the addition of DMSO, and the subscripts A and D denote alcohol and DMSO, respectively. The quantity $(C_A{}^0 - C_A)$ was obtained from $(A^0 - A)$ by using the Beer's law plot.

Acknowledgments. The author is grateful to Dr.

The Photoisomerization of Heteroatomic Eight π Electron Systems. Long-Range Coupling in Some Bicyclo[3.2.0]hepta-3,6-dienes[1]

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio. Received November 27, 1965

Abstract: The heteroatomic eight π electron systems N-carbethoxyazepine and 2,7-dimethyloxepin undergo light-induced valence tautomerism to bicyclo[3.2.0]hepta-3,6-dienes, a reaction paralleling that of cycloheptatrienes. Structure proof of the products has been achieved by spectroscopic methods. Application of double-resonance techniques to the nmr spectra of the photoisomers has permitted the complete derivation of chemical shift and coupling constant assignments. The variations in the magnitude of long-range coupling caused by the introduction of electronegative substituents are discussed.

The early unsuccessful attempts to prepare heterotropylidenes have usually been ascribed to the fact that they are isoelectronic with the cycloheptatrienide anion,[3] and as such were expected, on the basis of MO theory, to be endowed with unfavorable properties.[4,5] More recently, however, the synthesis of various derivatives of oxepin (1)[6] and 1H-azepine (2)[5,7] has been achieved, and such compounds are now readily available.[8] Although the ground-state properties of these interesting heterocycles have as yet not been completely defined, we have been led to a study of their excited-state behavior.
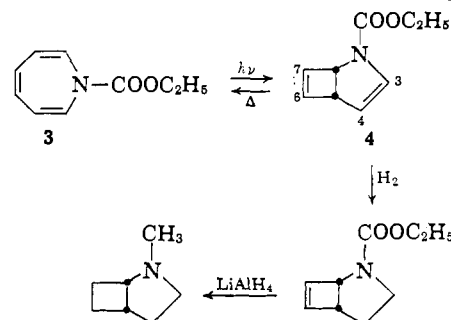

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Specifically, the present investigation of the photochemical transformations of N-carbethoxyazepine (3) and 2,7-dimethyloxepin (7) was conducted as part of our continuing interest in the photochemistry of unsaturated heterocyclic molecules.[9] In particular, it appeared of importance to determine if these eight π elec-

tron systems would undergo transformations from their electronically excited states paralleling, or differing, from those observed with cycloheptatrienes.[10] Because of the known ability of oxepin, for example, to undergo valence tautomerism to benzene epoxide with relative ease,[6] it was not clear how such molecules would behave under conditions of ultraviolet irradiation.

Results

When a 2% tetrahydrofuran solution of N-carbethoxyazepine (3) was irradiated under a nitrogen atmosphere with an unfiltered 450-w mercury arc for 2–3 days, there resulted the total disappearance of 3 and the concomitant formation of a single photoproduct. The progress of the reaction was followed by vapor phase chromatographic (vpc) analysis of aliquots removed periodically during the irradiation.[11] The resulting photoisomer was obtained as a very pale yellow oil (N-carbethoxyazepine is bright orange in color) in 43% yield by careful vacuum distillation. The isomeric nature of this photoproduct was delineated easily because of its facile thermal reversal to 3 when the distillation was effected at a bath temperature

(1) Unsaturated Heterocyclic Systems. XXIV. For paper XXIII of this series, see L. A. Paquette, *Proc. N. Y. Acad. Sci.*, in press.

(2) (a) Alfred P. Sloan Foundation Research Fellow; (b) National Science Foundation Summer Fellow, 1964.

(3) H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963).

(4) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 10.

(5) K. Hafner, *Angew. Chem.*, **75**, 1041 (1963).

(6) E. Vogel, R. Schubart, and W. A. Böll, *ibid.*, **76**, 535 (1964); E. Vogel, W. A. Böll, and H. Gunther, *Tetrahedron Letters*, 609 (1965).

(7) For a recent brief review of the azepine field, see L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4096 (1964); consult also F. D. Marsh and H. E. Simmons, *ibid.*, **87**, 3529 (1965).

(8) The parent systems of 1H-azepine and thiepin (as well as derivatives of the latter ring system) remain to be synthesized.

(9) (a) L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *J. Am. Chem. Soc.*, **87**, 3417 (1965); (b) L. A. Paquette, *ibid.*, **86**, 4092 (1964); (c) L. A. Paquette, *ibid.*, **86**, 500 (1964); (d) L. A. Paquette, *Tetrahedron Letters*, 2027 (1963); (e) L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, **85**, 765 (1963).
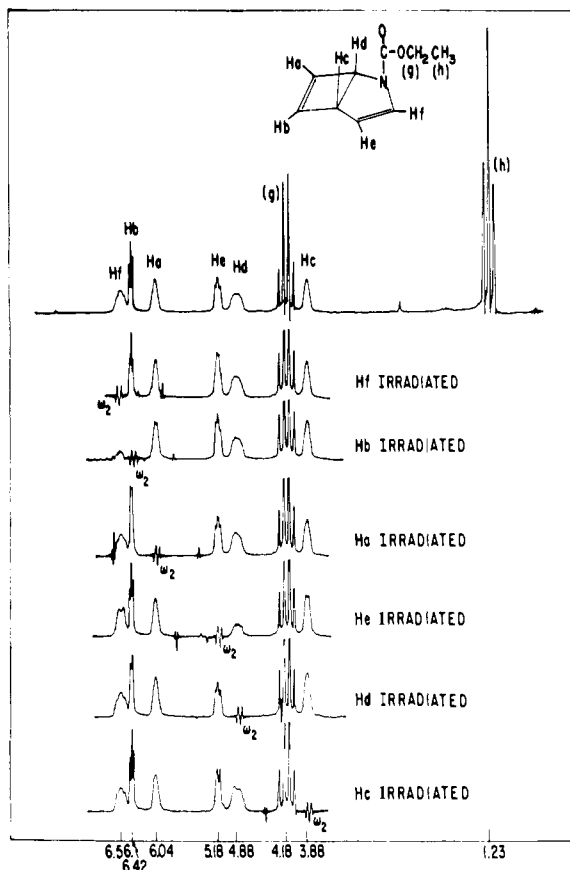
(10) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(11) The length of the irradiation period cannot be taken as a measure of the rate of the photochemical conversion, however, because of the buildup of a polymeric film on the quartz immersion well which diminished the quantum efficiency of the process. In this work the film was removed at approximate 24-hr interrvals.

Figure 1. 100-Mc nmr spectra of **4** in deuteriochloroform (δ units).

Figure 2. 100-Mc nmr spectra of **8** in deuteriochloroform (δ units).

above 125°. In agreement with structure **4**, this photoisomer exhibited infrared bands (in CCl₄) at 1720 (ester carbonyl), 1600 (enamide double bond), and 730 cm⁻¹ (*cis*-disubstituted double bond in strained ring). Its ultraviolet spectrum, λ_{max}^{EtOH} 229 mμ (ϵ 7400) and 248 mμ (ϵ 7500), was similar to that observed with other enamides.[12] The nuclear magnetic resonance (nmr) spectrum (Figure 1; for discussion, see below) likewise displayed features indicative of the valence tautomeric structure **4**. The bicyclic nature of the molecular framework was ascertained further by catalytic hydrogenation which proceeded with the consumption of 2 moles of hydrogen and gave rise to **5**. Lithium aluminum hydride reduction of **5** afforded **6** which was characterized as its picrate, mp 240–242° dec. By comparison, the picrates of 1-methyl-1-azacycloheptane and 7-methyl-7-azabicyclo[4.1.0]heptane display melting points of 220.5–221.5°[13a] and 128°,[13b] respectively.

In a similar fashion, irradiation of a 2% solution of 2,7-dimethyloxepin (**7**) in anhydrous ether under a nitrogen atmosphere was found to cause the slow disappearance of the starting heterocycle. After approximately 5.5–6 days, the conversion was found to be complete as judged by periodic vpc analyses.[14] After removal of the solvent at 0°, the major product (bicyclic

(12) See, for example, R. H. Mazur, *J. Org. Chem.*, **26**, 1289 (1961).

(13) (a) N. J. Leonard and W. K. Musker, *J. Am. Chem. Soc.*, **81**, 5631 (1959); (b) T. Taguchi and M. Eto, *ibid.*, **80**, 4075 (1958).

(14) Again in this instance, the deposition of a polymeric film on the quartz immersion well proved to be a problem. This opaque coating was likewise removed periodically. Despite this complicating factor, the photoisomerization of **7** did proceed at a rate slower than that observed for **3**.
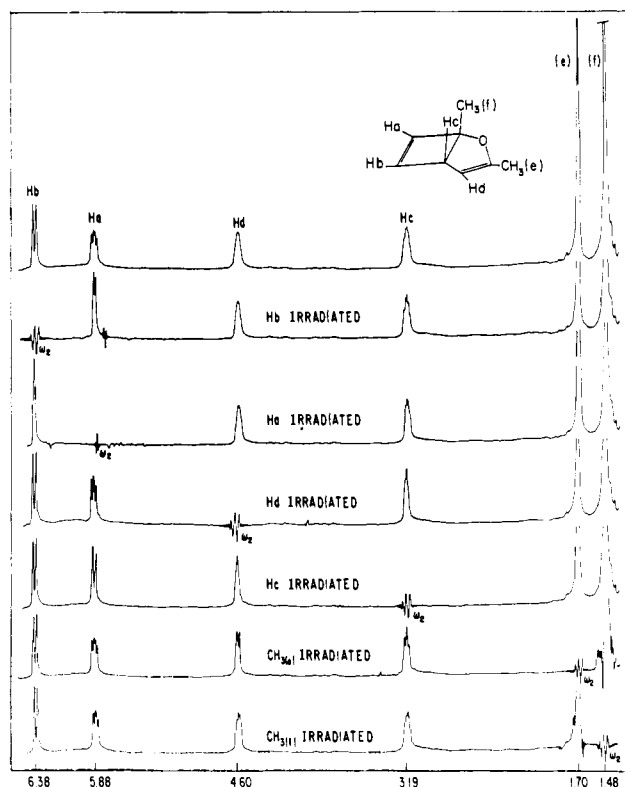
photoisomer **8**) was found to be the component most rapidly eluted from a vpc column packed with 20% Silicone SF96 on Chromosorb W (78°). Of the three remaining minor products observed in the gas chromatogram, only 2,7-dimethyloxepin (**7**) has been identified (apparently due to a quantity of **8** which had thermally reverted to **7** during the work-up procedure). The photoisomer could not be isolated by vacuum distillation because of its extreme sensitivity. Purification by
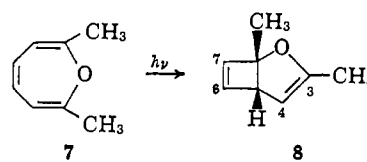
preparative scale vpc, on the other hand, did prove feasible; however, **8** appeared to be rapidly oxidized upon exposure to air, thus precluding elemental analysis. When handled or stored in an inert atmosphere, the pure substance appeared to be stable for a period of a few days. Shortly after exposure to the atmosphere, **8** rapidly is converted to one or more carbonyl-containing substances. The nature of this (these) material(s) is presently under investigation.

The structure of the photoproduct **8** was deduced on the basis of its spectral properties. Thus, its infrared spectrum (in CCl₄) displayed bands at 3030 and 730 (*cis*-disubstituted double bond in strained ring), and 1655 cm⁻¹ (vinyl ether); its ultraviolet spectrum displayed only slight absorption above 220 mμ. Final confirmation of the structure as **8** was available from its nmr (Figure 2; for discussion, see below) and mass spectra (Figure 3).
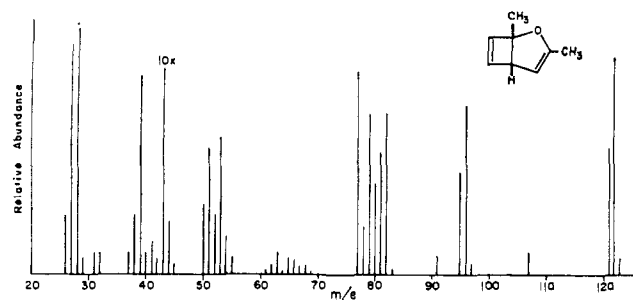
Figure 3. Mass spectrum of **8**.

The mass spectrum of **8** (Figure 3) contains an abundant molecular ion (a) and an almost equally intense peak corresponding to the M − 1 species b. This loss of a hydrogen atom from a, which *a priori* would be expected to be facile because of its allylic nature, leads to the conjugated cation b. The major portion of the remainder of the peaks are characteristic of 2,5-dimethylfuran whose fragmentation pattern has already been discussed at some length;[15] especially prominent in both spectra is the base peak at m/e 43. The particles responsible for the more abundant peaks are given by formulas c–h. The 2,5-dimethylfuran most likely arises from the concerted loss of neutral acetylene from ion a, a phenomenon known to be prominent in
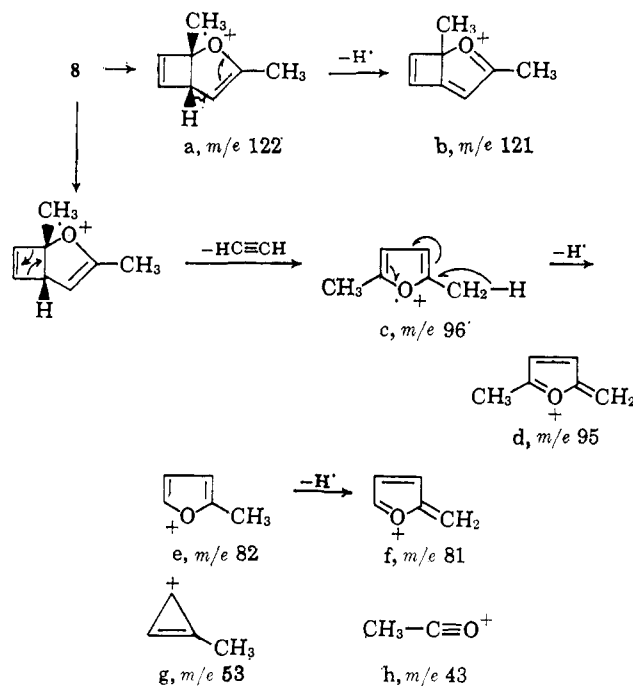
the mass spectral fragmentations of 2-oxabicyclo-[3.2.0]hept-6-enes.[16] The fragmentation pattern displayed in Figure 3 can therefore be accommodated uniquely by formula **8**.

The photochemical behavior of these heteroatomic eight π electron systems clearly parallels the general photoisomerization pathway of cycloheptatrienes and cycloheptadienes.[9, 10] Significantly, the rate of photoisomerization of 2,7-dimethyloxepin (**7**) is slower than that of

2,3-dihydrooxepin (**9**) by a factor of at least 50.[17] The distinct difference in photochemical properties of **7** and **9** must be a result of the presence of the additional double bond in the former case which apparently renders smooth electron redistribution to bicyclic product less favorable and allows a rapid return to starting material.

An examination of the photoisomerization pathway of 4-substituted carbomethoxyazepines and unsymmetrically substituted oxepins is presently in progress.

Application of Double Resonance to the Bicyclo-[3.2.0]hepta-3,6-dienes. Because nuclear spin information is readily transmitted through the π-electron systems of double bonds, and because the magnitude of such allylic and homoallylic couplings is in great part dependent upon the dihedral angle of the interacting protons,[18] the occurrence of such phenomena can be of great value in structural and conformational problems. However, little information is available regarding such long-range coupling in severely strained or distorted systems. Bent bicyclic structures such as **4** and **8** are unusually interesting because of the high degree of unsaturation and the unusual angular deformations associated with such molecules. Such bicyclo[3.2.0]hepta-3,6-dienes were expected to give rise to a myriad of interesting spin–spin interactions, and this was found to be the case. Analysis of the spectra of **4** and **8** was assisted substantially by the recent work of Paquette, *et al.*,[9a] which described complete chemical shift and coupling constant assignments for the 2-oxabicyclo[3.2.0]hept-6-ene system (**10**). Thus, by appropriate deuterium labeling of **10**, these workers demonstrated that the vinylic coupling J_{ab} was 2.8 cps

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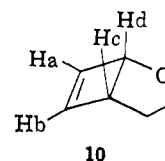
that the allylic coupling J_{bd} was likewise 2.8 cps, but that the other allylic coupling, J_{ac}, was interestingly only 1.5 cps. Since no major divergences in the dihedral angles of C–Hd and C–Hc relative to the cyclobutene π system are to be expected in this molecule (**10**), it appears likely that the differing electron density at the carbon atoms to which these protons are attached significantly affects the magnitude of the long-range coupling.[19]

The nmr spectrum of **4** (Figure 1) clearly demonstrates the existence of extensive long-range coupling. Of the two cyclobutene protons, Ha appears as a doublet (J = 2.6 cps) at δ 6.04 and Hb is seen as a triplet (J = 2.6 cps) at δ 6.42.[20] The illustrated decoupled spectra

(15) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of the Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 227.

(16) L. A. Paquette, J. H. Barrett, and S. Meyerson, results as yet unpublished.

(17) Irradiation of **7** with the 200-w mercury arc used in the 2,3-dihydrooxepin work[9a] was found to produce **8** only very slowly. At the end of a 1-week period, for example, only 60% (approximate) conversions were realized (as determined by vpc of aliquots); by comparison, 2,3-dihydrooxepin (**9**) is completely photoisomerized in 4 hr under these conditions.

(18) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 5.

(19) Slight variations in allylic coupling constants have been observed upon the introduction of various electronegative substituents (Br, Cl, OH, for example) in propene: E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960); A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, No. 34, 127 (1962).

(20) Certain of the shapes of the peaks in Figures 1 and 2 are not always clearly visible in the reduced photographs. As is usually the

substantiate the fact that the vinylic coupling J_{ab} is 2.6 cps, and that the allylic coupling J_{bd} corresponds to 2.6 cps; further examination of Figure 1 reveals that the other allylic coupling J_{ac} is virtually nonexistent (*i.e.*, <0.4 cps). These observations parallel the findings made earlier in the case of 10.[9a] The additional features of these spectra are equally revealing. For example, the other vinyl protons He and Hf, which appear as a four-line pattern centered at δ 5.18 and a broadened doublet at 6.56, respectively, display the following spin–spin interactions: J_{ef} = 4.8 cps, J_{ce} = 2.8 cps, and $J_{cf} \sim 0.5$ cps. Of particular interest is the observation that whereas J_{bc} approximates 0 cps, J_{ce} is relatively large (2.8 cps). An examination of Dreiding models of 4 reveals that the dihedral angles between the planes defined by $Hc-C_5-C_6$ and $Hb-C_6-C_5$ on the one hand, and $Hc-C_5-C_4$ and $He-C_4-C_5$ on the other hand, differ only very slightly. Therefore, application of one of the accepted criteria which apply to the magnitude of long-range coupling constants, namely dihedral angle, would be misleading in this instance. Convincingly, the introduction of a substituent whose electronegativity is different from hydrogen (O or N in the above examples) can significantly influence allylic coupling constants under appropriate conditions. Such effects can be produced by direct inductive effects on the C–H bond, changes in hybridization of the C–H bond, and the like. Therefore, any attempt to utilize the dihedral angle dependence of allylic coupling constants in structural analysis must allow for variation as a function of other substituents in the particular molecule. In other words, the same pitfalls that plague the use of vicinal proton coupling, recently summarized in a critical fashion by Karplus,[21] are applicable by analogy to long-range coupling.

The decoupled spectra of 8 (Figure 2) bear out and uniquely strengthen the above conclusions. It should be especially noted that J_{ab} = 2.8 cps, J_{ac} = 1.5 cps, $J_{bc} \sim 0$ cps, and J_{cd} = 2.2 cps.[22]

In conclusion, it is noteworthy that in 4 there is no observable coupling between Hb and He. A similar lack of coupling between the Hb and Hd protons of 8 was likewise indicated. Apparently no spin information of any magnitude is transmitted from the p orbitals of C-3 and C-4 to the p orbitals of C-6 and C-7 despite the W-plan arrangement of the p_z orbitals on C-4 and C-6. Recently, Russell, Chang, and Jefford[23] observed such a type of long-range coupling in the esr spectrum of the radical anion 11.
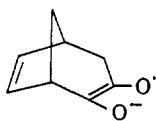
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case, the best spectra from the viewpoint of coupling constant analysis are obtained on neat samples. Unfortunately in the present instance the instability and scarcity of 4 and 8 precluded decoupling experiments on neat samples.

(21) M. Karplus, *J. Am. Chem. Soc.*, 85, 2870 (1963).

(22) Whereas J_{ac} in 10 is 1.5 cps the same coupling constant in 8 is nonobservable. Although some of this variation may be caused by a slight derivation in the dihedral angles involved, it is believed that the differing ionic substitution perturbations at C_5-Hc in 8 which are transmitted *via* the C_3-C_4 double bond have an appreciable effect.

(23) G. A. Russell, K. Y. Chang, and C. W. Jefford, *J. Am. Chem. Soc.*, 87, 4383 (1965).

Experimental Section[24]

Photoisomerization of N-Carbethoxyazepine (3). A solution of 6.45 g (0.04 mole) of 3[25] in 320 ml of tetrahydrofuran was irradiated at room temperature in a nitrogen atmosphere with an immersion-type Hanovia unfiltered 450-w lamp. The progress of the reaction was followed by vapor phase chromatography with a 10 ft × 0.25 in. aluminum column packed with 20% Silicone SF96 on Chromosorb W at 90°; after 48 hr, the reaction was complete.[11] The solvent was removed on a rotary evaporator and the remaining liquid was distilled. The fraction boiling at 45–85° (0.45 mm) was collected and redistilled to give 2.75 g (42.7%) of 4, bp 55–60° (0.45 mm) (short-path column), $n^{23}D$ 1.4988.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.22; H, 6.78; N, 8.52.

Thermal Conversion of 4 to 3. Small samples of 4 were sealed in glass ampoules under a nitrogen atmosphere. The ampoules were placed in a bath thermostated at 126.5°, and an ampoule was opened periodically and the contents were analyzed by vpc to follow the course of the reaction. The results are summarized in Table I. The reaction is somewhat complicated by further dimerization of 3 under these reaction conditions.

Table I[a]

Time, min	4, %	3, %
0	100	0
3	93.5	6.5
10	69.2	30.8
15	50	50
40	24	76
100	0	100

[a] All values are normalized to 100%.

Catalytic Hydrogenation of 2-Carbethoxy-2-azabicyclo[3.2.0]-hepta-3,6-diene (4). To approximately 100 mg of prereduced Adams[1] catalyst in 10 ml of tetrahydrofuran was added 940 mg (5.7 mmoles) of 4. Two equivalents of hydrogen was absorbed, at which point the catalyst was removed by filtration. The product (5) was shown to be *ca.* 95% pure by vpc and was used in the tetrahydrofuran solution directly for the subsequent reduction.

2-Methyl-2-azabicyclo[3.2.0]heptane (6). To a slurry of 250 mg (6.6 mmoles) of lithium aluminum hydride in 10 ml of tetrahydrofuran was added dropwise *ca.* 900 mg of 5 in 20 ml of tetrahydrofuran. The mixture was allowed to stir at room temperature for 18 hr and 0.25 ml of water, 0.25 ml of 30% sodium hydroxide solution, and 0.75 ml of water were added in that order. The resulting precipitate was separated by filtration and washed thoroughly with anhydrous tetrahydrofuran. To the combined filtrate and washings was added 20 ml of a saturated ethanolic picric acid solution. The solution was heated on a steam bath until all of the tetrahydrofuran had evaporated and the remaining ethanolic solution was allowed to cool slowly to room temperature. The precipitated crystals, 1.46 g (80.7% over-all), were removed by filtration and recrystallized from 75% ethanol to give the pure picrate of 6, mp 240–242° dec.

Anal. Calcd for $C_{13}H_{16}N_4O_7$: C, 45.88; H, 4.74; N, 16.47. Found: C, 45.96; H, 4.84; N, 16.61.

Photoisomerization of 2,7-Dimethyloxepin (7). A solution of 6.11 g (0.05 mole) of 7[26] in 300 ml of ether was irradiated at room temperature in a nitrogen atmosphere with an immersion-type Hanovia unfiltered 450-w lamp. The progress of the reaction was followed by vapor phase chromatography (same column as above,

(24) Melting points and boiling points are uncorrected. The infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer fitted with a sodium chloride prism. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The vpc analyses were obtained with an Aerograph A-90P gas chromatograph; helium was used as the carrier gas and percentage compositions reported refer to the relative areas observed for the different components. The decoupled spectra were obtained on a Varian HA-100 spectrometer operating in the frequency sweep mode; an audio frequency oscillator (HP 200 CD) was employed to supply the saturating field. The mass spectrum was obtained with a CEC Model 21-130 mass spectrometer.

(25) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, 29, 751 (1964).

(26) E. Vogel, R. Schubart, and W. A. Böll, *Angew. Chem. Intern. Ed. Engl.*, 3, 510 (1964).

but at 78°); after 132 hr, the reaction was complete.[14] The ether was removed by evaporation at 0° and the remaining oil was submitted to preparative vpc. One major and three minor components were observed (see text). Isolation of the major component gave a very sensitive colorless oil which, of necessity, was stored under helium or nitrogen. The spectral data were obtained on samples which showed the absence of impurities when reanalyzed by vpc.

The Photolysis of Spiro[2.5]octa-4,7-dien-6-one. Radical Fragmentation in the Photochemistry of 2,5-Cyclohexadienones[1]

David I. Schuster and Carl J. Polowczyk[2]

Contribution from the Department of Chemistry, New York University, University Heights, Bronx, New York   10453.   Received July 23, 1965

Abstract: The photolysis of spiro[2.5]octa-4,7-dien-6-one in ethyl ether gave four products in addition to polymer. The products were *p*-ethylphenol (**7**) and three compounds (**8, 9,** and **10**) which were 1:1 adducts of starting material and solvent. The structures of the adducts were determined by spectroscopy and by independent synthesis. The formation of reduction products and the incorporation of ether into the products demand the postulation of free-radical intermediates in this reaction. It is postulated that the excited state undergoes ring opening analogous to the cyclopropylcarbinyl–allylcarbinyl interconversion to give a diradical **13** which leads to **7, 8, 9,** and **10** by a succession of hydrogen abstraction and radical coupling reactions. The formation of **9** involves a novel hydrogen migration, the driving force of which is ascribed to formation of a neutral intermediate with all paired electrons. Formation of the products is found to be incompatible with ionic intermediates, indicating deviation from Chapman's "polar state concept" of photoreactions of 2,5-cyclohexadienones. Other examples of such deviation are cited and are found to belong to a hitherto unrecognized class of radical fragmentation reactions. The occurrence of such reactions in 2,5-cyclohexadienone photochemistry is compatible with a diradical structure for the excited state and argues against charge separation in the excited state.

The photochemical transformations of cross-conjugated cyclohexadienones have received considerable attention in recent years.[3] The kinds of rearrangements which have been observed in such reactions have led to the suggestions by several authors that ionic intermediates are involved at some stage of the reaction sequence.[3] Chapman has suggested a "polar state rule" in which the products of such reactions can be rationalized (eq 1) on the basis of transformations of a dipolar structure **2** derived from the dienone **1**.[3c] The origin of **2** has not been specified by Chapman, although others[4] have suggested that such a structure may be an adequate representation for the excited state involved in these reactions. Zimmerman and Schuster[3a] have postulated a mechanistic scheme (eq 2 and 3) which accounts for the eventual production of ionic intermediates from an (n,π*) excited state represented by the valence bond structures **3a–d**. The ionic structure **5** arises in a later stage of their postulated sequence following 3,5-bond formation to give **4** and electron demotion (**4 → 5**). Since **2** and **5** can be interconverted by the well-known cyclopropylcarbinyl–allylcarbinyl rearrangement,[5] any products which can be rationalized on the basis of one can just as well be rationalized on the basis of the other. Some theoretical arguments have also been used in favor of the more elaborate Zimmerman–Schuster scheme.[3a,b,6]

Despite the theoretical advantages[3a,b] of picturing the excited state in terms of valence bond structures **3**, no evidence had been presented prior to this work which *demanded* the intermediacy of diradicals prior to the product-determining ionic intermediates. A case was desired in which the "polar state concept"[3c] might give an incorrect prediction because of some structural feature of the dienone. A likely candidate was the spirodienone **6**, prepared originally by Baird and Winstein.[7] The "polar state" derived from **6** would be **6a**

(1) Part VI of a series on the photochemistry of unsaturated ketones. Part V: D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.,* **87**, 2515 (1965). A portion of the present paper was published in a preliminary communication: D. I. Schuster and C. J. Polowczyk, *ibid.,* **86**, 4502 (1964).

(2) National Institutes of Health Predoctoral Fellow, 1963–1964.

(3) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.,* **84**, 4527 (1962); (b) H. E. Zimmerman, *Advan. Photochem.,* **1**, 183 (1963); (c) O. L. Chapman, *ibid.,* **1**, 323 (1963); (d) P. J. Kropp, *J. Am. Chem. Soc.,* **86**, 4053 (1964).

(4) M. H. Fisch and J. H. Richards, *ibid.,* **85**, 3029 (1963).

(5) See (a) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.,* **81**, 4390 (1959); (b) R. Breslow in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 259–280.

(6) C. J. Polowczyk, Ph.D. Dissertation, New York University, June 1965.

(7) R. Baird and S. Winstein, *J. Am. Chem. Soc.,* **85**, 567 (1963);