Stirring was continued for an additional 3 hr; the mixture was then filtered and the ether washed ($NaHCO_3$), dried, and removed. The crude product showed nmr absorption at δ 2.07 (s, methyl ketone) and 11.3 ppm (t, aldehyde CH). The keto aldehyde was also heat sensitive and was thus carried directly to the keto acid by treatment with silver oxide according to the method of Campaigne and LeSeur.[21] The crude acid (20 g) was treated with 300 cm^3 of methanol with a few drops of added sulfuric acid overnight at room temperature. Methanol was removed and the residue was taken up in ether and washed (H_2O). The ether layer was dried and removed and a slightly yellow liquid was distilled to yield 12 g of clear liquid, bp 65° (15 mm) (31% from trimethylcyclohexene). This keto ester could be conveniently purified by preparative vpc on a 15 ft × $^3/_8$ in. Carbowax column maintained at 190–200°. SE-30 liquid phases were also adequate but less satisfactory. Both isomers showed sharp nmr absorption at δ 2.1 and 3.7 ppm (three protons each) and broad absorption centered around 2.1 and 0.9 ppm. The uv spectra were identical: λ_{max} 280 nm (ϵ 27, pentane).

Anal. Calcd for $C_{10}H_{18}O$: C, 64.49; H, 9.74. Found for *erythro*-IIa: C, 64.38; H, 9.71. Found for *threo*-IIa: C, 64.29; H, 9.79.

Identification of Olefin Isomers. *erythro*-Keto ester (1.3 g) I was irradiated for 5 hr in 20 cm^3 of pentane with a medium-pressure mercury arc using Pyrex filtering. The solvent was then removed and the mixture examined on a 15% SE-30 column, 15 ft × $^3/_8$ in. at 200° revealing starting material (retention time 20 min), two minor products at shorter times (16 and 18 min), and a major product at 6-min retention time. This low molecular weight product was collected from the SE-30 column and further purified on a 20% Carbowax 20M column, 15 ft × $^3/_8$ in., maintained at 110°. Two well-resolved components were observed here and were collected pure. These products were found to be identical with the two major products derived from the dehydration described below; the nmr characteristics of these products are summarized below in Table II.

Alternate Route to Methyl *cis*- and *trans*-2-Methyl-$\Delta^{2,3}$-pentenoate. The preparation and P_2O_5 dehydration of methyl β-methyl-β-hydroxypentanoate have been described by Kon and Nargand[9] and were repeated here with similar findings. Four products were observed on Carbowax 20M at 110° in a ratio of 20:55:20:5 given in order of increasing retention time. Pure samples of the first two are identical with the products derived from the photolysis of the keto ester. The other products appear to be α,β-unsaturated esters. See Table II. This agrees with the findings of the authors above that the β–γ unsaturated isomers represent the bulk of the dehydration mixture.

Quantitative Photolyses. Identical quantities of keto ester and an internal standard (tetradecane) together with varying amounts of isoprene (0–5 *M*) were diluted with pentane so that the ketone concentration was *ca.* 1 *M*. Equal amounts of these solutions were then sealed in 13-mm Pyrex tubes after three freeze–pump–thaw degassing cycles (ultimate pressure *ca.* 10^{-3} mm), and irradiated on a merry-go-round device. A medium-pressure Hg lamp together with Pyrex filtering was employed. Under these conditions the ketone absorbed >95% of the incident light even at the higher diene concentration. These samples were then analyzed in duplicate using matched 15 ft × $^1/_4$ in. 20% Carbowax 20M columns on a Hewlett-Packard F and M Model 5750 gas chromatograph equipped with flame ionization detector, with temperature programming between 110 and 200°.

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[21] N. Rabjohn, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 919.

The Chemistry of 1,4 Diradicals. II. The Interpretation of Spin Correlation Effects

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Abstract: The chemistry of 1,3 and 1,4 diradical species derived from different sources is discussed in terms of their origins and structures. Singlet diradicals produced from azo compounds and Norrish type II photoreactions behave differently from those produced *via* small ring pyrolyses. The properties of these and triplet diradicals are analyzed.

In recent years, many cycloaddition reactions[1] have provided strong evidence for the intermediacy of 1,4 diradicals. Attempts to generate these diradicals by alternate routes have been generally successful, although the species has never been directly observed (Chart I). 1,4 diradicals show three types of reactions in most systems: hydrogen atom transfers (internal disproportionation), ring closure to cyclobutanes, and cleavage to olefins. The stereospecificities of all three reactions have been the subjects of recent study; Bartlett and Porter[2] have studied the decomposition of Ia and Ib to cyclobutanes, Yang and Elliott[3] have studied the photoracemization of II resulting from γ hydrogen atom abstraction by the excited-state carbonyl, and Stephenson, Cavigli, and Parlett[4] have studied the photocleavage of III to *cis*- and *trans*-olefins subsequent to γ hydrogen abstraction. The striking feature of these studies is the large difference in product distribution when singlet or triplet precursors to the diradicals are used. Thus the above examples show high stereospecificity in the reactions which proceed from singlet precursors, and little or no selectivity in the triplet-derived reactions. Since it is reasonably certain that these reactions involve diradical intermediates,[4]

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[1] For example, see: G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, 28, 3297 (1963); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, 86, 622 (1964).

[2] P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

[3] N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

[4] L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid.*, **93**, 1984 (1971).

Chart I. Some Routes to 1,4 Diradicals

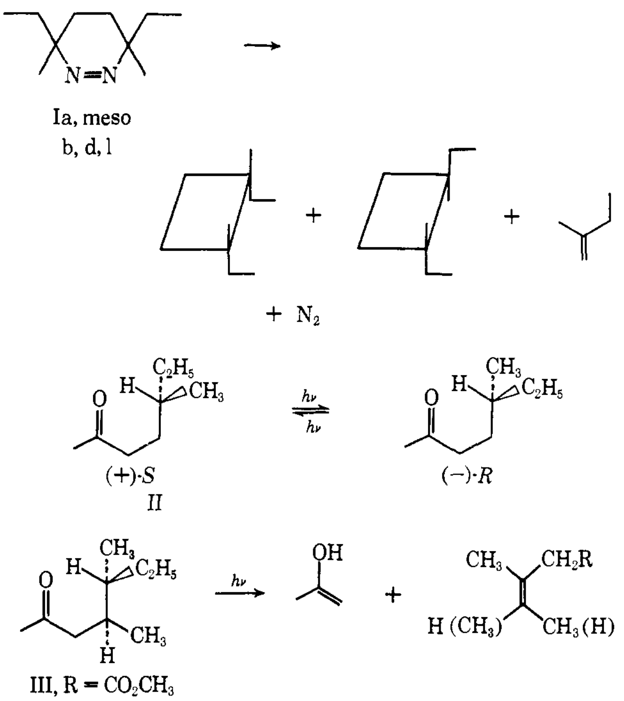
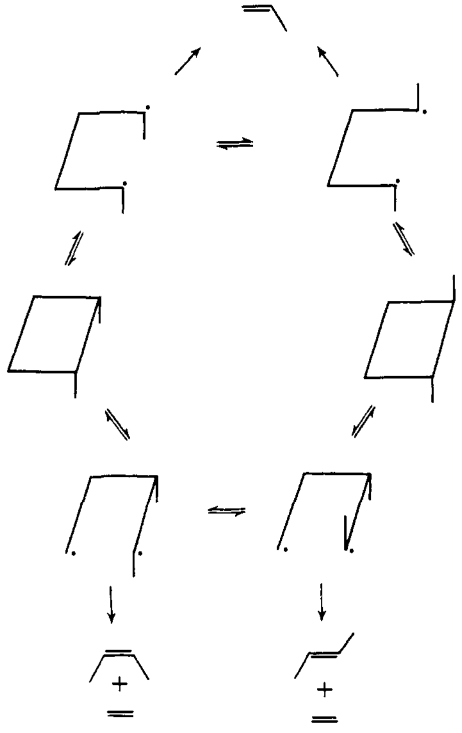


Chart II. Thermal Reactions of Dimethylcyclobutane



and since spin conservation considerations demand that the diradical intermediate be generated, at least initially, in the same spin state as its immediate precursor, it follows that these 1,4 diradicals show differences in behavior which depend on spin multiplicity. In the terminology of Bartlett, these reactions display a large spin correlation effect.

It is tempting to discuss such effects in terms of singlet and triplet 1,4 diradicals, differing only in spin states, with the triplet species unable to undergo bond-forming reactions until spin inversion to the singlet species occurs, a step presumably slow enough to permit extensive stereochemical scrambling. "The differences [in stereoselectivity] correspond to the expected longer lifetime of the triplet biradical . . . the parallel spins delay ring closure [and] allow rotation about all three single bonds separating the radical centers."[2] Unfortunately, this highly attractive explanation appears to be inconsistent with results in other systems, and below we seek an alternate hypothesis concerning spin correlation effects.

Singlet 1,4 Diradical. Cyclobutane pyrolysis reactions, which have been consistently analyzed in terms of 1,4 diradical intermediates,[5,6] show little stereospecificity, in marked contrast to the reactions of the singlet 1,4 diradicals studied by Bartlett, Stephenson, and Yang. An analysis of the pyrolysis of *cis*- or *trans*-1,2-dimethylcyclobutane studied by Walters[5a] will illustrate this point. The reaction was conducted at 425 ± 50° and at these temperatures can be understood in terms of singlet diradicals formed by breaking the 1,2 or 2,3 bonds (Chart II). It would appear that *all processes shown, bond rotation, ring closure, and cleavage, are competitive*. Of particular interest is the *cis*:*trans*-butene-2 ratio of *ca.* 1.8:1 in the initial stages of the pyrolysis of *cis*-1,2-dimethylcyclobutane and 1:9 beginning from the trans compound. Extrapolation of this result to room temperature shows that an even greater loss of stereochemical integrity would be anticipated.[7] In contrast, the singlet component of the room-temperature photolysis reaction reported by Stephenson and coworkers[4] yields olefins in cis:trans ratios of *ca.* 90:1.

The quantitative analysis of the pyrolysis system due to O'Neal and Benson[5b] is a further aid in visualizing the differences. The activation energy for cis–trans isomerization of the cyclobutane, postulated to occur *via* a 1,4 diradical was found to be 7.4 kcal/mol higher than the estimated energy difference[8] between cyclobutane and the diradical. Thus an activation energy of this magnitude is demanded for the ring-closure reaction in the diradical system of Walters. A similar estimate of E_a was made for the cleavage reaction. A bis tertiary diradical such as that reported by Bartlett and Porter would doubtless cross a barrier at least as high as the 7.4 kcal/mol required to close the Walters diradical. To account for the high stereospecificity observed in the Bartlett–Porter system would then require a bond rotation barrier of about 10 kcal/mol, which appeared to be remarkably high. Similarly high barriers to rotation would be required in the olefin-forming reactions studied by Stephenson to account for the high stereospecificity found.

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[5] (a) H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 4884 (1961); (b) E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

[6] However, see R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

[7] A thermochemical analysis of this system by O'Neal and Benson[5b] has indicated an activation energy of 7.4 kcal/mol for the cleavage reaction to olefins. It is known that the bond rotation rates and the cleavage rates are approximately the same in this system; both 2-butene isomers are formed. It seems unlikely that any bond rotation in the diradical system of Walters would possess an internal rotation barrier higher than 7.4, and much lower estimates might be made. Thus both the *A* factor and activation energies for bond rotation are expected to be smaller than the comparable activation parameters for cleavage in order to account for equal rates. Hence, at lower temperatures bond rotation would compete with the cleavage step even more favorably than the high-temperature numbers indicate.

[8] The estimate was corrected for gauche interactions in the conformations preceding ring closure, and for heat capacity changes between room temperature and 425°.

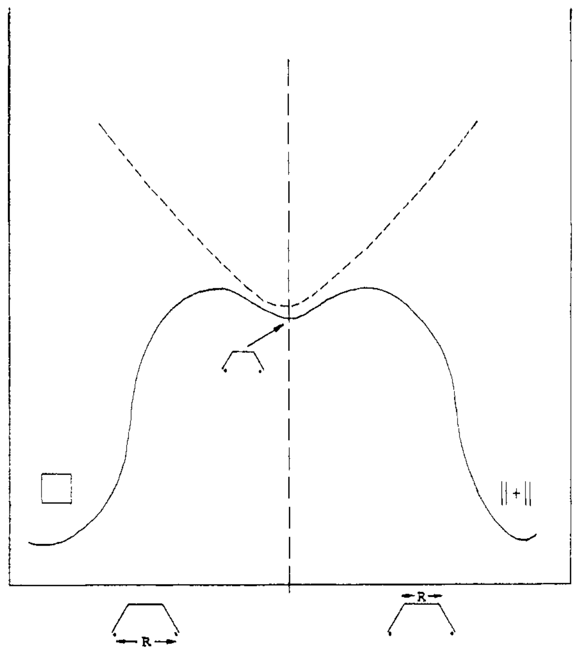

Figure 1. Potential energy surface for the 1,4 diradical.

If the barriers to internal rotation are much less than 10 kcal/mol then the reactions of the singlet 1,4 diradical formed in the photoreactions of Stephenson and Yang, or the thermal reactions of Bartlett, are not those which would be expected if the species were formed *via* cyclobutane pyrolyses. On the other hand, recent work of Berson, Tompkins, and Jones[9] indicates that rotational barriers in tertiary radicals may be quite high. However, inclusion of even lower barriers in the analysis of the triplet diradical systems (*vide infra*) gives rise to inconsistencies. Thus we conclude that the bulk of the singlet diradical species produced in the reactions carried out by Bartlett, Stephenson, and Yang cannot be that described by the shallow minimum at the top of the solid curve in Figure 1.

Triplet 1,4 Diradical. Discrepancies develop in an examination of the triplet component of diradical-forming reactions, where the lack of stereospecificity demands that bond rotation rates compete with overall closure and cleavage rates. The bond rotation rate constant, according to our estimates,[10] must be $\cong 10^6$–10^8 sec^{-1} for barriers of 5–8 kcal/mol. Thus the overall closure or cleavage rate constant of the triplet must be *ca.* 10^4–10^6 sec^{-1}. *This is much too slow to be the spin inversion rate constant.* The fluctuating magnetic and electric fields produced by the relatively loose oscillations of the 1,4 diradical together with the small anticipated singlet–triplet energy spacing make it likely that this spin inversion rate constant would be substantially greater than the spin inversion rate constants for aromatic hydrocarbon excited triplet decay, which lie between 10^3 and 10^6 sec^{-1} at room temperature. The application of even higher barriers to internal rotation cannot improve this situation, even though the A factors would be expected to increase since the motion would begin to possess more of the characteristics of a torsion rather than a free rotation.

Since the stereospecificity exhibited in the reactions of this triplet species seems to be similar to the extrapolated behavior of the 1,4 diradical intermediate implicated in the cyclobutane pyrolysis, it is attractive to postulate rapid spin inversion of the triplet intermediate to the singlet intermediate described by the shallow minimum in the potential energy surface of Figure 1. This leads us to draw the potential energy surfaces for the singlet and triplet diradicals quite close to one another in regions of large R (referring in this case to 1,4 bond distance) in Figure 1; a result required as $R \rightarrow \infty$. It is clear that *some* rate-limiting step(s) must exist other than bond rotation. We conclude that these slow steps are ring closure or cleavage, and not spin inversion to a singlet species which can ring close or cleave rapidly.

In summary, normal barriers to internal rotation (5–8 kcal/mol) are not consistent with the singlet diradical results; higher barriers (10 kcal/mol), while accommodating the singlet diradical results, give rise to anomalously long triplet diradical lifetimes. Thus either presuppositions concerning spin inversion lifetimes are inaccurate or the usual interpretation of spin correlation effects is incorrect. As noted above, our discussion presumes that the latter is true.

Discussion

A common feature of the Bartlett, Stephenson, and Yang routes to the 1,4 diradical is the production of a species with excess energy relative to any point on the solid curve in Figure 1.[11] The stereospecificity of these reactions can thus be ascertained by determining the point on the potential energy curve to which the species falls when vibrationally deactivated, since the behavior of the intermediates in the cyclobutane pyrolysis reactions is known. High stereospecificity could be maintained if the species were deactivated into either of the deep minima of Figure 1 and avoided the shallow 1,4 diradical minimum, since vibrational deactivation should compete very favorably with bond rotations. In thermally equilibrated 1,4 diradicals the exothermic 1,4 bond forming step is initially countered by incipient ring strain of the cyclobutane system, rendering this transformation slow. In the vibrationally "hot" 1,4 diradical species this ring strain barrier is easily overcome, regions of energy space involving small 1,4 bond distances are easily accessible, and vibrational deactivation to cyclobutane is more likely. In equivalent terms, potential energy surfaces should exist which allow deactivation of the hot diradical to cyclobutane and involve no appreciable apparent barrier to ring closure.[12] Using similar arguments one can also

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[9] J. A. Berson, D. C. Tompkins, and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 5799 (1970). However, if cleavage is appreciably faster than ring closure in the tetramethylcyclobutane system, this conclusion may not be valid.

[10] Based on the method of Golden, *et al.* (D. M. Golden, S. Furuyama, and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 57 (1969)), we estimate this rate constant as $\log k = 11.5 - (E_a/2.3RT)$. Conveniently at room temperature the barrier to rotation is approximately equal to E_a.

[11] For example the singlet excited state of a ketone would have ~100 kcal/mol of electronic energy. The various bond-breaking processes which lead to a diradical are endothermic by ~60 kcal/mol leaving 40 kcal/mol excess.

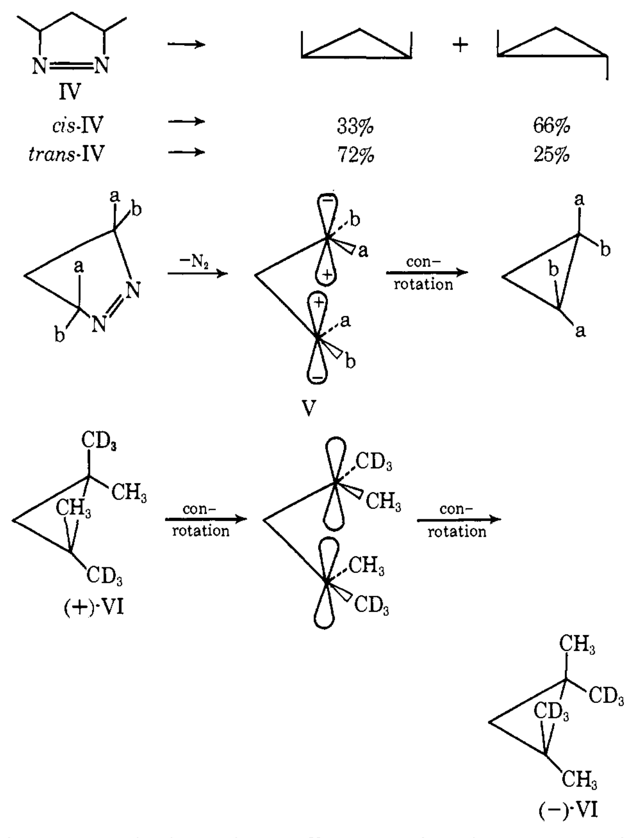
[12] Studies of chemically and photochemically activated species have been common in the gas phase.[13] The behavior of such species is generally analyzed successfully in terms of quasi-equilibrium theories such as the RRK treatment, which describe reaction rate constants as $k = A(1 - E^*/E)^{s-1}$ (with E^* = critical energy for the reaction of interest, E = energy of the "hot" species, and S = number of effective oscillators). In the limit of large E the reaction rate constant clearly approaches the A factor. Since the A factors for the bond-forming steps are higher

postulate fast deactivation of the diradical to olefins.[14]

The triplet portion of the diradical reactions does not have such possibilities. In the regions above the deep minima in Figure 1 the triplet potential energy surface is strongly repulsive (dotted line). Provided that vibrational deactivation is fast relative to spin inversion, the triplet diradical vibrationally deactivates to a region close to that described as the shallow region of the potential energy surface. It would appear that these vibrationally relaxed triplet species are similar to the singlet diradical species generated in cyclobutane pyrolyses in terms of inability to preserve stereochemistry, and there seems to be no need to postulate long triplet–singlet interconversion rates to account for lack of stereospecificity. Calculations of spin inversion rates would require then either a substantial number of assumptions, or data which are now lacking.

1,3 Diradical. As in the 1,4 diradical system, different modes of generation give 1,3 diradicals with strikingly different properties. Cyclopropane pyrolysis reactions show little or no stereospecificity, while an alternate route to the 1,3 diradical, the thermolysis of pyrazolines, leads to significant maintenance of stereochemical integrity in the products. Particularly interesting are the results of Crawford[15] who has studied the decomposition of both *cis-* and *trans*-3,5-dimethylpyrazoline (IV) and reports an unusual stereochemical crossover in the product cyclopropanes (see Chart III). The results were neatly explained by Hoffmann[16] using extended Hückel calculations, which indicated an energy minimum for a planar π type diradical V, which prefers a conrotatory ring closure. Since the extrusion of nitrogen seems likely to occur in a "cis" manner this leads to overall inversion of configuration, *cis*-dimethylpyrazoline yielding *trans*-dimethylcyclopropane.

Chart III. The 1,3 Diradical



On the other hand, pyrolyses of optically active cyclopropanes (VI for example), reactions studied by Berson[17] and Bergman,[18] demonstrate that most probably a potential energy surface exists for the cyclopropane pyrolytic ring opening which is of lower energy than that calculated by Hoffmann to involve a π type diradical. Thus, in line with the analyses of many other workers,[5] the results of Berson[17] and Bergman[18] are most conveniently understood in terms of a long-lived 1,3 diradical with relatively free rotation of the two ends and a large barrier to ring closure (~10 kcal), factors which ensure significant stereochemical scrambling. At best, only weak support for the mechanism outlined in Chart III for the racemization of VI could be found.

Once again the feature which leads to a peculiar behavior of the azo-derived diradical is the fact that it is generated in a thermally activated state. Since the earlier work of Crawford strongly suggests that the configuration of the five-membered ring which leads to nitrogen extrusion would form a diradical intermediate with strong geometric resemblance to π-cyclopropane, it would not be unreasonable that diradicals produced in this manner would use the potential energy surface calculated by Hoffmann during vibrational deactivation to cyclopropane. As in the case of the 1,4 diradical, it is the vibrationally excited 1,3 diradical which is able to explore these high potential energy surfaces, energetically unattainable by the thermally equilibrated species. It is not clear at this time if the lack of high stereospecificity reflects greater leakage to the "thermally equilibrated" diradical, or only that the symmetry principles do not place large constraints on this system.[19]

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than those for rotation[7] in the 1,4 diradical, the trend toward high stereospecificity noted for the reactions of the high-energy diradicals would be expected. It is not clear to what extent such a theory is applicable to solution-phase studies where vibrational deactivation is expected to be rapid ($k = 10^{12}$–10^{13} sec^{-1}). It is probable, however, that vibrational deactivation will proceed without significant loss of stereochemical integrity since even as the rotation rate constant approaches its limit of $k_{\mathrm{rot}} = A_{\mathrm{rot}} \cong 10^{11.5}$ sec^{-1}, it competes only inefficiently with the deactivation step. The data of Bartlett, Stephenson, and Yang require that the singlet diradical species formed in their reactions be deactivated directly to cyclobutane, olefins, or disproportionation products, without the intervention of long-lived, thermally equilibrated, 1,4 diradicals—a result accommodated by our analysis.

(13) B. S. Rabinovitch and M. C. Flowers, *Quart. Rev., Chem. Soc.*, 122 (1964).

(14) This sequence requires the postulation of a single species, the diradical, which can partition to both two ethylenes or cyclobutane. In the limit of significant 1,4 interactions in this species the sequence would violate orbital symmetry principles. For geometrical reasons there seems to be no need to invoke large 1,4 interactions in the species. Indeed, the thermal-concerted extrusion of nitrogen from an azo compound, which produced a strongly interacting radical pair, would itself represent a disallowed 2 + 2 cycloreversion. The identical behavior observed in the direct irradiation of the azo compound, a reaction which could produce products *via* a concerted extrusion of nitrogen, also supports this point of view.

(15) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, 88, 3963 (1966).

(16) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

(17) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968).

(18) W. L. Carter and R. G. Bergman, *ibid.*, **90**, 7344 (1968); R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969). This paper contains an extensive analysis of cyclization–rotation rate ratios in diradical systems.

(19) P. D. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971). These authors present an alternate explanation for this effect.