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J. J. Tufariello, L. T. C. Lee
Department of Chemistry, State University of New York at Buffalo
Buffalo, New York 14214

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Spin Inversion and Bond Rotation in 1,3-Diradicals

Sir:

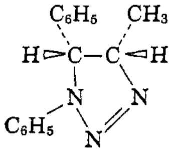
Skell's hypothesis relating electron spin multiplicity and stereospecificity in the addition of carbenes to olefins[1] rests on the assumption that σ-bond rotation is more rapid than spin inversion. The observed nonstereospecific addition of triplet carbene is thus attributed to bond rotations in the intermediate triplet 1,3-diradical prior to the relatively slow spin-inversion process.[2] Singlet carbene addition to olefin occurs with spin conservation and is observed to be stereospecific. Although the validity of Skell's hypothesis is widely recognized, it has been noted that firm evidence supporting the assumption that σ-bond rotation is more rapid than spin inversion in 1,3-diradicals is currently lacking.[3] Furthermore, chemical evidence bearing on this point has been obtained through investigation of carbene and nitrene[4] reactions. Since it is not clear whether additions of singlet carbene to olefin involve 1,3-diradical intermediates,[1,2] valid comparisons of the stereochemical behavior of singlet and triplet 1,3-diradicals have not been possible. We report here our observations of such diradicals, generated by a noncarbene path.

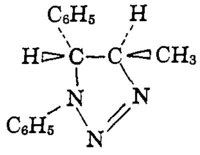
Table I. Direct Photodecomposition[a,b]

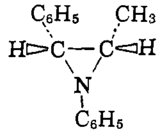
Triazoline[c]	*cis*-Aziridine III, %	*trans*-Aziridine IV, %	Imine V, %
I, cis	65	17	18
II, *trans*	22	66	12

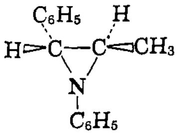
[a] Hanovia Type A, 550 w, Pyrex filter, 25°. [b] ± 4%. [c] Initial concentration: 0.042 M in benzene.

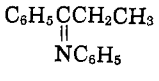
Triazolines I and II were prepared by the stereospecific addition of phenyl azide to *cis*- and *trans*-β-methylstyrenes. Structures I and II are fully supported by elemental analysis,[5] nmr spectra,[5] the reported stereospecificity,[6] and the orientational selectivity of azide–olefin addition,[7] as well as by the nature of the decomposition products. Direct irradiation of solutions of I or II produced different mixtures of the same three products: *cis*-aziridine III,[8] *trans*-aziridine IV,[8] and propiophenone anil V (Table I). Interrupted runs revealed no *cis–trans* triazoline interconversion, and the products were photostable under the conditions employed. Within experimental error, the same product distributions were observed (Table I) with oxygen rigorously excluded from the system or in the presence of 4.9 M piperylene. Similarly, quantum yields for nitrogen evolution (313 mμ) from I and II were unaffected by oxygen.


I, *cis*


II, *trans*

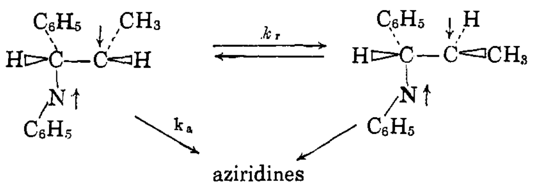

III, *cis*


IV, *trans*


$C_6H_5\underset{\underset{NC_6H_5}{\|}}{C}CH_2CH_3$

V

The failure of triplet quenchers to alter the characteristics of the reaction is indicative of reaction from an excited singlet state. The product distribution data (Table I) show predominant retention of initial geometry in the aziridine products. It thus appears that the intermediate singlet 1,3-diradical undergoes ring closure to aziridine more rapidly than bond rotation ($k_a > k_r$).[9] Similar retention of geometry has been reported for the photo- and thermal decompositions of 1-pyrazolines.[10]



Under photosensitizing conditions (366 mμ, benzophenone), I and II give the products shown in Table II. Appropriate control experiments demonstrated the photostability of the products and the absence of triazoline isomerization prior to decomposition. No other products were detected.

Table II. Benzophenone-Sensitized Photodecomposition[a,b]

Triazoline	*cis*-Aziridine III, %	*trans* Aziridine IV, %	Imine V, %
I, *cis*	60	36	4
II, *trans*	54	42	4

[a] See footnotes *a*, *b*, *c*, Table I. [b] Benzophenone, 0.028 M.

Photodecomposition of azo compounds by triplet energy transfer is well documented.[11] Loss of singlet nitrogen[11b] from excited triplet triazoline results in a triplet 1,3-diradical, a species which must undergo spin inversion before closure to aziridine.

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[1] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

[2] For pertinent references see P. P. Gaspar and G. S. Hammond in W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, Chapter 12.

[3] Reference 2, p 260; W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

[4] W. Lwowski and J. S. McConaghy, *J. Am. Chem. Soc.*, **87**, 5490 (1965); A. G. Anastassiou, *ibid.*, **88**, 2322 (1966).

[5] A full report dealing with the mechanism of triazoline photodecomposition will appear shortly.

[6] R. Huisgen and G. Szeimies, *Chem. Ber.*, **98**, 1153 (1965).

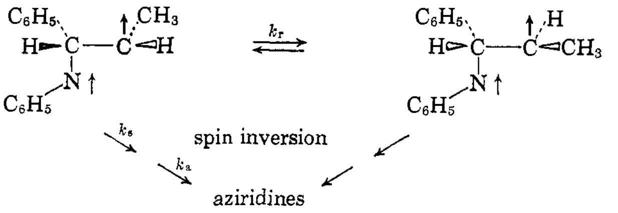
[7] For references see P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libby, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).

[8] J. A. Deyrup and R. B. Greenwald, *ibid.*, **87**, 4538 (1965).

[9] The origin of the imine product and evidence for a one-step expulsion of nitrogen from excited triazoline will be discussed in a forthcoming article.[5]

[10] C. G. Overberger, R. E. Zangaro, and J. P. Anselme, *J. Org. Chem.*, 31, 2046 (1966); T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **82**, 5251 (1960).

[11] (a) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (b) S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).



Because ring closure should be rapid, as in direct photolysis, the loss of stereospecificity suggests that spin inversion is slower than bond rotation ($k_s < k_r$). The similarity of product composition from I and II indicates equilibration of triplet diradicals is approached, if not actually obtained. Predominance of the thermodynamically less stable *cis*-aziridine may reflect rate differences in the ring-closure process.

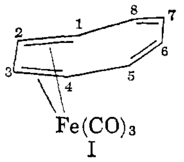
In summary, predominant retention of geometry is observed in the direct photolysis. Thus, ring closure is more rapid than bond rotation in the singlet 1,3-diradical. On the other hand, rotational equilibrium is approached under conditions leading to a triplet 1,3-diradical. It is therefore concluded that spin inversion is slow relative to σ-bond rotation. The results provide confirmatory evidence for Skell's proposal.[1]

P. Scheiner
Mobil Oil Corporation, Research Department
Central Research Division Laboratory, Princeton, New Jersey
Received July 25, 1966

Valence Tautomerism in Cyclooctatetraene–IronTricarbonyl

Sir:

Cyclooctatetraene–iron tricarbonyl is an interesting complex in that it is one of the first systems isolated which indicated that certain olefin–metal π complexes might be capable of undergoing extremely rapid valence tautomerism. Dickens and Lipscomb[1] have shown that in the solid state the arrangement of the atoms are as indicated in I; in this system the iron atom is bonded to one conjugated diene unit with the remaining two double bonds not being involved in coordination to the metal atom. In order to explain the observed single proton nmr absorption at τ 4.76 for the complex these authors suggested that some dynamic effect was occurring in solution.



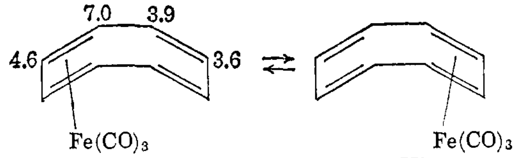
I

Recently Winstein and co-workers[2] have reported that at $-150°$ the spectrum of this complex consists of two peaks of equal areas separated by 80 cps and have taken this as evidence that at this temperature the dynamic effect has been stopped and the system is "frozen" into structure I. We have also been studying this and related systems, and while we agree with the experimental data reported by these workers, we wish to report an alternate interpretation of these results.

The spectrum of I at $-120°$ consists of two absorptions of equal areas at τ 4.06 and 5.44.[3] Winstein and co-workers attribute the low-field absorption to the four olefinic protons and the high-field absorption to the four protons of the diene–iron tricarbonyl moiety in I. However, it is characteristic of derivatives of butadiene–iron tricarbonyl complexes that there is a large difference in chemical shift between the internal hydrogens (2 and 3 in I) and the terminal hydrogens (1 and 4) of the diene ligand. In a series of 39 butadiene–iron tricarbonyl complexes studied either in our laboratories or reported by other workers, these two types of protons are invariably found to be separated by 80 cps or more; the internal protons and the terminal protons for cyclic diene complexes typically fall in the range τ 4.5–5.0 and 6.5–7.3, respectively.[4] Particularly on the basis of the absence of absorption in the neighborhood of τ 7.0 we therefore consider that the observed spectrum at $-150°$ does not correspond to the rigid system I.

Evidence that absorptions at higher fields than τ 5.5 are involved in system I is indicated from a study of substituted cyclooctatetraene–iron tricarbonyl complexes. In addition to the parent system we have also found a temperature-dependent nmr spectrum of the $Fe(CO)_3$ complexes of methyl-, ethyl-, phenyl-, triphenylmethyl-, and carbomethoxycyclooctatetraene.[5] At $+30°$, the spectrum of the methyl derivative consists of a doublet centered at τ 4.33, a triplet at 4.92, and a doublet at 5.50, having areas of 3, 2.3 and 1.8, respectively; the methyl group appears as a sharp singlet at τ 8.13 (area 3). At $-120°$ the spectrum is drastically changed and consists of approximately equal areas centered at τ 4.05 and 5.62 with widths at half-height of 16 and 21 cps, respectively; the CH_3 absorptions remain at τ 8.1. It is clear that at room temperature the absorption at τ 5.50 results from averaging of protons in different chemical environments; since olefinic character must be involved in this averaging process, then in some contributing structures these protons must absorb at considerably higher values in order that the average value be τ 5.5. That the introduction of the methyl group has not given rise to any sigificant change in chemical shift of the ring protons in the methyl derivative as compared to the parent system is indicated by the fact that the weighted average of the three regions of absorption in the room-temperature spectrum of the methyl complex is τ 4.8, which is identical with that of the single peak found for the parent system at room temperature.

It seems to us that a more reasonable way of accommodating the appearance of the spectrum of cyclooctatetraene–iron tricarbonyl at $-150°$ is to assume that it is undergoing isomerization indicated by IIa $\rightleftarrows$ IIb at this temperature.



IIa IIb

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(1) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

(2) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

(3) Reported at the Robert A. Welch Symposium on Organometallic Compounds, Nov 1965. The proceedings of this meeting are currently in press.

(4) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 12 (1964).

(5) Details of the variation in the nmr spectrum of these complexes will be published later.