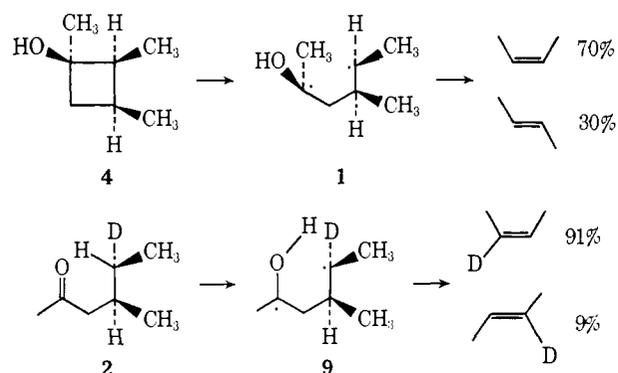


A detailed comparison of two of the reactions in Table I illustrates this point. Photoreaction of ketone **2** will produce diradical **9** which in turn gives the 2-butenes



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.<sup>12</sup> 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  $n, \pi^*$  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 theory<sup>13</sup> 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.<sup>14</sup>

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 pressure<sup>15</sup> 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-

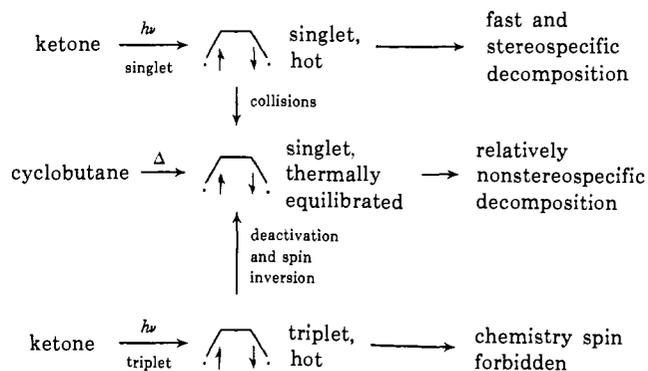
(12) (a) N. J. Turro and D. S. Weiss, *J. Amer. Chem. Soc.*, **90**, 2185 (1968); (b) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Bartrop, and J. D. Coyle, *ibid.*, **93**, 7213 (1971).

(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 Rabinovitch<sup>16</sup> 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;<sup>17</sup> other reports, for example the recent study of O'Neal,<sup>18</sup> indicate that the triplet diradical should scramble stereochemistry extensively. This point requires substantial added study before it can be resolved completely.

**Acknowledgment.** The authors wish to thank E. I. du Pont de Nemours and Company for their generous support *via* a du Pont University Science and Engineering Grant.

(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 C<sub>18</sub>-Tetraene Ketone in the Retinal Series. Synthesis of the Hindered 7-Cis Isomers<sup>1</sup>

Sir:

The chemical properties of conjugated diene<sup>2</sup> and triene triplets<sup>3</sup> suggest the presence of a common intermediate or rapidly equilibrating intermediates. The relaxed triplets are believed to have a perpendicular  $\pi$ -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).

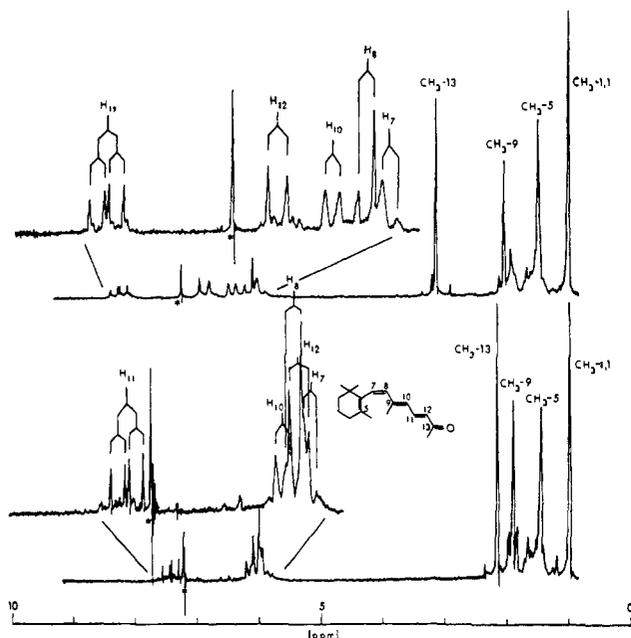
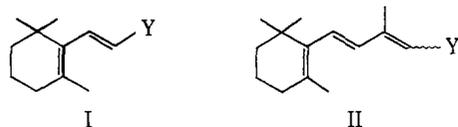


Figure 1. PMR spectra of 7-cis  $\beta$ -C<sub>18</sub> ketone in CDCl<sub>3</sub> locked on TMS (lower) and after addition of Eu(fod)<sub>3</sub>-shift reagent (upper). \*  $\equiv$  benzene.

energy. Such conclusions are in agreement with results of extended HMO and semiempirical SCF-CI calculations.<sup>4</sup> On the other hand, these calculations also predict in longer polyenes a change of relative stability of the planar triplet as compared to the twisted. This prediction, however, has not been verified by experiments. A reversal of ordering of relaxed polyene triplets could profoundly change photochemical properties of polyenes, particularly in hindered polyenes such as compounds related to 7-cis isomers of retinal, a system of considerable interest to us. We now believe to have obtained experimental evidence in support of the calculated results, and in the process of this study we have prepared useful precursors to presently unknown 7-cis isomers of retinal.<sup>5</sup>

We reported that under selective sensitization conditions,  $\beta$ -ionyl (I) and several  $\beta$ -ionylidene derivatives (IIa-c)<sup>6</sup> undergo one-way geometric isomerization to the 7-cis isomers. Subsequently, we found, initially to our dismay, that the corresponding triene aldehyde (IIc), a key intermediate in the synthesis of vitamin A



- a, Y = H  
b, Y = CO<sub>2</sub>R  
c, Y = CN  
d, Y = CHO

and carotene, failed to produce 7-cis isomers under a variety of conditions for sensitized irradiation.<sup>7</sup> Addi-

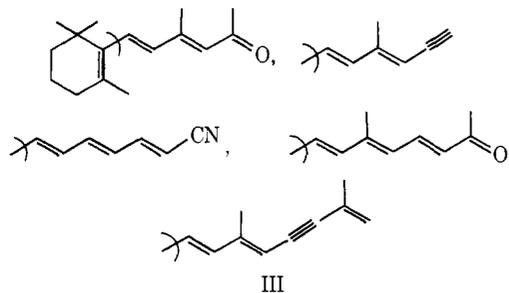
(4) (a) R. Hoffmann, *Tetrahedron*, 521 (1966); (b) N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 4427 (1971).

(5) Only six isomers all with the 7-trans geometry are known. Isomers with 7-cis geometry involving 1,6-methyl, methyl interaction were once thought to be too sterically hindered for preparation. Two of these contain the slightly less hindered 11-cis geometry. For a comprehensive review of vitamin A and carotene see O. Isler, Ed., "Carotenoids," Birkhauser Verlag, Basel and Stuttgart, 1971.

(6) V. Ramamurthy, Y. Butt, C. Yang, P. Yang, and R. S. H. Liu, *J. Org. Chem.*, **38**, 1247 (1973).

tional experiments showed that this lack of chemical reactivity is apparently an intrinsic property of the triplets. First, with 9,10-dimethyl-1,2-benzanthracene ( $E_T = 44.3$  kcal/mol)<sup>7</sup> as sensitizer we showed that IIc (up to  $8.0 \times 10^{-3}$  M) has a negligible effect on its fluorescence intensity. Clearly, the failure to form 7-cis isomers is not due to removal of donor excitation through some forms of singlet quenching. At the same time, triplet energy transfer apparently did take place because isomerization around the 9,10 double bond occurred reaching a 60:40 7,9-ditrans and 7-trans-9-cis isomer ratio. To confirm that this represents a genuine photostationary composition, irradiation of the 7-cis isomers was conducted. The compounds were synthesized by partial reduction of a mixture of 7-cis isomers of IIc by diisobutylaluminum hydride followed by chromatographic separation on silica gel columns: 7-cis nmr 1.52 s (C<sub>5</sub>-CH<sub>3</sub>), 6.22 d,  $J = 12.0$  Hz (H<sub>7</sub>), 6.04 d,  $J = 12.0$  Hz (H<sub>8</sub>), 5.88 d,  $J = 8.0$  Hz (H<sub>10</sub>), 9.98 ppm d,  $J = 8.0$  Hz, H<sub>2</sub>(CHO); 7,9-dicis 1.52 s (C<sub>5</sub>-CH<sub>3</sub>), 6.28 d,  $J = 12.0$  Hz (H<sub>7</sub>), 6.92 d,  $J = 12.0$  Hz (H<sub>8</sub>), 5.68 d,  $J = 3.0$  Hz (H<sub>10</sub>), 10.02 d,  $J = 8.0$  Hz (CHO).<sup>8</sup> The C<sub>5</sub>-Me signals are 0.14 ppm upfield from the corresponding signals in the 7-trans isomers, characteristic of all 7-cis isomers in this series.<sup>9</sup> Upon sensitized irradiation<sup>7</sup> of either a mixture of these 7-cis isomers or either single isomer, a mixture containing only the two 7-trans isomers was obtained with an isomer ratio identical with that starting from the 7-trans isomers.

This selective decay also exists in higher polyenes in this series. Some of the examples we have examined so far are shown below.



Of particular interest are two 7-cis isomers of the C<sub>18</sub>-tetraene ketone (possible precursors to 7-cis retinal), obtained by base-catalyzed condensation of acetone with the 7-cis isomers of IIc. The nmr spectrum of one of the two ketone isomers (7-cis), with and without Fluoroshift,<sup>10</sup> is shown in Figure 1 as a representative example. Similar unambiguous assignments can be made for the 7,9-dicis isomer<sup>11</sup>: 7-cis H<sub>7</sub> 5.95 d,

(7) With Corning 0-51 filter and 9-fluorenone ( $E_T = 51$  kcal/mol) benzanthrone, (47.0), or benzanthracene (47.2) as sensitizer. For sensitizer excitation energies see W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(8) Other spectroscopic properties, which will be reported in full in the future, agree with the assignments.

(9) This conclusion was based on observation with more than 20 pairs of geometric isomers in this series, prepared by Mr. Ramamurthy in our laboratory. The upfield shift of C<sub>5</sub>-CH<sub>3</sub> in the cis isomers is clearly due to shielding by the exo-cyclic alkenyl chain which assumes a conformation perpendicular to the ring. For a nmr study of some of these compounds see V. Ramamurthy, T. T. Bopp, and R. S. H. Liu, *Tetrahedron Lett.*, 3915 (1972).

(10) R. E. Sievers and R. E. Rondeau, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(11) The newly formed double bond from the condensation reaction, therefore, has the trans geometry. This is in agreement with results with the 7-trans-IIc: M. Mousseron-Canet and J.-C. Mani, *Bull. Soc. Chim. Fr.*, 3285, 3291 (1966).

H<sub>8</sub> 6.09 d, H<sub>10</sub> 6.18 d, H<sub>11</sub> 7.46 dxd, H<sub>12</sub> 6.06 ppm d,  $J_{7,8} = 12.5$  and  $J_{11,12} = 14.5$  Hz; 7,9-dicis H<sub>7</sub> 5.97 d, H<sub>8</sub> 6.60 d, H<sub>10</sub> 6.14 d, H<sub>11</sub> 7.52 dxd, H<sub>12</sub> 6.03 d,  $J_{7,8} = 12.0$ ,  $J_{11,12} = 15$  Hz). Direct or sensitized irradiation of these tetraene ketone isomers results in conversion to a mixture of the 7-trans isomers as indicated by complete replacement of the singlet at 1.50 ppm (C<sub>5</sub>-Me in 7-cis isomers) by a broad lower field singlet between 1.70 and 1.75 ppm, corresponding to the C<sub>5</sub>-Me's in 7-trans isomers.

An obvious trend in this series of compounds is that geometric isomerization around the 7,8-double bond,<sup>12</sup> when the conjugation involves four double bonds or longer, shows a decay ratio prohibitively in favor of the trans. This somewhat unexpected result, however, can be rationalized by the excited state torsional potential curve around the 7,8-bond. Because of higher ground state and S<sub>0</sub> → T<sub>1</sub> excitation energies, cis triplets are expected to be much higher in energy than the trans. If one further assumes, in agreement with the calculated results for tetraenes,<sup>4a</sup> that any intermediate structures in going from trans to cis are higher in energy than the trans, when one expects excitation from either isomer will result in the exclusive formation of the trans. The photochemical results, therefore, simply reflect the distorted shape of the potential curve. It is worth noting that the excited state potential curve for the slightly less hindered 11-cis-retinal is available in the literature<sup>13</sup> which takes the general shape of our postulated model for the 7-cis compounds. It is also interesting to note that extension of our results would predict that 7-cis-retinal isomers should not be present in significant amounts in the photostationary state mixture. This agrees with present knowledge of retinal photochemistry which is based on study starting from the 7-trans isomers.<sup>14</sup> A more definitive confirmation of this prediction would be irradiation of the 7-cis isomers. The preparation of such hindered retinal isomers is in progress in our laboratory.<sup>15</sup>

(12) IId is probably more appropriately considered as a tetraene. For example, the triplet energy of a trienealdehyde (43.5 kcal/mol) is known to be much lower than that of hexatriene (48): D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(13) (a) J. R. Wiesenfeld and E. W. Abrahamson, *Photochem. Photobiol.*, **8**, 487 (1968); (b) J. Langlet, B. Pullman, and H. Berthod, *C. R. Acad. Sci.*, 1616 (1969).

(14) A. Kropf and R. Hubbard, *Photochem. Photobiol.*, **12**, 249 (1970).

(15) This work was supported by the National Eye Institute, Public Health Service, Research Grant No. EY-AM 00918.

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### A Laboratory Model for the Biosynthesis of Cyclopropane Rings. Copper-Catalyzed Cyclopropanation of Olefins by Sulfur Ylides

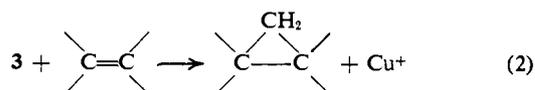
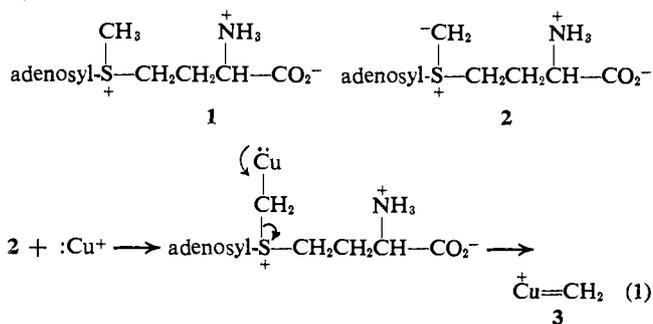
Sir:

The biosynthesis of the cyclopropane ring in a number of natural products is known to occur by the transfer of a methylene group from the methyl group of *S*-adenosylmethionine (1) to an unactivated olefin such as an oleic ester.<sup>1</sup> It has been suggested<sup>2</sup> that the process in-

(1) J. H. Law, *Accounts Chem. Res.*, **4**, 199 (1971).

(2) (a) S. Pohl, J. H. Law, and R. Ryhage, *Biochim. Biophys. Acta*, **70**, 583 (1963); (b) E. Lederer, *Biochem. J.*, **93**, 449 (1964).

volves the corresponding ylide (2) but a viable scheme for the *in vivo* methylene transfer from 2 to the olefin has never been advanced. The copper-induced cyclopropanation of unactivated olefins by diazoalkanes<sup>3</sup> and the electronic and behavioral analogy between diazoalkanes and ylides<sup>4,5</sup> suggest that transition metal-induced transfer of a methylene group from 2 to the olefin *via* a metal-carbene complex (such as 3) may be occurring. Equations 1 and 2 illustrate the process for the case of copper(I);<sup>4</sup> copper(II) salts used in diazoalkane decompositions may be reduced to copper(I) *in situ*.<sup>5</sup> It is of considerable interest to note that the binding of the metal ion to the ylide (2), derived from *S*-adenosylmethionine (1), and/or the cleavage of the C-S bond may be facilitated by strain-free chelate formation involving strategically placed electronegative atoms (see 4).<sup>6</sup>



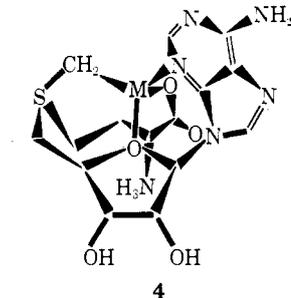
The credibility of this biosynthetic scheme has been demonstrated by the cyclopropanation of the following olefins by diphenylsulfonium methylide (5) in tetrahydrofuran solution at room temperature in the presence of the soluble complex cupric acetylacetonate (glpc yields, based on sulfonium salt, in parentheses): 1-heptene (39%), isobutyl vinyl ether (45%), *trans*-2-octene (48%), *cis*-2-octene (41%), cyclohexene (35%), 3-methylcyclohexene (31%, two stereoisomers produced), tetramethylethylene (yield not determined).<sup>7,8</sup>

(3) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973); V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970); C. W. Cowell and A. Ledwith, *Quart. Rev.*, *Chem. Soc.*, **24**, 119 (1970).

(4) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967).

(5) Ylides have recently been used as models for diazoalkanes in a mechanistic study of the copper-induced decomposition of the latter: R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 3300 (1973).

(6) The tetrahedral bonding of the metal is appropriate for a d<sup>10</sup> complex.



(7) The only other reported example of metal ion induced cyclopropanation by an ylide is that of Trost who recognized the analogy between diazoalkanes and ylides.<sup>4</sup> He demonstrated that 7-benzoylnorcaradiene is generated in 5% yield by reaction of the stabilized ylide dimethylsulfonium phenacylide and cyclohexene in the presence of cupric sulfate.

(8) No reaction occurs without the catalyst.