energy may be removed from a molecule in a single collision. This suggests a lifetime in hydrocarbon solution for the hot species of 10^{-10} – 10^{-11} sec. This is roughly the same time scale we expect for the cleavage and rotation motions, but we can be no more quantitative at this time.

The lifetime and associated loss of stereochemical integrity in the triplet species are also interesting points which cannot yet be addressed with certainty. It is clear from the present interpretation (see Scheme I) that at least part of the nonspecificity of the triplet diradical reactions can be ascribed to the ultimate intervention of the thermally equilibrated singlet diradical. Indeed, it is not obvious in the present case that the triplet diradical itself scrambles at all;¹⁷ other reports, for example the recent study of O'Neal,¹⁸ indicate that the triplet diradical should scramble stereochemistry extensively. This point requires substantial added study before it can be resolved completely.

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(16) Y. N. Lin and B. S. Rabinovitch, *J. Phys. Chem.*, **74**, 3151 (1970).

(17) A comparison of the loss of stereochemistry from the thermally equilibrated singlet derived from our pyrolyses, with the triplet diradical of Casey (ref 3), shows no very substantial difference.

(18) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Amer. Chem. Soc.*, **96**, 3351 (1974).

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Preferred Directions of Photoisomerization of Ionylideneacetaldehyde and the C₁₈-Tetraene Ketone in the Retinal Series. Synthesis of the Hindered 7-Cis Isomers¹

Sir:

The chemical properties of conjugated diene² and triene triplets³ suggest the presence of a common intermediate or rapidly equilibrating intermediates. The relaxed triplets are believed to have a perpendicular π -system with the planar structure somewhat higher in

(1) Photochemistry of Polyenes VII. No. VI of the series is R. S. H. Liu, Y. Butt, and W. G. Herkstroeter, *J. Chem. Soc., Chem. Commun.*, 799 (1973).

(2) See, e.g., J. Saltiel, *et al.*, *Org. Photochem.*, **3**, 1 (1973).

(3) R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, **93**, 1532 (1971).