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The Photolysis of Spiro[2.5]octa-1,4-dien-3-one in Ethyl Ether. A Note on the Mechanism of Photolysis of 2,5-Cyclohexadienones¹

Sir:

Photolyses of crossconjugated cyclohexadienones in solution have led to rearranged products whose structures suggested that their mode of formation involved ionic intermediates.² However, it has been postulated^{2a,3} that radical intermediates might well precede the product-determining ionic intermediates, although the necessity for this added mechanistic complication has not been accepted universally.⁴ We now report a novel photochemical reaction of a 2,5-cyclohexadienone which requires the postulation of radical intermediates to explain adequately the results.

The substrate, spiro[2.5]octa-1,4-dien-3-one (I), was prepared according to the procedure of Baird and Winstein^{5,6} and was crystallized at low temperatures before photolysis. The photolysis of I in ethyl ether with a Hanovia 450-watt high pressure mercury arc with a Pyrex filter was followed by ultraviolet spectra of aliquots withdrawn during the reaction. The dienone has λ_{\max} 261 $m\mu$ ⁵ and new maxima appeared at 225 and 280 $m\mu$ while the peak at 261 $m\mu$ diminished. When the source was turned off during photolysis, the relative peak heights in the ultraviolet spectrum did not change for an indefinite period, and on reillumina-

TABLE I

PHOTOLYSIS OF SPIRO[2.5]OCTA-1,4-DIEN-3-ONE (I)

Runs	1 ^a	2 ^a	3 ^a	4 ^a	5 ^b
Dienone I, moles $\times 10^{3c}$	1.3	1.7	2.3	2.5	0.22
Concn. of I in ether, moles/l. $\times 10^{3c}$	4.1	5.4	7.6	1.6	0.64
Products, mole % based on I					
<i>p</i> -Ethylphenol (II)	50	30	10	20	53
Acetal (III)	<i>d</i>	4	2.2	3.8	<i>d</i>
IV + V ^e	21	28	18	16	17.5 ^f
PolymERIC and unidentified photoproducts	<i>d</i>	<i>d</i>	71	59	<i>d</i>

^a Yields determined by weighing of isolated material. ^b Yields determined by g.l.c. ^c Based on ultraviolet spectrum of ethereal solution and ϵ at 261 $m\mu$ of 23,000.⁵ ^d Undetermined. ^e Combined yield of unseparated mixture of IV and V. ^f Analysis by g.l.c. indicates mixture of 37% IV and 63% V.

(1) Part III of a series: The Photochemistry of Unsaturated Ketones. Part II: D. I. Schuster, M. J. Nash, and M. L. Kantor, *Tetrahedron Letters*, No. 22, 1375 (1964). Part I: D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, No. 27, 1911 (1963).

(2) For reviews, see (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); (b) O. L. Chapman in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 323-420.

(3) H. E. Zimmerman in ref. 2b, pp. 183-208.

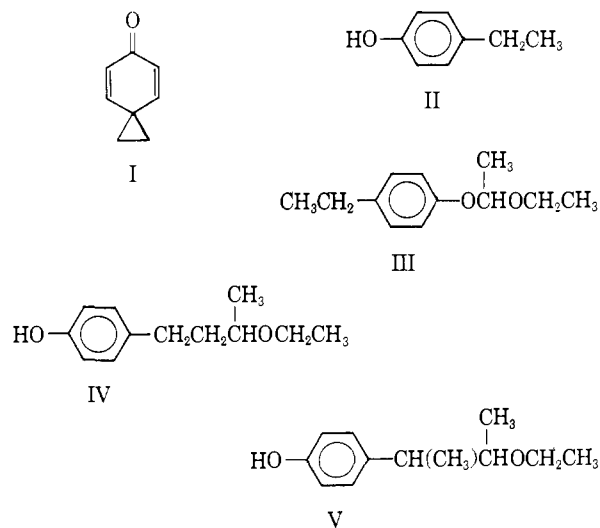
(4) See ref. 2b and G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

(5) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963); **79**, 4238 (1957).

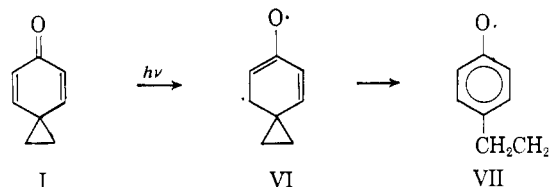
(6) We are indebted to Professor Winstein and Dr. Baird for detailed procedures for the preparation of I prior to their full publication.

tion the reaction resumed at an unchanged rate. A control sample of dienone in ether which was not irradiated showed no change. All evidence indicates that other thermal reactions of the dienone,⁵ not initiated by photolysis, were not competing with the photochemical reaction.

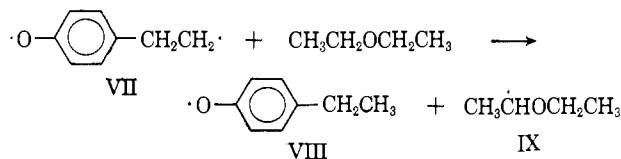
The products were isolated by column chromatography on silica gel and molecular distillation and are given with yields in Table I. The structures of III, IV, and V (mixture of diastereomers) were elucidated by analysis of n.m.r. and mass spectra and were confirmed by independent synthesis.⁷ Isolation of reduc-



tion products and incorporation of ether into the products necessitate postulation of radical intermediates in this reaction. The exact modes of formation of III, IV, and V are unknown, but preliminary mechanistic suggestions seem appropriate. Excitation of I appears to give diradical VII either directly or *via* VI.⁸ Ring opening of VI to VII⁹ is anticipated not



only because of the formation of the benzene ring but also by analogy with the model cyclopropylcarbonyl radical.¹⁰ The reactive primary radical VII would most likely abstract an α -hydrogen from ether to give



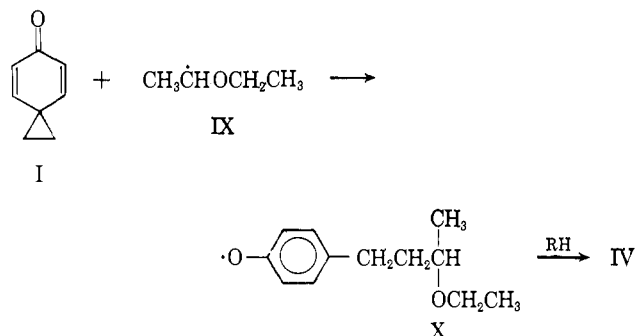
(7) Details will be given in the full paper. Satisfactory elemental analyses have been obtained for all new compounds.

(8) The cyclopropane ring is favorably situated geometrically to interact directly with the π -system in I, as has been noted in the ultraviolet spectrum of I.⁵

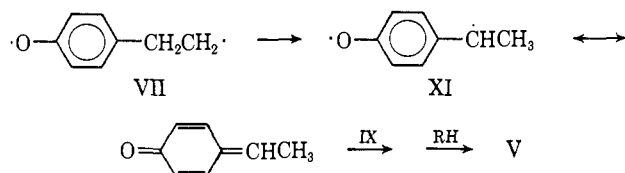
(9) Ring opening has been observed in the vapor-phase photolysis of acetylcyclopropane: J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(10) (a) D. I. Schuster, Ph. D. Dissertation, California Institute of Technology, 1961; (b) R. Breslow in "Molecular Rearrangements," Vol. 1, P. De Mayo, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 291-294.

the relatively stable radicals VIII and IX. Products II and III are generated by hydrogen abstraction and coupling of VIII and IX. While coupling of VII and IX, possibly after hydrogen abstraction by oxygen of VII, would ultimately give IV, this product could arise by a radical displacement on I (ground state) by IX, followed by hydrogen abstraction.¹¹ Formation of



V is formally a rearrangement reaction. The vibrational excitation of VII and the driving force for formation of XI may be sufficiently great that rearrange-



ment by 1,2-hydrogen migration occurs to an extent unexpected by analogy with the β -phenylethyl radical¹³ or other model radical systems.¹⁴ Coupling of XI and IX would then lead to V. Alternatively, hydrogen abstraction from the benzylic carbon of *p*-ethylphenol (II) gives a radical which would give V by coupling with IX.¹⁵ Finally, isolation and preliminary characterization of some dimers and polymers give results in accord with this scheme.

Since the reactions which ensue on photolysis of I are due to $n \rightarrow \pi^*$ excitation of a chromophore which is formally analogous to that of santonin, 4,4-diphenylcyclohexadienone, and other 2,5-cyclohexadienones, it is tempting to interpret our results as evidence for the formation of diradicals as primary intermediates on $n \rightarrow \pi^*$ excitation of all such dienones, and that differences in the photochemistry arise in subsequent steps. However, it is possible that our results are quite irrelevant with respect to these other systems. Current experiments will hopefully resolve the points at issue.¹⁶

(11) Radical displacements, while rare, are known in cyclopropane chemistry.¹² This would be the first case of a carbon-carbon radical displacement reaction.

(12) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

(13) L. H. Slaugh, *ibid.*, **81**, 2262 (1959).

(14) C. Walling in ref. 10b, pp. 416-423.

(15) Recent incomplete studies on the ratio of IV to V as a function of concentration of I make it appear more likely that both products are derived from a common intermediate (such as VII) *via* reactions in a solvent cage.

(16) This work was supported in part by a grant from the Army Research Office (Durham).

(17) National Institutes of Health Predoctoral Fellow, 1963-1964.

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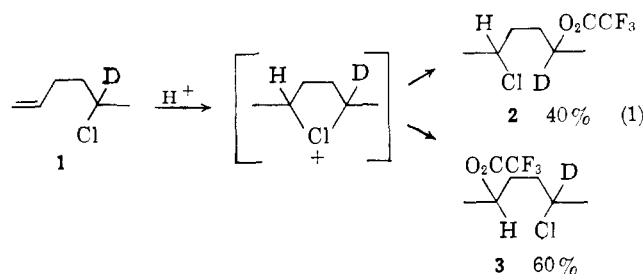
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A 1,4-Chlorine Shift and an Estimate of the Rate Enhancement Owing to Chlorine Participation in the Addition of Trifluoroacetic Acid to 5-Chloro-1-hexene

Sir:

We have found that reaction of 5-chloro-1-hexene-5-*d*, **1**, with trifluoroacetic acid gives 5-chloro-2-hexyl-2-*d* trifluoroacetate, **2**, the product of a 1,4-chlorine shift, which may arise *via* a cyclic chloronium ion intermediate, as shown in eq. 1. Based on n.m.r. analysis



of the distilled products obtained in 52% yield from 1.48 g. of **1**, 60% of "normal addition product," **3**, is formed, along with 40% of **2**. The corresponding reaction products from the nondeuterated chloride, 5-chloro-1-hexene, were identified as the expected diastereomeric 5-chloro-2-hexyl trifluoroacetates by elementary analysis,¹ infrared analysis, gas chromatography (two peaks attributable to diastereomers: 20-ft. Dow-Corning 550 silicone column, 100°), and n.m.r. analysis at 60 Mc. (CH_3CHCl ; methyl doublet at δ 1.50 and poorly resolved sextuplet at δ 4.00; $\text{CH}_3\text{-CHO}_2\text{CCF}_3$, methyl doublet at δ 1.33 and unresolved multiplet at δ 5.08, in the pure liquid containing a trace of tetramethylsilane). The n.m.r. spectra of the deuterated reaction products showed, in addition to methyl doublets of reduced intensity, broadened single peaks approximately in the middle of the doublets, attributable to the groups CH_3CDCl and $\text{CH}_3\text{CDO}_2\text{-CCF}_3$, in which the H-D coupling constant is small. The per cent of chlorine shift was calculated from the ratios of the areas of the doublet and "unsplit" peaks in each methyl region. Both measured ratios were within 2% of the value reported above, and these values could be approximately confirmed by integration of the low-field region of the spectrum.

A second series of experiments has enabled us to estimate the rate acceleration associated with chlorine participation in the addition of trifluoroacetic acid to 5-chloro-1-alkenes, and to show that the above-mentioned product distribution (eq. 1) may be the result of a competition between ordinary Markonikov addition and addition proceeding *via* a cyclic chloronium ion, which has a 50% probability of opening at C-2 or C-5 if secondary isotope effects are negligible. The reactivity of a series of ω -chloro-1-alkenes was determined (Table I) and the rate data was plotted (Fig. 1) in a form previously shown to give a straight line when the inductive rate depression falls off by a constant factor per methylene group.²

(1) *Anal.* Calcd. for $\text{C}_8\text{H}_{12}\text{ClF}_3\text{O}_2$: C, 41.30; H, 5.19. Found: C, 41.28; H, 5.17.

(2) (a) P. E. Peterson and C. Casey, *Tetrahedron Letters*, 1569 (1963).

(b) In Fig. 1, $\Delta \log k$ is the difference in the logarithms of the rate constants for the ω -chloro-1-alkenes and the corresponding unsubstituted alkenes. Reasonable values for errors in $\Delta \log k$, as indicated in Fig. 1, were calculated by assuming that $\pm 5\%$ error might be present in *each* rate constant.