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.

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation, is gratefully acknowledged. In addition, the authors are particularly indebted to Dr. Ross Pitcher, Varian Associates Application Laboratory, Pittsburgh, Pa., for the 100-Mc nmr spectra and to Professor Glenn Berchtold, Massachusetts Institute of Technology, for the mass spectrum. We wish to thank Dr. M. Hermes, Central Research Department, E. I. du Pont de Nemours and Co., and Professor E. Vogel, Universität Köln, Germany, for informing us of the results of their photochemical studies with N-carbethoxyazepine and oxepin, respectively, prior to publication.

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

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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**

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[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).

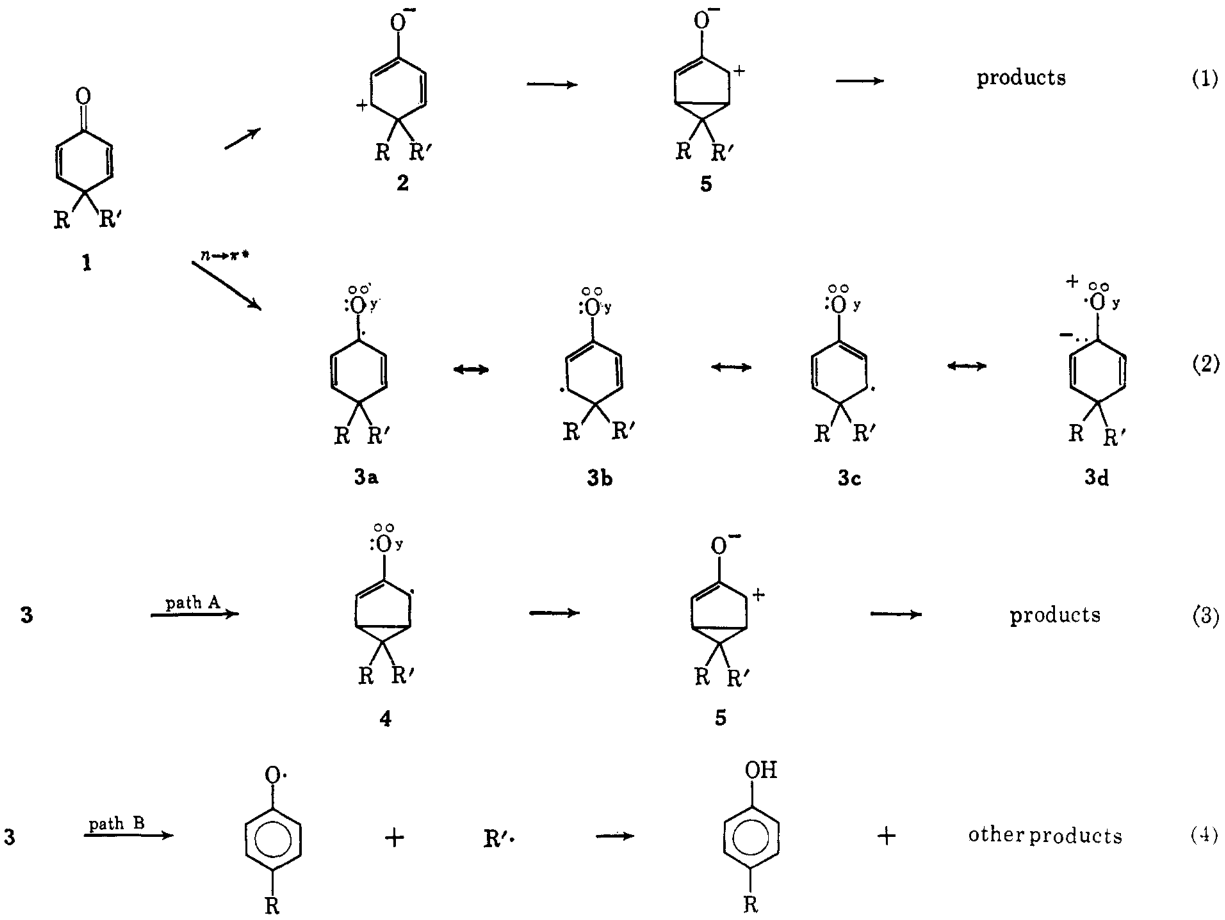
[4] M. H. Fisch and J. H. Richards, *ibid.*, **85**, 3029 (1963).

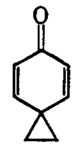
[5] See (a) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (b) R. Breslow in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 259–280.

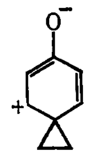
[6] C. J. Polowczyk, Ph.D. Dissertation, New York University, June 1965.

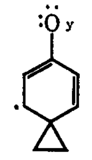
[7] R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963);

Scheme I




6


6a


6b

while the excited state according to the Zimmerman–Schuster scheme[3a] would be **6b**. A differentiation between these two possible intermediates seemed possible on the basis of the known differences in behavior of cyclopropylcarbinyl cations and radicals.[5,8] A photochemical study of spirodienone **6** was therefore undertaken.

Results

The synthesis of the spirodienone **6** was repeated.[7] As found by Winstein and Baird,[7] a yield of no more than 2–4% was achieved in the last step. The recrystallized dienone had properties corresponding in all details to those described by Winstein and Baird.[7] The photochemical reaction was initially studied in ethyl ether and it was in this solvent alone of those studied that the results were most interesting and most readily interpretable. Except for the few comments at the end referring to photolyses in other solvents, the results and discussion below refer to the reactions carried out in ethyl ether.

The photochemical reaction could be conveniently followed by ultraviolet spectroscopy on aliquots withdrawn during the reaction. In ethyl ether, the dienone has a maximum at 261 mμ while new maxima appeared during photolysis at 225 and 280 mμ. The disappearance of dienone cleanly followed a zero-order rate expression, with a rate constant of 3×10^{-8} mole l.$^{-1}$ hr^{-1}.[9] The lamp was turned off during one run, and it was found that the relative heights of the maxima at 225, 261, and 280 mμ did not change during a 48-hr period; subsequent reillumination led to continued diminution of the 261-mμ peak and enhancement of the 225- and 280-mμ peaks at a zero-order rate identical with that before the lamp was extinguished. A control sample of the dienone in ether which was not irradiated showed no change during a 3-month period. The reaction was usually complete after 24 hr. Some material was deposited on the walls of the flask during the irradiation.

The residue remaining after removal of solvent was examined in various runs by thin layer chromatography and gas–liquid partition chromatography. Although initial glpc results indicated a simple product mixture, tlc demonstrated the full complexity of the mixture. The mixture was separable into an ether-soluble and ether-insoluble portion and the ether-soluble portion was chromatographed on silica gel. The fractions were analyzed using tlc and those fractions of similar composition were combined and analyzed by infrared, ultraviolet, nuclear magnetic resonance (nmr), and mass spectrometry. A portion of the material put on the

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79, 4238 (1957). We are indebted to Professor Winstein and Dr. Baird for detailed procedures for the preparation of 6 prior to the full publication of their results.

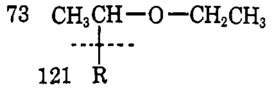
(8) D. I. Schuster, Ph.D. Dissertation, California Institute of Technology, 1961; Breslow in ref 5b, pp 289–294.

(9) For full discussion and interpretation of the kinetic data, see ref 6.

chromatography column was found to be completely nonmobile under the experimental conditions.

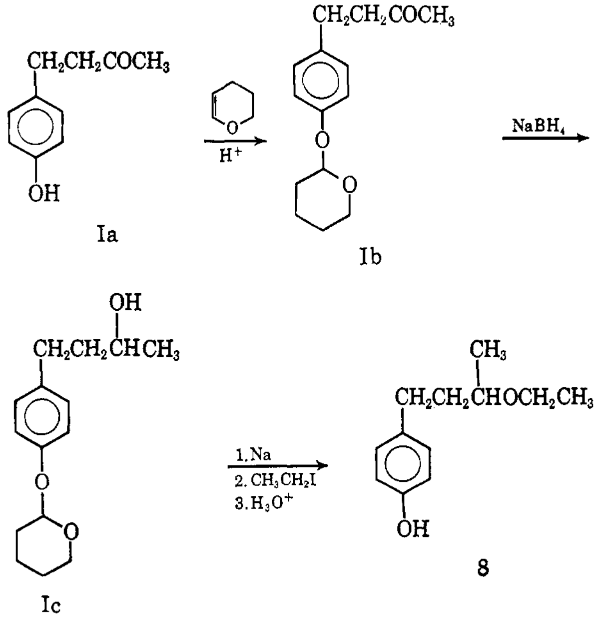
The largest chromatography fraction (referred to as fraction A) was homogeneous by tlc, and was identified as *p*-ethylphenol (**7**) by direct comparison with an authentic sample.

The second largest fraction (fraction B) was also homogeneous by tlc. A mass spectrum of this material showed a parent peak at 194 with strong peaks at 121 and 73. Since dienone **6** has a molecular weight of 120, it was clear that the product involved incorporation of one molecule of ethyl ether (molecular weight 74) and, moreover, that the product probably involved the partial structure given below which would be expected to cleave on electron impact into a fragment with *m*/*e* 73. The fact that the peak at *m*/*e* 121 was so prominent suggested that the other fragment, R^+, was also appreciably stabilized. The infrared and ultraviolet spectra indicated the material was aromatic and had a hydroxyl band and ether linkages. The nmr spectra which were initially obtained were limited by the minute amounts of chromatographically pure material available, but were in qualitative accord with the information available from the other spectra. On the basis of the above information and some preliminary mechanistic speculation, the structure 1-*p*-hydroxyphenyl-3-ethoxybutane (**8**) was postulated for fraction B. Since the material was not available in sufficient quantity for structure proof by degradation, the approach was to synthesize **8** by an independent route. This synthesis is outlined in Chart I.



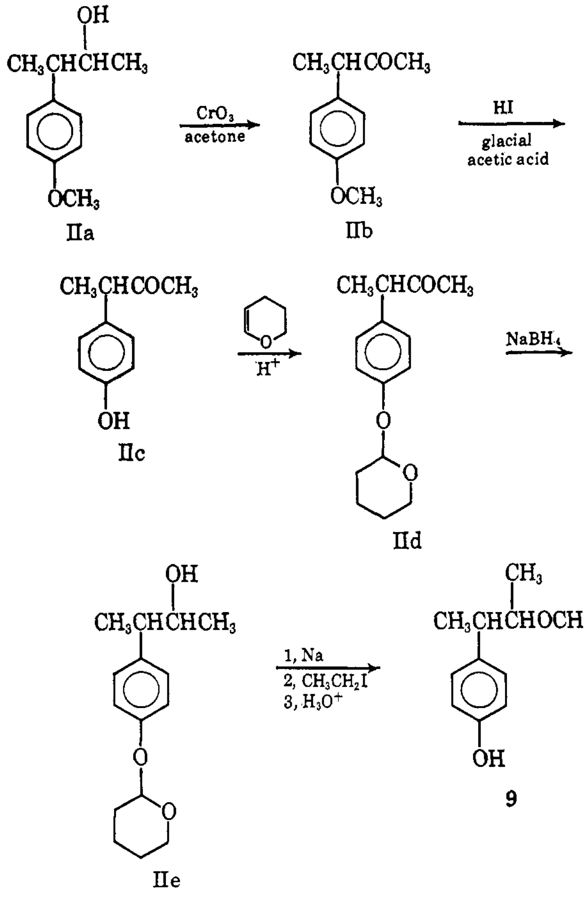
$$\begin{array}{l} 73\ \ CH_3\underset{\substack{|\\ R}}{C}H{-}O{-}CH_2CH_3 \\ 121 \end{array}$$

Chart I



The infrared spectrum of **8** obtained by this route was remarkably like that of fraction B, but not identical in all details, while its ultraviolet spectrum was virtually identical with that of B. Strong similarities were found on comparison of the nmr spectra of B and **8**, but there were important differences. The relative intensities of the resonances ascribed to the benzylic protons at 2.5 ppm (all relative to internal tetramethylsilane) and the aliphatic methylene group at 1.7 ppm were both greater in **8** than in fraction B. Moreover, **8** clearly showed an A_2B_2 pattern characteristic of a *para*-disubstituted benzene, while the pattern in the same region (centered at 6.7 ppm) for B was more complex. Finally, the patterns in the aliphatic region of 0.9 to 1.3 ppm are quite different in the two spectra. A closely split multiplet in **8** at 3.4 ppm, for three protons on ether carbon, corresponded well to a similar pattern in B, which, in earlier less well-resolved spectra, had appeared as a broad resonance corresponding to three protons. The over-all similarity in spectra of **8** and B indicated that our structural hypothesis needed slight adjustment. The greater intensity of the nmr resonances for B at 0.9 to 1.3 ppm, coupled with the other data, suggested that a third methyl group was present, and accordingly a synthesis of the isomeric compound 2-*p*-hydroxyphenyl-3-ethoxybutane (**9**) was devised.

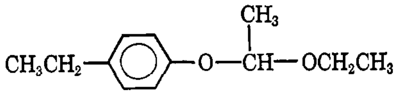
Chart II



The synthesis of **9** is outlined in Chart II. The striking similarity of the infrared and ultraviolet spectra of **8** and **9** was immediately apparent. The nmr spectrum of **9** was in accord with the proposed structure. As with **8** and B, a highly split multiplet corresponding to the three protons on the α carbons of an ether was noted at 3.4 ppm, as was an A_2B_2 pattern of a *para*-disubstituted benzene. As expected, the resonance found in **8** at 1.7 ppm was absent in **9**, while the benzylic proton resonance at 2.5 ppm in **9** corresponded to one proton and the multiplet at 0.9 to 1.3 ppm to nine protons. It was also evident that the nmr spectra of **9** and B were not identical. However, the nmr spectrum of B could be closely approximated by a spectrum of a mixture of **8** and **9** in the proportions of approximately 1:1.8. While the two spectra are nearly superimposable (*e.g.*, the unsymmetrical appearance of the aromatic protons at 6.3 ppm is exactly duplicated), small but significant details of the pattern in the aliphatic region at 0.9 to 1.3 ppm could not be exactly duplicated. We believe that this difference in the spectra is not due to an error in structure assignment; compound **9** is necessarily a mixture of two racemic diastereomers, each with its own characteristic nmr spectrum. The diastereomeric composition of **9** as obtained by the route in Chart II would *a priori* not be the same as in **9** produced photochemically from **6**. These small differences would be sufficient to explain the deviations in the nmr spectra of the two mixtures.

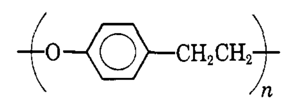
The assignment of B was corroborated by glpc analysis. Only one spot was obtained by tlc under a variety of conditions, the R_f of which was identical with those of the synthetic isomers **8** and **9**. With the synthetic material available, glpc conditions were established for separation of **8** and **9**. Fraction B showed two peaks under these glpc conditions and admixture with samples of **8** and **9** showed only peak enhancement, with no new peaks or shoulders appearing in the chromatogram. The composition of the mixture in B was determined using thermal conductivity factors obtained independently for **8** and **9** with an internal standard.

A very small chromatography fraction (fraction C) was identified by comparison of spectra with those of compound **10**, which was synthesized in the course of the investigation of the structure of B. The acetal **10** was synthesized by reaction between *p*-ethylphenol and ethyl vinyl ether, according to the procedure of Reppe.[10] Acetal **10** reacted with acidic 2,4-dinitrophenylhydrazine reagent to give acetaldehyde 2,4-DNPH. Further substantiation for the structure **10** was obtained from the nmr spectrum. The aromatic A_2B_2 pattern (6.8 ppm), the quartet for the hydrogen on the acetal carbon (5.3 ppm), the quartet for the methylene attached to the ring (2 H, 2.6 ppm), and the methyl resonances (9 H, 1.0 to 1.4 ppm) all appeared as expected for **10**. It was interesting to note that the resonance for the methylene protons of the ethoxy group appeared at 3.6 ppm not as a quartet but in a more complicated pattern. This is reasonable since these two protons are not identical but rather have a diastereomeric relationship.[11]



10

Another small chromatography fraction (D) was also isolated, but in quantities too small for structural studies. Spectra (infrared and nmr) of the ether-insoluble reaction product and the chromatographically nonmobile material indicated close relationship to the other isolated products. Evidence for aromatic moieties and ether linkages was clear, and we tentativey suggest that these materials are small polymer (dimers, trimers, etc.) of the starting material with the general structure



It is likely that some ethyl ether has been incorporated into these products as well.

The results of a number of runs of the photolysis of dienone **6** in ethyl ether are given in Tables I and II.

Table I. Results of Photolysis of Spiro[2.5]octa-4,7-dien-6-one (**6**) in Ethyl Ether. Products Isolated by Column Chromatography

			Products[a]			
Run	Dienone **6**, moles × 10³	Concn of **6** in ether, moles/l. × 10³	**7**	**10**	**8** + **9**[b]	Polymers and unidentified products
1	1.3	4.1	50	*c*	21	*c*
2	1.7	5.4	30	4	28	*c*
3	2.3	7.6	10	2.2	18	71
4	2.5	1.6	20	3.8	16	59
5	0.22	0.64	53	*c*	17.5	*c*

[a] Mole %, based on spirodienone **6**. [b] Products **8** and **9** are not separated under these conditions; see text. [c] Undetermined.

Table II. Gas–Liquid Partition Chromatographic Analysis of Products of Photolysis of Spiro[2.5]octa-4,7-dien-6-one (**6**) in Ethyl Ether[a]

		Products[c]			
Run	Concn of **6** in ether,[b] moles/l. × 10³	*p*-Ethylphenol (**7**)[d]	1-*p*-Hydroxyphenyl-3-ethoxybutane (**8**)	2-*p*-Hydroxyphenyl-3-ethoxybutane (**9**)	Ratio of **9**/**8**
6	0.69	51.4	8.8	15.8	1.8
7	1.3	47.8	5.0	8.4	1.7
8	1.3	52	3.4	6.8	2.0
9	2.7	40.8	4.6	7.8	1.7
10	2.7	48	4.2	8.4	2.0

[a] *sym*-Trichlorophenol used as an internal standard. For retention times of all components, see the Experimental Section. [b] Determined on the basis of ultraviolet absorption at 260 mμ, using ε 23,000.[7] [c] Expressed as mole %, based on reacted spirodienone **6**. [d] Contains a small contribution of **7** produced under these conditions from acetal **10**.

Possible thermal reactions of the dienone **6** in ethyl ether were investigated. A solution of **6** in ether was heated in a sealed tube at 100° for 2 hr, and ultraviolet spectroscopy indicated that 80% of the dienone had not reacted. After a 24-hr run, the dienone was entirely consumed giving polymer. Analysis by glpc showed that none of the products isolated from the photolyses (**7**, **8**, **9**, and **10**) were produced in the thermal runs, within the limits of our analytical method. A control experiment showed that **7**, **8**, and **9** are stable under the conditions of the thermal reaction, while **10** is thermally unstable.

The photolysis of **6** in solvents other than ether was briefly investigated. The solvents studied included toluene, acetonitrile, *t*-butyl alcohol, benzene, and hexane. In all solvents except toluene, no *p*-ethylphenol (**7**) could be isolated or detected, and apparently

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[10] W. Reppe, *et al.*, *Ann.*, **601**, 81 (1956).

[11] See K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 94.

only polymer was formed. In toluene, the yield of **7** was 11%, considerably less than the yield in the ether runs. Reactions of **6** in toluene at 200° for 6 hr afforded some bibenzyl, indicating that radicals were apparently produced in these reactions. No products derived from **6** other than polymer could be detected. In a control run in which a solution of **7** in toluene was heated at 200° for 6 hr, over 99% of the phenol was recovered.

In an attempt to study nonphotochemical radical reactions of **6** in ethyl ether, particularly induced decomposition, the decomposition of di-*t*-butyl peroxylate[12] in an ethereal solution of **6** was briefly investigated. The product mixture gave a very complex glpc tracing in which peaks appeared with retention times identical with those of *t*-butyl alcohol and *p*-ethylphenol (**7**) under the same conditions. The acetal **10** gives **7** under these same glpc conditions, and hence it is not possible to tell how much, if any, **7** arose from **10**, and how much was present as a product component. It was clear that the reaction mixture did not contain either of the isomers **8** or **9**. That ether radicals, $CH_3\dot{C}HOCH_2CH_3$, were produced was shown by a peak in the chromatogram which had the same retention time as an authentic sample of the *meso* ether dimer **11**.[13] No peak corresponding to ether dimer **11** was found on glpc analysis of the mixture from photolysis of dienone **6** in ethyl ether.

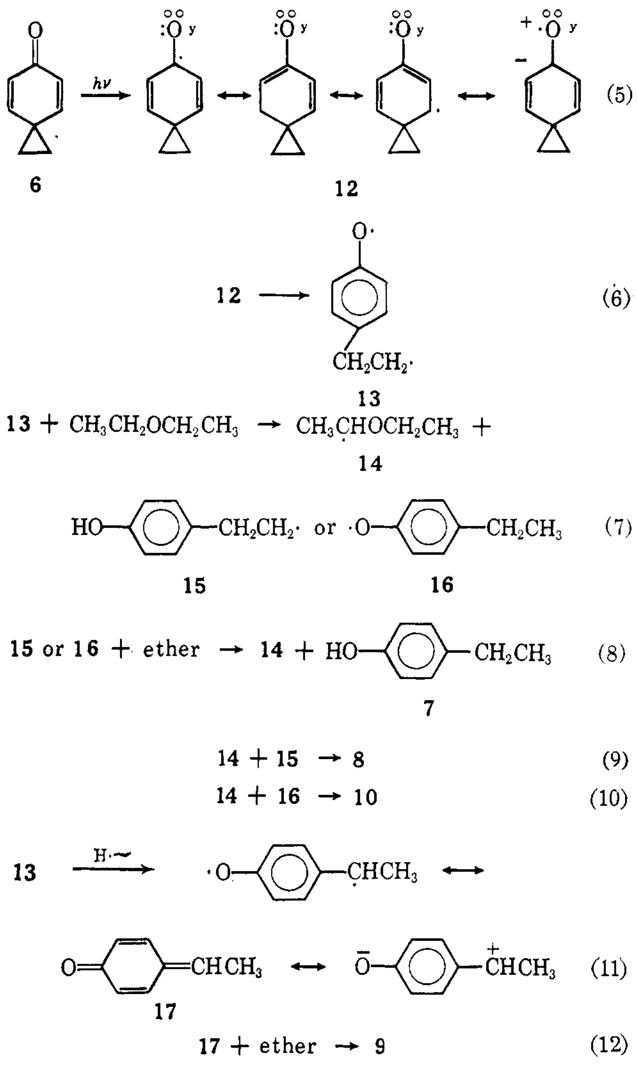
$$CH_3CH_2OCH(CH_3)CH(CH_3)OCH_2CH_3$$

11

Discussion

The course of the photochemical reaction of spirodienone **6** in ethyl ether, leading to reduction and to reaction with the solvent, requires the intermediacy of free radicals and can be rationalized as in Scheme II.

Scheme II



The problem as to whether initial excitation gives the ring-opened diradical **13** directly, or whether an intermediate depicted as **12** is involved, is not answered by the experimental results. The ring opening of **12** is favored not only because of the concomitant production of the aromatic ring system, but also because this is the expected path of reaction for a cyclopropylcarbinyl radical.[5,8] Such radicals generated in a variety of ways invariably open to give allylcarbinyl radicals, which then lead to the observed products. In favorably substituted cases, the reverse reaction occurs and initially produced allylcarbinyl radicals can give products derived from the related cyclopropylcarbinyl radical.[14]

It seems safe to assume, to a first approximation, that the two sites of unpaired electron density in **13** will react more or less independently. Hydrogen abstraction from ether at both radical sites to give **15** and **16** and the stabilized ether radical **14** (eq 7) seems reasonable.

Some evidence on the question of activated radicals in these reactions[15,16] is provided from experiments on the thermal behavior of spirodienone **6**. These thermal reactions, observed also in earlier work,[7] lead only to polymer, and hence are distinctly different from the photochemical reactions leading, in ether, to **7**, **8**, **9**, and **10**. Thus, it appears as if the thermal reactions do not involve the diradical **13**, and that the thermally derived polymer (formed in the solid state as well as in solution) *may* arise from direct attack of one dienone molecule on another. It could be argued[16] that the photochemical and thermal reactions do in fact involve the same intermediates, except that in the photochemical reactions the intermediates are generated with more potential energy than in the thermal reactions, such that reactions of high activation energy occur in the photochemical reactions which are not observable in the thermal sealed-tube reactions. For this argument to be valid, it must then be assumed that reactions with solvent of the photochemically produced diradical in a vibrationally excited ground electronic state occur more

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[12] P. D. Bartlett, R. E. Pincock, and E. P. Benzing, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

[13] The sample of **11** was very kindly provided by Drs. R. Srinivasan and S. Cremer of the Thomas J. Watson Research Center of IBM Corp., Yorktown Heights, N. Y.

[14] M. E. H. Howden, Ph.D. Dissertation, California Institute of Technology, 1962.

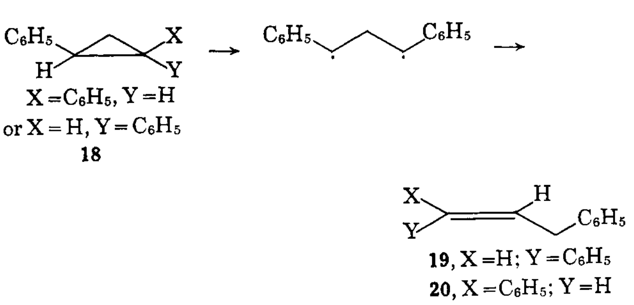
[15] The possibility that highly activated radical intermediates are involved must be considered. Hammond's "principle of maximum awkwardness"[16] states that "a highly excited molecule will find paths of decay which involve a minimum decrease in energy in each individual step." Thus, **14**, **15**, and **16** might still contain a significant portion of the original excitation energy (80–90 kcal/mole, corresponding to n → π* absorption of **6** between 320 and 350 mμ). The radical–radical reactions leading to **8**, **9**, and **10** would be quite rapid under these conditions, and there would be little chance for diffusion of radicals away from the solvent cage. Nonetheless the intervention of highly activated radicals in this system appears remote (*vide infra*).

[16] G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

rapidly than vibrational deactivation by collision, which seems highly unlikely, since rate constants for vibrational deactivation are at least on the order of 10^{11} $\sec^{-1}$.[17,18] Also, it would be most unusual if the abstraction reactions (eq 7) were of particularly high activation energy, since the α hydrogens of ether are readily abstracted by radicals.[19] Thus, if similar radical intermediates were involved in the thermal reactions in ether and toluene and in the photochemical runs, some *p*-ethylphenol (**7**) ought to have been observed in the products of the sealed-tube reactions. The facts are otherwise. The failure to observe the photochemical products from thermal runs in ether (**7**, **8**, and **9**) and toluene (**7** only) cannot be ascribed to their instability since control experiments show that these materials are recoverable under the reaction conditions; **10**, however, does not survive under these same conditions.[20]

The hydrogen migration suggested (eq 11) as the route for conversion of radical **13** to **17**, and eventually to rearranged product **9**, may appear unreasonable since hydrogen migration does not occur to a detectable extent in ground-state radical chemistry.[21-23] Thus, Walling summarizes the situation with the statement that "the preponderance of evidence indicates that 1,2 shifts of alkyl or hydrogen do not occur to a detectable extent during the lifetimes of radicals in well-defined systems at ordinary temperatures." [21] However, in this case, rearrangement of the diradical **13** can proceed to form a molecule (**17**) without any unpaired electrons.[24] This driving force is absent in the case of monoradicals.[21-23]

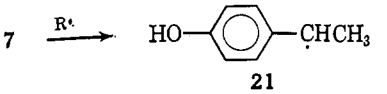
Another example of such a hydrogen rearrangement in a diradical generated photochemically in solution has been provided by Griffin and co-workers[25] who found that photolysis of *cis*- or *trans*-1,2-diphenylcyclopropane (**18**) gave, among other products, *cis*- and *trans*-1,3-diphenylpropene (**19** and **20**). Moreover irradiation of **20** led in part to a reversal of the reaction, again presumably *via* hydrogen migrations in an intermediate diradical. Such hydrogen migrations have been observed previously in vapor phase photolyses,[26] but extension of these results to the liquid phase is not necessarily expected because of the problem of rapid vibrational quenching in solution.



X = C_6H_5, Y = H or X = H, Y = C_6H_5 **18**

19, X = H; Y = C_6H_5
20, X = C_6H_5; Y = H

An alternative scheme which leads to the rearranged product **9** is pictured below. This involves hydrogen abstraction from *p*-ethylphenol (**7**), followed by reaction with ether radicals.



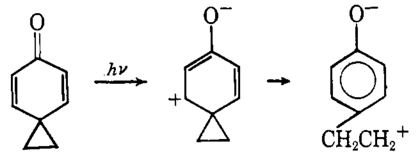
21

$$\mathbf{21} + \mathbf{14} \rightarrow \mathbf{9}$$

While this alternative mechanism cannot be rigorously excluded at this time, it appears unlikely. The ratio of products **9**/**8** is relatively insensitive to variations in the concentration of spirodienone (see Table II). This suggests that **8** and **9** are directly derived competitively from the same intermediate, presumably the diradical **13**. If **7** were an intermediate in the formation of **9**, the ratio of **9**/**8** would have increased markedly in runs 4 and 5 (Table II) since more **7** was available in these runs than in the others. Such a trend is not borne out by experiment. A direct demonstration of the hydrogen migration is possible using deuterium-labeled dienone **6**, the synthesis and photolysis of which is now under investigation.

Finally, the last step in Scheme II (eq 12), involving reaction of ether with the quinoid structure **17**, may be either a dark or a photochemical reaction. The latter would be analogous to the photoaddition of ether to 9,10-phenanthroquinone and related compounds.[27]

If the polar state concept[3c] were applicable to the photolysis of **6**, the intermediates **22** and **23** would be



6 **22** **23**

involved. Considering the ease of hydrogen migrations in carbonium ions when a more stable structure could arise by such a rearrangement, it would be expected that **23** would rearrange to give the same quinoid intermediate **17** suggested earlier.

$$\mathbf{23} \xrightarrow{\text{H}^{-}\sim} \mathbf{17} \xrightarrow[\text{ether}]{h\nu} \mathbf{9}$$

Thus, it might be possible to account on this basis for formation of the rearranged product **9**, but it would be difficult to account for the formation of reduction product (*p*-ethylphenol) and products **8** and **10**. Thus, **10** would have to be formed by the unlikely series of reactions

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(17) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

(18) A case in which a photochemical reaction has been interpreted as occurring *via* vibrationally excited ground states in solution has been reported by E. F. Ullman and W. A. Henderson, Jr., *ibid.*, **86**, 5050 (1964).

(19) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 478–479.

(20) An argument based on the assumption that thermal opening of the cyclopropane ring could give a radical which would react differently from **13** does not seem reasonable. Any unpaired electron density generated at the 4 position of the dienone system would surely be delocalized to some extent on oxygen to give a species that would be expected to react like **13**, *i.e.*, by hydrogen abstraction.

(21) C. Walling, in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., p 416.

(22) L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

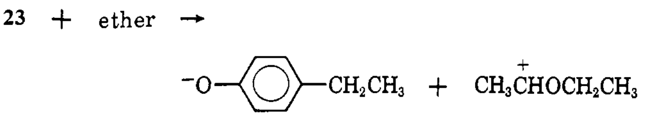
(23) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

(24) It should also be noted that the various valence bond structures written for **17** can contribute to the hybrid only if their multiplicity is the same, *i.e.*, singlet. Further implications with respect to the electronic state of **13** are not clear, however, since spin inversion might be concomitant with the rearrangement **13** → **17**.

(25) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965).

(26) See J. N. Pitts and I. Norman, *ibid.*, **76**, 4815 (1954).

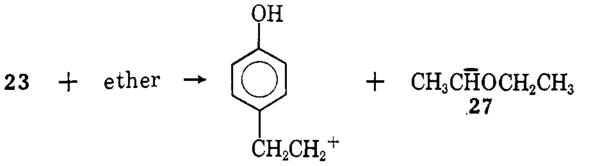
(27) M. B. Rubin, *J. Org. Chem.*, **28**, 1949 (1963).



24 **25**

24 + **25** → **10**

Even more objectionable is the route to **8** from **23** which would necessarily involve proton abstraction from ether, a most unusual and unlikely event.

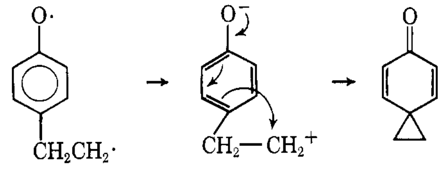


27

26

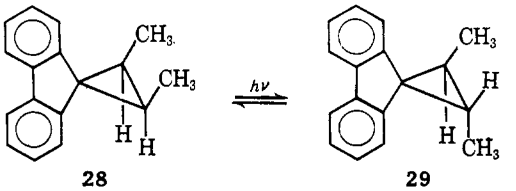
26 + **27** → **8**

However, if **23** is involved in the reaction, the most likely course of reaction would not be reaction with ethyl ether, but rather ring closure to give the starting material. This reaction would be a classic example of Ar$_1^-$-3 participation[7] and would be especially favorable in a nonsolvating medium such as ethyl ether. A determination of the quantum yield for disappearance of dienone gave a value of 0.06; the above scheme which regenerates spirodienone after photoactivation is a tempting rationalization for a quantum yield significantly less than unity. If induced decomposition of dienone, leading possibly to polymer, were taking place to a significant extent it would affect the quantum yield in the reverse direction.



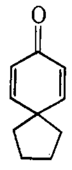
13 **23** **6**

Numerous examples of photoinduced ring opening of cyclopropanes have been reported. Excitation of an aromatic system with 2537-A light, followed by ring opening, has been observed for the diphenylcyclopropanes,[25] cyclopropylphenylmethane,[28] and the *cis–trans* isomers **28** and **29**.[29] Cyclopropane ring opening following n → π* excitation is known from the classic vapor phase study of methyl cyclopropyl ketone[26] and photolysis of dibenzoylcyclopropanes in solution.[30] These reactions have been interpreted on the basis of formation of intermediate diradicals. The interpretation given here of the photochemistry of **6**, in which ring opening to a diradical follows n → π* excitation, is consistent with the earlier studies.



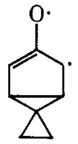
28 **29**

The formation of species exhibiting radical-like behavior on photolysis of **6** is compatible with a diradical structure for the excited state, and thus supports the Zimmerman postulate.[3a,b] Whether this excited state is best represented as **12** or **13** or some other structure remains unresolved. Clearly, though, the intermediacy of dipolar structures such as **22** must be excluded *in this case.* Extension of these results to other dienones is tenuous because of the peculiar properties of the cyclopropane ring. In addition to strain effects, conjugative interaction between the cyclopropane ring and the rest of the chromophore is particularly favorable in **6** because of the geometry of the molecule.[31]



i

Nevertheless, it is interesting to generalize these results in terms of two competitive pathways which are available for reaction of the (n,π*) excited state, depicted as **3**, in competition with radiative and nonradiative decay to ground states. Path A (eq 3 in Scheme I) leads to 3,5-bond formation, while path B (eq 4) gives a phenol by radical fragmentation. Path A, part of the route postulated by Zimmerman[3a,b] to account for formation of zwitterionic intermediates in almost all previously studied 2,5-cyclohexadienone photolyses, is particularly unfavorable in the case of **12**, as generated from **6**, because of the formation of the highly strained spiropentane intermediate **30**. In this case, reaction *via* path B is more attractive since it leads to opening of the strained cyclopropane ring with concomitant formation of an aromatic system (**12** → **13**, eq 6).



30

Since most of the 2,5-cyclohexadienones studied heretofore reacted *via* path A[3] (formation of aromatic systems by expulsion of a 4 substituent is usually not observed), it must be concluded that usually path A (eq 3) is more favorable energetically than path B (eq 4). Thus, path B can only be observed when the strain encountered in path A is unduly great (as in the case of **30**), or if one of the 4 substituents could lead to a stabilized radical R′. Since almost all dienones studied previously had phenyl or primary alkyl groups at C$_4$,[3] it is not surprising in retrospect that only path A was observed. Schuster and Patel[32a] have

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(28) P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **30**, 539 (1965).

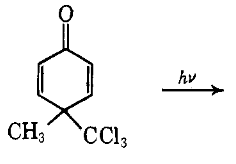
(29) W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, No. 12, 791 (1963).

(30) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963).

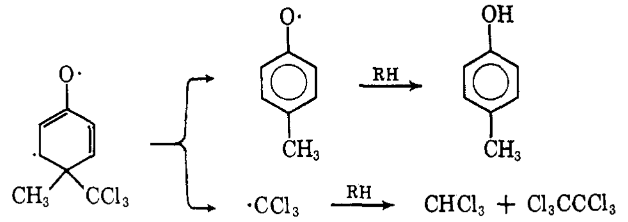
(31) The ultraviolet spectrum of **6**[7] shows λ_{max} 261 mμ in ether and 271 mμ in *t*-butyl alcohol (ε 22,200), while the ultraviolet spectrum of i shows λ_{max} in methanol at 242 mμ (ε 16,000): R. Baird and S. Winstein, *ibid.*, **84**, 788 (1962).

(32) (a) D. I. Schuster and D. J. Patel, *ibid.*, **87**, 2515 (1965). (b) The possibility cannot be discounted, as pointed out by a referee, that the "abnormal" behavior of **6** and **31** and a few other dienones is due to a different excited state in these cases in contrast with that involved in "normal" dienone photochemistry, *i.e.*, a dipolar structure for the ex-

presented several examples of radical fragmentation observed in earlier studies (which involve expulsion of heteroatom groups, such as acetoxy or methoxy) along with a seemingly unambiguous example of carbon–carbon fragmentation. Thus, photolysis of the dienone **31** in a variety of solvents gave a high yield of *p*-cresol together with chloroform and hexachloroethane.[32] In the case of **31** the competing reaction by path A does not involve the formation of a highly strained intermediate, in contrast to **6**.[32c] Thus, the



31



radical fragmentation route is probably quite general and should be observed in a number of favorable cases. These examples of radical fragmentation support the conclusion that the photochemistry of 2,5-cyclohexadienones involves initial formation of excited states in which charge separation is not appreciably developed.[32b]

Experimental Section[33]

Spiro[2.5]octa-4,7-diene-6-one. (6). Although a detailed description of the preparation of spirodienone **6** has been reported,[7] considerable difficulty was experienced in reproducing the results and, in our hands, certain modifications of the original scheme were more satisfactory. It should be emphasized that careful preparation of all glassware used in these experiments according to the instructions of Baird and Winstein[7] is necessary to achieve satisfactory results.

For consistent results Harshaw alumina AL-101-P was used. Harshaw alumina (1800 g) was treated with a potassium hydroxide (180 g) solution in water (135 g). The mixture was ball milled for 12 hr. The basic alumina prepared in this manner was allowed to stand for at least 24 hr, and each batch was separately standardized for optimum flow rate. To basic alumina (260 g) packed as a wet slurry in a 59-mm diameter column was added 2-*p*-hydroxyphenylethyl bromide[7,34] (2.6 g) in anhydrous ether (30 ml) using gentle air pressure. Fresh ether was added so as to achieve an initial flow rate of approximately 50 ml/min. Samples of eluent were collected at intervals corresponding to changes in flow rate of 10 ml/min and the best flow rates in terms of yield and purity of dienone were determined by ultraviolet analysis of fractions. The dienone has λ_{max} 260 mμ[7] and the phenolic contaminants λ_{max} 225 mμ. The flow rate established for a particular batch of alumina was used for all runs on that alumina preparation. Those fractions which showed only the 260-mμ peak in the ultraviolet were further utilized.

The ethereal dienone solutions were analyzed using the absorbance at 260 mμ (ϵ 22,000).[7] Yields varied between 2 and 4%. The ethereal solutions were concentrated to 100 ml and dried over anhydrous sodium carbonate, and concentrated to about 6 ml. Freshly distilled dry pentane (6 ml) was added and the dienone was recrystallized at −5°[35] as colorless needles which, on standing or heating, were converted to an ether-insoluble polymer. A freshly prepared sample melted over a range of 42 to 45° (lit[7] mp 40–43° and 43–46°). The melting point was obscured since the liquid rapidly polymerized to an infusible white solid. For photolysis in ether the solid was redissolved in ether freshly distilled from lithium aluminum hydride. Alternatively, the solid was kept in a drybox at room temperature and was later dissolved in the appropriate solvent.

Photolysis of Spirodienone 6. All glassware used in the operations was specially washed and treated, as described by Baird and Winstein.[7] The irradiation flask (made by Eck and Krebs Inc., Long Island City, N. Y.) was designed to fit around a Hanovia quartz immersion well. The flask was fitted with a side arm to a condenser, a nitrogen inlet tube at the bottom, and an outlet fitted with a stopcock near the bottom. The solutions were stirred magnetically. A Hanovia 450-w, high-pressure mercury arc inside a Pyrex filter sleeve was used in all runs. The dienone solutions were purged for 20–30 min with dry nitrogen purified by passage through alkaline pyrogallol, concentrated sulfuric acid, and ethereal or dioxane solutions of benzophenone ketyl. After purging, the flask was maintained in an atmosphere of nitrogen, a control sample was removed, and the lamp was fired.

For rate studies, aliquots were removed until the solvent level reached the top of the arc. In analytical runs, photolysis was continued for the time extrapolated from the rate studies and the extent of the photolysis checked by ultraviolet spectroscopy. The time of the photolysis depended on the amount of dienone and varied between 24 and 72 hr. When the source was turned off in midrun, the relative peak heights in the ultraviolet spectrum did not change for an indefinite period; reillumination led to reaction at an unchanged rate. A dark control sample of dienone in ether showed no change over 60 days.

Dienone Photolysis in Ethyl Ether. Rate Studies. Aliquots were diluted and their ultraviolet spectra were determined. The absorbance at 260 mμ fell off linearly with time. A zero-order rate constant of 3 × 10^{-8} mole l.$^{-1}$ hr^{-1} was calculated from the slope of the straight line plots. In the concentration ranges employed, Beer's law was obeyed.

Dienone Photolysis in Ethyl Ether. Chromatographic Separation of Products. In analytical runs, the optimum scale and concentration which maximized the yield of nonpolymeric products was found to be 100 mg of spirodienone **6** in 330 ml of ether. Irradiation was 85–90% complete in 25 hr, as estimated from the ultraviolet spectra.

Photomixture amounting to 392 mg was isolated from irradiation in three portions of 300 mg of spirodienone **6** in ethyl ether. The mixture was chromatographed on 50 g of Davison No. 950 silica gel. Fractions of 8 ml were combined on the basis of similarity of thin layer chromatograms of selected eluate fractions. For full details of procedure and methods of analysis, see ref 6.

Fractions 31–75, eluted with 3:50 ether-pentane, were combined and distilled in a "Kugelrohr"[36] at 100° (1 mm). The material collected was uniform by tlc, giving a single spot at R_f 0.95. A positive dinitrophenylhydrazone test was observed both on the tlc spot and on the isolated oil. When authentic ethyl *p*-ethylphenyl acetal of acetaldehyde (**10**, see below) and this fraction, labeled fraction C, were run on the same tlc plate, identical R_f's of 0.90 were obtained. Infrared spectra of C and **10** were identical.

Fractions 76–130, also eluted with 3:50 ether–pentane, were combined and recrystallized from freshly distilled pentane at −5°.

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cited state might appertain in the majority of cases. This distinction might involve, for example, simply a difference between the properties of (n,π^*) and (π,π^*) excited states. This problem can only be resolved by a detailed characterization of the various excited states directly, a study which is already in progress and which we have considered theoretically.[6] Our main point here is to demonstrate that the divergent behavior of **6** and **31** can be understood in terms of the competitive reaction paths outlined above, although other explanations may prove equally satisfactory. The necessity for additional experimental evidence should be obvious.

(32c) Note Added in Proof. Evidence that **31** reacts *via* path A and path B through a common diradical intermediate has recently been obtained: D. I. Schuster and D. J. Patel., *J. Am. Chem. Soc.*, in press.

(33) All boiling points and melting points are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103C instrument operating at an ionizing potential of 70 v, ultraviolet spectra on a Cary 15 recording spectrophotometer, infrared spectra on a Perkin-Elmer Model 137 Infracord spectrophotometer and on a Baird-Atomic Model KM-1 spectrophotometer, and nuclear magnetic resonance spectra on a Varian Model A-60 spectrometer with tetramethylsilane as an internal standard.

(34) This material is a vicious skin irritant and must be handled so as to avoid contact with the skin.

(35) This temperature gave consistently better results than the Dry Ice–acetone bath suggested by Baird and Winstein.[7]

(36) R. Graeve and G. H. Wahl, Jr., *J. Chem. Educ.*, **41**, 279 (1964).

Colorless needles were obtained which were sublimed at room temperature at about 1 mm to yield material, mp 45°, undepressed by admixture with authentic *p*-ethylphenol (**7**). Selected aliquots of fractions 76–130 also had the same retention time (on a 6-ft Carbowax column at 150°, helium flow rate 100 ml/min) as authentic *p*-ethylphenol.

Fractions 131–200, eluted with 1:5 ether–pentane, were combined and distilled in a "Kugelrohr"[36] at 100° and 1 mm. The oil obtained, designated fraction B, was homogeneous by tlc. The mass spectrum of this material showed a parent peak at *m/e* 194 and intense fragments at *m/e* 121, 107, 73 (base peak), 57, and 45. The nmr spectrum of B is described in the text. The infrared spectrum showed a hydroxyl band at 3400 cm^{-1}, aromatic bands at 1500 and 1600 cm^{-1}, no carbonyl bands, and strong broad bands in the region 1050–1250 cm^{-1} ascribable to C–O absorption in alcohols and ethers.

Fractions 201–210 (fraction C, 5 mg), eluted with 1:2 ether–pentane, were not investigated further.

Fractions A and B were identified as described in the Results section (above). The results of several runs of the photolysis of spirodienone **6** are given in Table I.

Quantitative Glpc Analysis of Products from Dienone Photolysis in Ethyl Ether. Conditions were established for the separation of the two components of fraction B (above), 1-*p*-hydroxyphenyl-3-ethoxybutane (**8**) and 2-*p*-hydroxyphenyl-3-ethoxybutane (**9**), using the synthetic samples made by the procedures given below, on a 6-ft 0.25-in. copper tube packed with 10% Dow 710 silicone oil on Chromosorb P (60–80). The helium flow rate was 200 ml/min at a column temperature of 180°. A Perkin-Elmer Model 254C gas chromatograph was used. Under these conditions, the retention times for *p*-ethylphenol and synthetic **8** and **9** were 2.4, 10.6, and 14.4 min, respectively. The three components of the photolysis mixture had identical retention times as the standards, by simultaneous injection. Quantitative analysis of the photomixtures was carried out using *sym*-trichlorophenol as an internal standard (retention time 6.2 min). The composition of the photomixture in five runs is reported in Table II.

Thermal Reactions of Dienone 6 in Ether and Toluene. A solution of 10 mg of recrystallized dienone **6** in 35 ml of ether was placed in a carefully neutralized Pyrex tube. The ethereal solution was purged with nitrogen in a liquid nitrogen bath and sealed under an atmosphere of nitrogen. The tube was heated at 100° for 2 hr, and the solution was then allowed to cool overnight. Ultraviolet spectroscopy showed that less than 2 mg of dienone had been destroyed. A fresh solution was prepared and was heated for 24 hr at 100°. The ultraviolet spectra showed only phenolic absorption maxima at 225 and a shoulder at 285 mμ. Glpc analysis with a trichlorophenol internal standard showed no *p*-ethylphenol or **8** or **9**. White polymer remained in the tube. A control mixture of **7**, **8**, and **9** in ether heated to 100° for 12 hr was recoverable by the above technique in greater than 90% yields. Similarly, only polymer and no *p*-ethylphenol resulted from heating a toluene solution of the dienone for 6 hr at 200°. Similar treatment of a toluene solution of *p*-ethylphenol led to recovery of greater than 99% of the phenol.

Photolysis of Spirodienone 6 in Toluene. Twenty-five milligrams of spirodienone **6** in 350 ml of toluene was photolyzed for 24 hr. *sym*-Trichlorophenol (13.3 mg) was added and the mixture was analyzed by glpc. The yield of *p*-ethylphenol was 11%.

Preparative tlc afforded *p*-ethylphenol and bibenzyl, whose identities were confirmed by infrared and nmr spectral comparison with authentic samples.

Photolysis of Spirodienone 6 in *t*-Butyl Alcohol and Acetonitrile. The irradiation apparatus was modified to allow 30° water to circulate in the inner jacket. Recrystallized dienone (100 mg) was suspended in purified *t*-butyl alcohol, fp 25–26°, and residual ether was removed. The course of the photolysis was followed by ultraviolet spectroscopy, $\lambda_{\max}^{t\text{-BuOH}}$ 270 mμ (lit[7] 271 mμ). The photolysis was much more rapid in this solvent than in ethyl ether, reaction time of 16 hr *vs.* 36 hr. The *t*-butyl alcohol was removed *in vacuo*, and the residue was examined by tlc. A complicated chromatogram was obtained with the majority of the material appearing as an ill-defined smear from the origin to R_f 0.45. No spot was observed corresponding in R_f to *p*-ethylphenol (**7**). Chromatography on silica gel gave a series of fractions, none of which contained **7** (glpc). The infrared spectra were like that of the chromatographically nonmobile material found in the ether photomixture. Similar results were obtained on photolysis in purified acetonitrile.

Quantum Yield Determination. The apparatus consisted of a Hanovia 100-w low-pressure mercury arc, a focusing lens, a water filter, and ruby and Pyrex glass filters as suggested by Srinivasan,[37] to limit the exciting wavelength to mainly 3130 A. The procedure was based on that described by Masson, Boekelheide, and Noyes,[38] using a uranyl oxalate actinometer. A value of 0.55 for the quantum yield for disappearance of oxalate at 3130 A was used.[38] The intensity of radiation passing though the filters was found to be 5×10^{18} quanta/hr. Over a 30-hr period, the reaction of 1.62×10^{-6} mole of dienone required 1.5×10^{19} quanta, corresponding to a quantum yield for disappearance of dienone of 0.065.

Acetaldehyde *p*-ethylphenyl ethyl acetal (10) was made by the model procedure of Reppe, *et al.*[10] A solution of ethyl vinyl ether (8 g, 0.11 mole) and α-chloroethyl ethyl ether (2 drops) was added dropwise to a solution of *p*-ethylphenol (11.7 g, 0.096 mole) in 7 ml of anhydrous ether at 15°. After 0.5 hr of additional stirring, the ethereal solution was extracted twice with 10% sodium hydroxide, dried over anhydrous sodium carbonate, concentrated, and distilled through a 6-in. Vigreux column to give 13.3 g (70% yield) of the acetal as a colorless liquid, bp 99–100.5° (7 mm). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.10; H, 9.34. Found: C, 74.23; H, 9.65.

The nmr spectrum of the acetal is described in the text. The infrared spectrum is in accord with the structure. Further confirmation was achieved by hydrolysis of the compound in the presence of acidic 2,4-dinitrophenylhydrazine solution to give a derivative, mp 166°. Two 2,4-dinitrophenylhydrazones of acetaldehyde are reported,[39] one mp 147° and the other mp 168°. Extraction of the aqueous acid solution from the hydrolysis afforded *p*-ethylphenol, characterized by comparison of infrared and glpc data with an authentic sample.

***p*-Pyranyloxybenzylacetone (Ib).** A solution of *p*-hydroxybenzylacetone[40] (13 g, 0.08 mole) and 30 ml of dry, freshly distilled dihydropyran was treated with 6 drops of concentrated hydrochloric acid in an ice bath. After 15 min the solution was warmed until dark in color. Extraction with 10% sodium hydroxide resulted in recovery of 3.5 g of starting material. The dark residue (41 g) was chromatographed on silica gel (500 g) with 10% ether–pentane to give a nonaromatic (infrared) yellow oil. Further elution with 1:1 ether–pentane gave an aromatic oil, thought to be *p*-pyranyloxybenzylacetone, which was distilled through a 6-in Vigreux column to yield 6.5 g (32%) of material, bp 162° (1.5–2.0 mm). *Anal.* Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.41; H, 8.29. The infrared spectrum was in accord with the assigned structure.

1-*p*-Pyranyloxyphenyl-3-butanol (Ic). A solution of *p*-pyranyloxybenzylacetone (6.5 g, 0.026 mole) in 10% aqueous ethanol containing sodium hydroxide (0.1 g) was treated with sodium borohydride (0.8 g) with stirring at ice bath temperatures. After 2 hr, the ice bath was removed, and stirring was continued overnight. The solution was evaporated to $^1/_3$ volume, diluted with water, and extracted with ether. The ether layer was dried over sodium carbonate, concentrated, and distilled to give 1-*p*-pyranyloxyphenyl-3-butanol (4.8 g, 70%), bp 174° (0.15 mm). *Anal.* Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.80. Found: C, 72.04; H, 8.94.

The infrared spectrum of **1c** had no carbonyl bands and had the usual strong bands assigned to hydroxyl, ether, and benzenoid moieties.

1-*p*-Hydroxyphenyl-3-ethoxybutane (8). A solution of 1-*p*-pyranyloxyphenyl-3-butanol (4.5 g, 0.018 mole) in 10 ml of anhydrous ether was treated with sodium (0.37 g, 0.016 g-atom) at reflux for 24 hr. Additional ether (10 ml) was added and the mixture was heated at reflux for 72 hr. Ethyl iodide (6 g) was added and stirring was continued for 24 hr. The solution was filtered and concentrated, and the residual oil (1.5 g) was chromatographed on silica gel. Elution with 10% ether–pentane gave a fraction showing pyranyl and benzenoid but no hydroxyl absorption in the infrared. Tlc showed a single spot. This oil (1.5 g) was hydrolyzed by heating on a steam bath with 15 ml of 1:2 water–ethanol containing 10 drops of concentrated hydrochloric acid. The solution was extracted with ether, dried over sodium sulfate, and distilled using a

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(37) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

(38) C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry," Vol. II, A. Weissberger, Ed., 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, pp 289–299.

(39) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

(40) G. Zemplen, R. Bognar, and L. Boskovitz, *Chem. Ber.*, **77B**, 785 (1944).

"Kugelrohr"[36] at 0.15 mm and 125° giving 0.6 g (0.003 mole, 17%) of 1-*p*-hydroxyphenyl-3-ethoxybutane. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.71; H, 8.91. C-Methyl determination (Kuhn–Roth): Calcd, 15.46. Found, 14.79.

The product had one spot on tlc, R_f 0.45. The nmr spectrum is described in the text. The infrared spectrum, in accord with the structure, has strong hydroxyl, ether, and benzenoid, but no carbonyl bands.

2-*p*-Anisyl-3-butanone (IIb). A solution of 2-*p*-anisyl-3-butanol[41] (30 g, 0.17 mole) in 50 ml of purified acetone was treated with a freshly prepared solution of chromic acid in acetone at 0.5°. The extent of oxidation was estimated by infrared spectroscopy on aliquots. When the reaction was complete, the solution was diluted with water and extracted with ether, and the ether layer was washed with 5% sodium bicarbonate solution, dried over sodium sulfate, and concentrated. The resulting oil was distilled through a 6-in. Vigreux column to give 16.0 g of material, bp 84–88° (7 mm). This oil was not homogeneous by tlc but chromatography on silica gel, using 10% ether in pentane as eluent, gave 13.6 g (42.3%) of homogeneous material. The infrared spectrum of the material showed no OH bands and had a strong carbonyl band at 1710 cm^{-1}. *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.89; H, 7.98.

2-*p*-Hydroxyphenyl-3-butanone (IIc). 2-*p*-Anisyl-3-butanone (13.0 g, 0.075 mole) was heated with 20 ml of glacial acetic acid and 15 ml of concentrated hydrogen iodide at reflux overnight. The resulting solution was cooled, diluted with water, and extracted with ether. The ether extract was washed with water, 5% sodium bicarbonate solution, and then with three portions of 10% sodium hydroxide solution. The basic solution was quickly acidified with concentrated hydrochloric acid and extracted with ether. The ethereal layer was washed with water and 5% sodium bicarbonate solution, dried over sodium sulfate, concentrated, and distilled in a short-path apparatus to yield 9.2 g (74%) of product. *Anal.* Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.80; H, 7.33. The infrared spectrum of this material had strong bands for hydroxyl (3400 cm^{-1}) and carbonyl (1710 cm^{-1}) and the usual aromatic bands.

2-*p*-Pyranyloxyphenyl-3-butanone (IId). 2-*p*-Hydroxyphenyl-3-butanone (8.5 g, 0.05 mole) was dissolved in dihydropyran (20 ml), treated with 6 drops of concentrated hydrochloric acid, and allowed to stand for 0.5 hr in an ice bath. Dilution with ether (40 ml) followed by extraction with water and 10% sodium hydroxide solution gave an ether solution which was dried over anhydrous sodium carbonate and concentrated to yield a thick, brownish oil. This oil on short-path distillation gave 2-*p*-pyranyloxyphenyl-3-butanone (5.8 g 46%), bp 127–128° (0.03–0.05 mm). *Anal.* Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.35; H, 7.99. The infrared spectrum, which contained no hydroxyl bands, was in accord with the structure.

2-*p*-Pyranyloxyphenyl-3-butanol (IIe). 2-*p*-Pyranyloxyphenyl-3-butanone (5.0 g, 0.02 mole) was dissolved in 95% ethanol (20 ml) and enough water was added to maintain a slight turbidity. Sodium borohydride was added (1.1 g, 0.03 mole) in small amounts with stirring, the mixture was stirred for 6 hr, diluted with water, extracted three times with ether, and the extracts were dried over anhydrous sodium sulfate and concentrated. The resulting oil was distilled through a short-path apparatus to yield 3-*p*-pyranyloxyphenyl-2-butanol (4.0 g, 80%), bp 133–134° (0.02–0.03 mm). *Anal.* Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.55; H, 8.97. The infrared spectrum had a hydroxyl band at 3400 cm^{-1} and no carbonyl bands and was otherwise similar to that of IId.

2-*p*-Hydroxyphenyl-3-ethoxybutane (9). 2-*p*-Pyranyloxyphenyl-3-butanol (3.5 g, 0.014 mole) was treated with sodium dispersion (70% in mineral spirits) in benzene solution. The dispersion was added dropwise until the initial vigorous reaction subsided. After 20 min of additional stirring, ethyl iodide (20 g) was added, the mixture stirred for 72 hr, and then filtered and concentrated. The residue was distilled in a "Kugelrohr"[36] at 100° (0.1 mm). The product was not homogeneous by tlc and was purified by column chromatography on silica gel, using the conditions established for the photolysis mixture (see above). The purified material gave a single spot on tlc with R_f 0.5, identical with that given by 1-*p*-hydroxyphenyl-3-ethoxybutane (**8**) and photolysis fraction B. The chromatographically purified product was redistilled to give 0.1 g (3.5%) of 2-*p*-hydroxyphenyl-3-ethoxybutane. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.61; H, 9.63.

The infrared spectrum of **9** is extraordinarily similar to that of **8**, differing only in some fine structure. The nmr spectrum is described in the text.

Reaction of Spirodienone (6), Ethyl Ether, and Di-*t*-butyl Peroxylate. Di-*t*-butyl peroxylate, prepared by the procedure of Bartlett, Pincock, and Benzing,[12] had mp 51–52° (lit[12] 50.5–51.5°). An aliquot of an ethereal solution of 50 mg of dienone **6** (from its ultraviolet spectrum) was diluted to 100 ml with ether. The solution was cooled to −20° and 0.15 g of di-*t*-butyl peroxylate was added. The solution was then purged of oxygen[12] by cooling in a Dry Ice–acetone bath and then in liquid nitrogen until the ether solidified. The flask was evacuated to a pressure of 0.08 mm, nitrogen was admitted, and the flask contents was warmed to Dry Ice–acetone temperatures where it reliquified. The procedure of cooling, evacuation, etc., was repeated three times. The sample was then warmed to room temperature in a nitrogen atmosphere and kept there for 18 hr. The ether was evaporated leaving an oil containing a small amount of white solid, whose infrared spectrum showed unreacted di-*t*-butyl peroxylate, as well as bands typical of *para*-substituted benzene derivatives seen previously. A portion of the oil was examined by glpc as above and neither **8** nor **9** was observed; a trace peak corresponding to *p*-ethylphenol was observed. On the same column at 100° and 100 ml/min peaks corresponding to *t*-butyl alcohol and ether dimer **11**[13] were found. No evidence for the presence of **8** or **9** in the sample was obtained by preparative tlc.

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