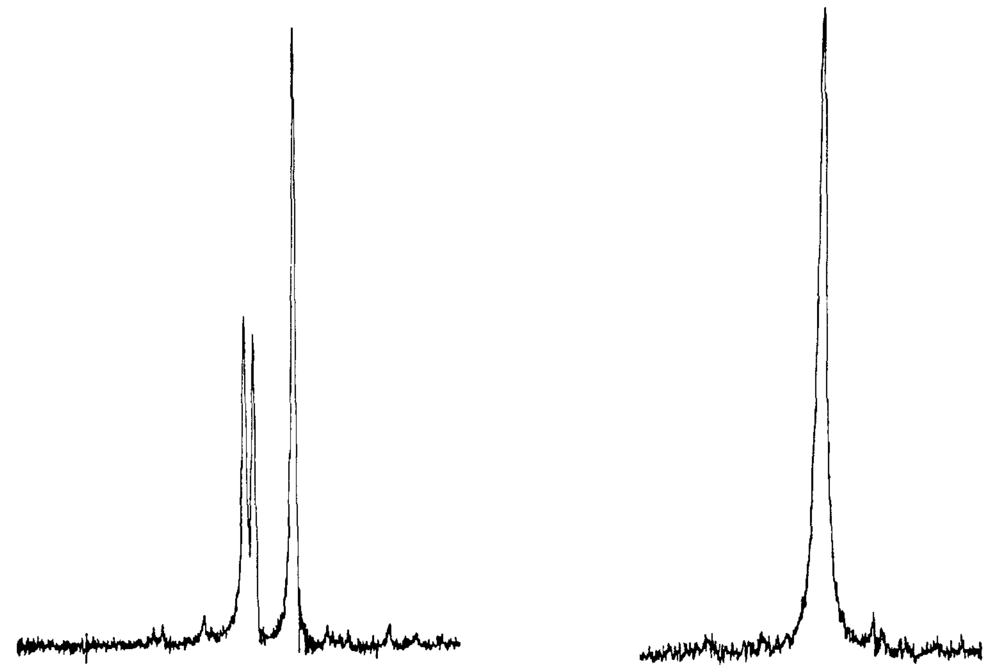
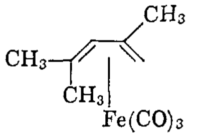


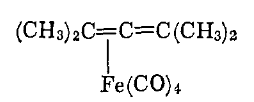
Figure 1. Nmr spectrum of $C_7H_{12}Fe(CO)_4$ taken in CS_2 at −60° (left) and + 30° (right).

case of degenerate valence tautomerism in an allene complex in which the ligand–metal interaction alternates between the two orthogonal π molecular orbitals of the allene system.

Reaction of tetramethylallene with $Fe_2(CO)_9$ produces two complexes having the molecular formulas $C_7H_{12}Fe(CO)_4$ (A) and $C_7H_{12}Fe(CO)_3$ (B).[3,4] Compound A, which is formed in predominant amount when limited quantities of $Fe_2(CO)_9$ are employed, is converted upon prolonged heating or, more rapidly, by reaction with $Fe_2(CO)_9$ into the substance B. Compound B is identified as 2,4-dimethyl-1,3-pentadiene-iron tricarbonyl (I) by its nmr spectrum and by oxidative degradation which liberates a hydrocarbon identical with authentic 2,4-dimethyl-1,3-pentadiene. Compound A gives mainly tetramethylallene upon oxidative degradation and is assigned the olefin–$Fe(CO)_4$ formulation II analogous to other monoolefin–$Fe(CO)_4$ complexes.



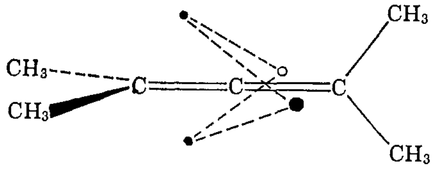
I



$$\underset{\displaystyle Fe(CO)_4}{(CH_3)_2C{=}\overset{|}{C}{=}C(CH_3)_2}$$

II

Taken in carbon disulfide at room temperature, the nmr spectrum of II exhibits only a single absorption at τ 8.16 (Figure 1). However, upon lowering the temperature, the spectrum changes until at −60° it involves three single bands at τ 7.97, 8.02, and 8.23, having areas 1:1:2; this latter pattern is now consistent with a structure involving coordination of the allene to the iron by means of one double bond as in II.



III

The nature of this temperature dependence indicates that the $Fe(CO)_4$ unit is rapidly moving from one π molecular orbital to the second orthogonal one and at room temperature it is tracing a path indicated by the dotted lines in formula III. The activation energy for the process is determined to be 9.0 ± 2.0 kcal.[5] The intramolecular character of the rearrangement is indicated by the appearance of two singlets in the room-temperature nmr spectrum of a mixture of the complex and tetramethylallene.

Keller, B. A. Shoulders, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 4760 (1966); E B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *ibid.*, **88**, 3158 (1966); J. E. Mahler, D. A. K. Jones, and R. Pettit, *ibid.*, **86**, 3589 (1964); R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 785 (1964).

(3) Determined by elemental and mass spectrometric analysis. Compound A produces triphenylphosphine–$Fe(CO)_4$ upon reaction with triphenylphosphine.

(4) The compound $C_6H_8Fe_2(CO)_6$ produced in the reaction between allene and $Fe_3(CO)_{12}$ is also reported to exhibit valence tautomerism [A. Nakamura, *Bull. Chem. Soc. Japan*, **39**, 543 (1966)]. We have prepared this same material from allene and $Fe_2(CO)_9$ but have been unable to demonstrate that the very small change in nmr chemical shifts displayed upon varying the temperature requires such an interpretation.

(5) We thank Mr. A. Liles for the determination of this value.

(6) The authors thank the U. S. Army Research Office (Durham) and the Robert A. Welch Foundation for financial assistance. We also thank General Aniline and Film Corp. for a generous gift of iron carbonyl.

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Received March 2, 1967

Sensitized Photolyses of 3-Sulfolenes, Mechanism of Photochemical Sulfur Dioxide Extrusion from Sulfones

Sir:

It has been proposed that photochemical SO_2 extrusion from sulfones occurs by concerted fragmentation of a vibrationally excited ground state, $S^0{}_n$, produced by internal conversion from S^1 or intersystem crossing from T^1.[1] We present evidence which suggests that in the case of sensitized photolyses of 3-

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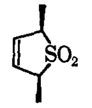
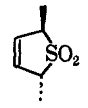
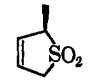
(1) M. P. Cava, R. H. Schlessinger, and J. P. Van Meter, *J. Am. Chem. Soc.*, **86**, 3173 (1964).

sulfolenes fragmentation occurs mainly from an electronically excited state, probably T^1, prior to crossing into the ground state.

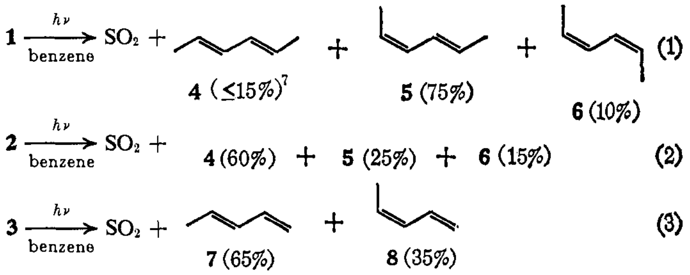
The 3-sulfolenes, **1**–**3**, were prepared according to Backer,[2] as was described recently.[3,4] Irradiations were carried out in a merry-go-round apparatus[5] using a 200-w high pressure Hanovia mercury lamp and a Vycor filter (cut-off $\lambda \leq 2200$ A). Quartz ampoules were employed. Samples were degassed. The apparatus was immersed in a water bath thermostated at 30°. Analyses were by vapor phase chromatography on a 20 ft × $^1/_8$ in. column packed with 15% β,β'-oxydipropionitrile on Chromosorb P. Purified benzene,[6] containing methylcyclohexane as internal standard, was used as solvent. Irradiations were interrupted at low 3-sulfolene → 1,3-diene conversions (≤2%). The 3-sulfolenes were irradiated in the presence of 2,5-dimethyl-2,4-hexadiene. In the case of **1** irradiation results were corrected for competing thermal decomposition. No such correction was required for **2** and **3**.


1


2(*dl*)


3(*dl*)

Irradiations in which the 3-sulfolene concentrations were 0.063 *M* and the added 1,3-diene concentration was 0.018 *M* led to 1,3-diene photoproduct compositions which did not vary with irradiation time. The results are shown in eq 1–3.

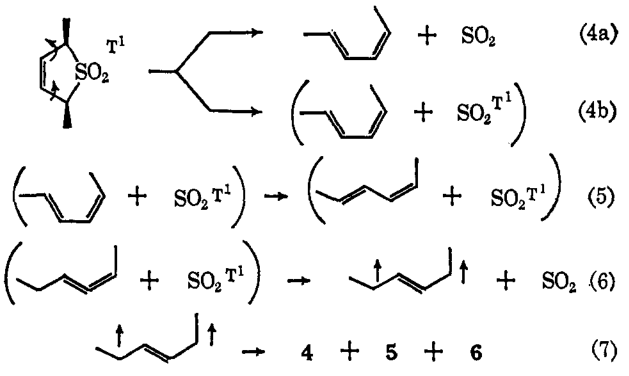


Essentially all the incident radiation was absorbed by the solvent. Benzene has been shown to be a photosensitizer for the *cis–trans* isomerization of alkenes.[8] The key step in these isomerizations is triplet excitation transfer from benzene to the alkene.[8] Therefore, triplet excitation transfer from benzene to each 3-sulfolene should lead to efficient formation of 3-sulfolene triplets. 1,3-Diene photoproducts should also accept triplet excitation from benzene[9] and may interact with benzene singlet states.[10] Excitation of the 1,3-diene photoproducts would have led to *cis–trans* isomerization. However, this was avoided by irradiating the 3-sulfolenes in the presence of the added 1,3-dienes. The compositions shown in eq 1–3 are those in which the 1,3-dienes are initially produced.

Thermal SO_2 extrusion from *cis-* and *trans*-dimethyldihydrothiophene dioxides has been shown to proceed exclusively in a disrotatory manner (**1** → **4**; **2** → **5**).[3,4] This is the direction predicted for concerted fragmentation of the ground state by the orbital symmetry considerations of Woodward and Hoffmann.[3,4,11,12] The thermal decomposition of sulfolene **3** is also stereospecific and gives *trans*-1,3-pentadiene (**6**).[13,14] Therefore, if the photolyses were to proceed by way of vibrationally excited ground-state intermediates, the reactions would be **1** → **4**, **2** → **5**, and **3** → **7**. The results in eq 1–3 lead to the conclusion that the ground-state mechanism does not obtain.

Application of the Woodward–Hoffmann orbital symmetry considerations to the system suggests that concerted fragmentation should be allowed photochemically and that the conrotatory mode should be favored.[15] The data are in accord with this prediction. In each case concerted conrotatory fragmentation would lead to the major diene photoproduct.

The following mechanism (shown for **1**) is proposed in which parentheses designate solvent cage. An important feature of the mechanism is that the major product-forming step (4a) must be accompanied by intersystem crossing. This is necessary since the steric course of the reaction is dictated by the orbital symmetry demands of the excited state. Concerted formation of *s-cis*-diene triplets can be ruled out as an important process because the triplets would be expected to interconvert rapidly[5] and would lead to identical product mixtures from **1** and **2**. Equations 4b–7 account for the formation of the minor diene products. Triplet excitation transfer from SO_2 (E_T = 74 kcal/mole[16]) to the neighboring diene (E_T = 53–60 kcal/mole[9]) is exothermic and should compete with diffusive separation from the solvent cage.[9] The formation of **6** leads us to postulate step 5. This step would not be required if one were willing to propose that *s-cis*-1,3-diene triplets can decay to **6**. This possibility was rejected on steric grounds and because it can be inferred from studies involving sensitized dimerization[9] and



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[2] H. J. Backer, J. Strating, and C. M. H. Kool, *Rec. Trav. Chim.*, **58**, 778 (1939).

[3] W. L. Mock, *J. Am. Chem. Soc.*, **88**, 2857 (1966).

[4] S. C. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

[5] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

[6] The procedure recommended by Dr. R. Steinmetz was used. See W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

[7] Due to the sizable correction for thermal decomposition only an upper limit for the yield of **4** can be given at this time.

[8] M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966), and references cited therein.

[9] R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

[10] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665, 3893 (1966).

[11] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

[12] R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

[13] D. Craig, *ibid.*, **65**, 1006 (1943).

[14] We used the thermal decomposition reaction for sulfolenes **1** and 2 as one criterion of purity.

[15] We thank Professor R. Hoffmann for cautioning us concerning the limited predictive power of the symmetry considerations as applied to the lowest electronically excited state of the system in question.

[16] K. F. Greenough and A. B. F. Duncan, *J. Am. Chem. Soc.*, **83**, 555 (1961).

cis–trans isomerization[5] of 1,3-dienes that decay from *s-cis* triplets should favor the *trans,trans*-diene isomer.

Acknowledgment. This research was supported in part by a grant from the Research Corporation and Grant GP-5159 from the National Science Foundation.

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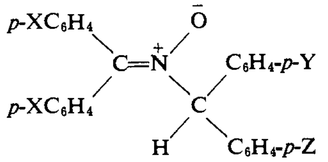
Received March 15, 1967

A Homolytic Mechanism for the Thermal Isomerization and Decomposition of N-Benzhydryl-α,α-diaryl Nitrones

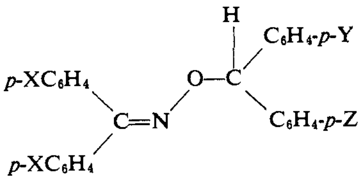
Sir:

In 1950 Cope and Haven[1] reported that α,α-diphenyl-N-benzhydryl nitrone (Ia) undergoes a nearly quantitative rearrangement to benzophenone O-benzhydryloxime (IIa) when heated above its melting point. The disappearance of Ia in dilute solutions of diethyl Carbitol exhibited good first-order kinetics. The rate data reported[1] in the temperature range of 160–176° lead to an Arrhenius activation energy of about 37 kcal/mole and an entropy of activation of approximately 6 eu. On the basis of these kinetic data and seemingly apparent similarities of this reaction with other amine oxide rearrangements,[2] these authors postulated a concerted intramolecular mechanism involving a quasi-three-membered-ring transition state. An alternate route which they dismissed as unlikely, namely an initial ionization to form an oxime anion and a benzhydryl cation, could not, however, be ruled out on the basis of the experimental evidence.

Recently we reported the preparation of several nitrones (Ia–d) and the corresponding isomeric oxime O-ethers (IIa–d).[3] Our original intent was a more detailed kinetic probe of this reaction which might serve to distinguish between these two mechanisms.



Ia, X = Y = Z = H
b, X = Y = H; Z = CH_3
c, X = CH_3; Y = Z = H
d, X = Cl; Y = Z = H



IIa, X = Y = Z = H
b, X = Y = H; Z = CH_3
c, X = CH_3; Y = Z = H
d, X = Cl; X = Z = H

In the course of our kinetic experiments we observed that the ultraviolet spectra of our "infinity" solutions differed somewhat from that of the expected oxime O-ether. Furthermore, the product isolation from a rearrangement under kinetic conditions (dilute solution in diethyl Carbitol) reported previously[1] accounts for less than 79% of starting nitrone. Because of these uncertainties we decided to repeat the product analysis. A thoroughly degassed solution of 100 mg of Ia in 75 ml of diethyl Carbitol was sealed in a Pyrex bulb and heated at 144° for 46 hr. The resulting solution was concentrated to remove solvent and the residue was carefully chromatographed through a column packed with acid-washed alumina. A clean separation led to the isolation and characterization of *three compounds: sym*-tetraphenylethane (16 mg), benzophenone O-benzhydryloxime (IIa) (44 mg), and benzophenone oxime (12 mg).[4]

The first and third products isolated are most easily accounted for by assuming the intermediacy of benzhydryl and diphenyliminoxy[5] free radicals. This suggests that the first step in this reaction sequence may be a *homolytic dissociation at the carbon–nitrogen single bond.*

The rate constants for the disappearance of Ia–d in diethyl Carbitol at 144° all differ from each other by less than a factor of 2. Our kinetic data for the decomposition of Ia in the same solvent over the temperature range 130 to 160° yield an activation energy of 38.8 ± 0.3 kcal/mole and an entropy of activation of 11 eu, in fair agreement with the data of Cope and Haven. The activation parameters for Id are nearly identical (E_a = 37.9 ± 0.2 kcal/mole, $\Delta S^{\ne}$ = 9 eu). The insensitivity of decomposition rates to substituent changes is consistent with an initial homolytic cleavage of the carbon–nitrogen single bond. It also appears that the large positive entropy of activation is more easily accommodated by a homolytic dissociation in the transition state than it was assuming a concerted rearrangement.

Recently we have obtained additional evidence for the intermediacy of radicals during the decomposition of Ia by using epr methods. Radicals were observed in degassed solutions (*ca.* 0.1 *M*) of Ia in diethyl Carbitol at temperatures between 100 and 180°. We also observed radicals in melts of pure Ia above 160°.[6] The failure to observe a signal when benzophenone O-benzhydryloxime (IIa) was examined under comparable conditions precludes this rearrangement product as a source of the radicals. The stability of IIa under conditions in which the nitrone readily decomposes was confirmed by the nearly quantitative (99%) recovery of a sample of IIa which had been heated in diethyl Carbitol for 48 hr at 144°.

On the basis of these observations we propose Scheme I for the decomposition of Ia in diethyl Carbitol.

The reasons for the relatively high yields[7] of oxime

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[1] A. C. Cope and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **72**, 4896 (1950).

[2] (a) J. Meisenheimer, *Ber.*, **52**, 1667 (1919); (b) J. Meisenheimer, H. Greeske, and A. Willmersdorf, *ibid.*, **55**, 513 (1922); (c) R. F. Kleinschmidt and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 1929 (1944).

[3] E. J. Grubbs, J. D. McCullough, Jr., B. H. Weber, and J. R. Maley, *J. Org. Chem.*, 31, 1098 (1966).

[4] This represents a total product balance of 72%. Small amounts of several other components which were eluted later have not been characterized yet.

[5] Iminoxy radicals have been recently generated by the oxidation of oximes with ceric ammonium nitrate or lead tetraacetate. See, for example: (a) J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 1446 (1964); (b) M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 1985 (1964); (c) B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 234 (1964); (d) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., B*, 3119 (1966); (e) J. W. Lown, *ibid., B*, 441 (1966); and (f) *ibid., B*, 644 (1966).

[6] The nature of the observed radicals will constitute a portion of a forthcoming publication.

[7] Cope[1] reported a 96% conversion of Ia to IIa when this nitrone was heated at 200° for 0.5 hr. Our highest yield in a thermal rearrange-