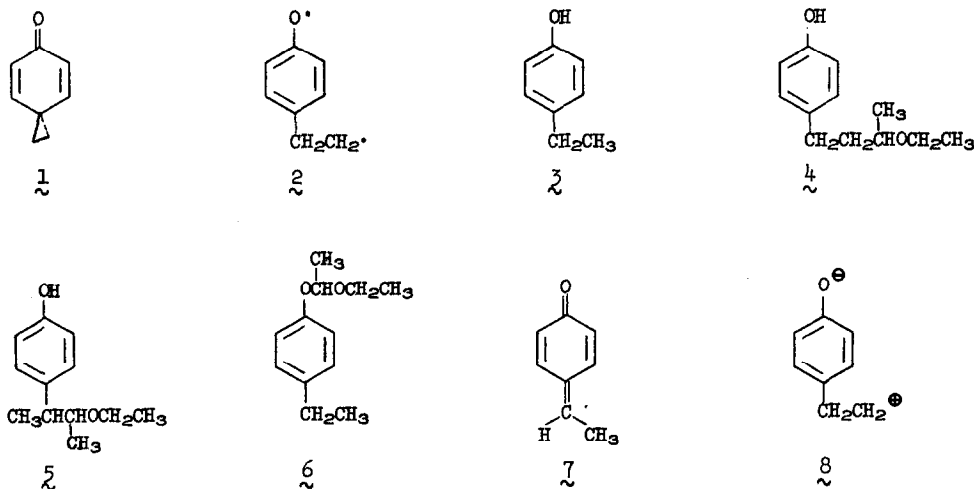


PHOTOLYSIS OF HINDERED
SPIRO[2.5]OCTA-4,7-DIEN-6-ONES

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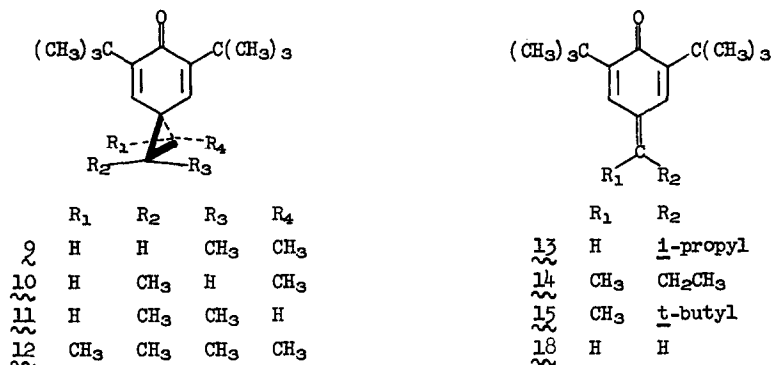
(Received in USA 21 August 1967)

We have recently succeeded in preparing a series of spiro[2.5]octa-4,7-dien-6-ones (1) and find the photochemistry of these compounds to differ from that reported (2a-c) for the parent dienone 1 (3a-c). Schuster and coworkers report that irradiation ($>2800\text{\AA}$) of an ethereal solution of 1 leads to intermediate diradical 2 which subsequently reacts with solvent to give 3, 4, 5, and 6. To account for phenol 5, formed in yields of 6.8-15.8%, a novel hydrogen atom shift was postulated to give rise to quinone methide 7 which, although not detected, was suggested as a precursor to 5. The dipolar species, 8, a reasonable precursor of 7, was rejected since it was deemed unlikely to lead to products 3, 4, and 6, but rather would be expected to regenerate the original spirodienone. On the basis of the observed products and the results of deuterium labeling studies, these workers favor diradical spirodienone excited states.



We find that the photolysis of several alkylated spirodienones leads to a more complicated sequence of events in that not one but three simultaneous photoreactions are observed.

Irradiation of $4.5 \times 10^{-3}M$, cyclohexane solutions of cis-1,2-dimethyl-5,7-di-t-butyl-spiro[2.5]octa-4,7-dien-6-one, 9, (Rayonet Photochemical Reactor, 8 2537Å lamps, nitrogen swept quartz vessels, 8-15°C) causes initial photoisomerization to the corresponding trans isomer, 10, with slower concomitant formation of two isomeric quinone methides, 13 and 14, in a time dependent ratio. Both spirodienones are consumed before a photostationary cis:trans ratio is established. Similar irradiation of $4.2 \times 10^{-3}M$ solutions of the pure trans spirodienone, 10,



leads to barely detectable amounts of 9 before essentially complete conversion (ca. 3.5 hrs.) to a mixture (ca. 1.1:1.0) of quinone methides 13 and 14. High quinone methide yields (85% by nmr) may be obtained by stopping the photolysis at the optimum time.

Table I summarizes the time dependence of the 9:10 and 13:14 ratios upon irradiation of the cis-spirodienone, 9, as determined from the vinyl proton region of the nmr spectrum of the total mixture. Figure 1 shows this region of the nmr spectrum after a two hr. irradiation period. The cis and trans dimethylspirooctadienones cannot be readily distinguished by other common analytical methods.

Photoconversion of spiro[2.5]octa-4,7-dien-6-ones to quinone methides extends to the 1,1-dimethyl spirodienone 11 (prepared by the method described in (1) and previously reported in (3c) and to the 1,1,2,2-tetramethyl spirodienone 12 and may be general. Irradiation of $4.5 \times 10^{-3}M$ cyclohexane solutions of 11 (RPR, 16 2537Å lamps) leads to a mixture of quinone methides 13 and 14 (ca. 9.4:1.0 ratio after 1.5 hrs; ca. 6.0:1.0 ratio after 5 hrs.). Similar irradiation of a $6.5 \times 10^{-3}M$ solution of 12 leads to quinone methide 15, a conversion which is facile in ether as well as in cyclohexane.

FIGURE 1 Vinyl Proton Region of the NMR Spectrum of the Product Mixture from a Two Hour Irradiation of the cis-Spirodienone, 9

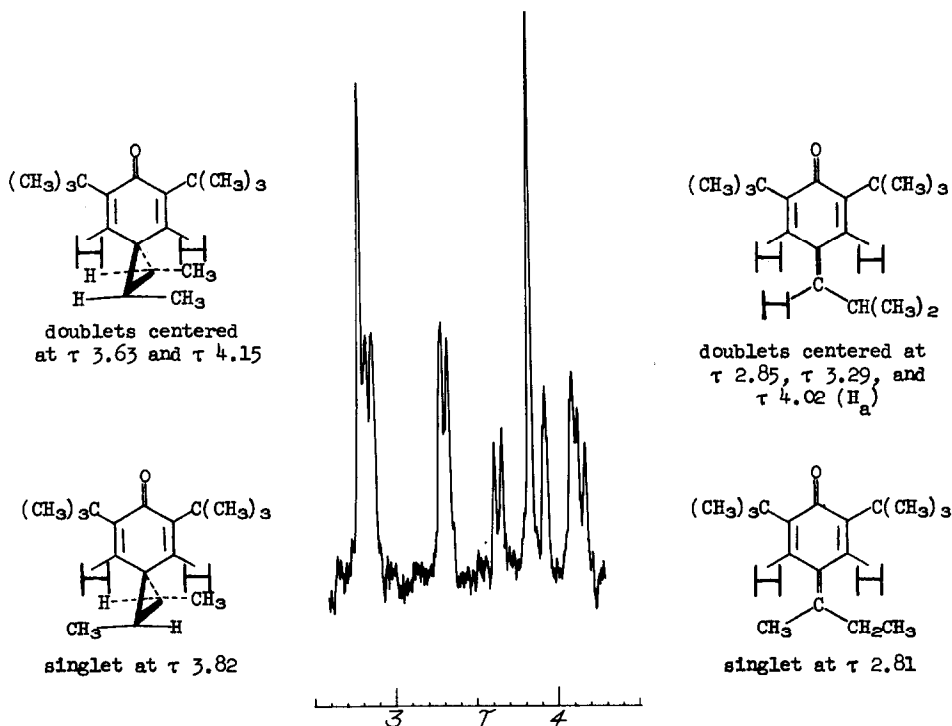


TABLE I^a Time Dependence of the Products of Irradiation of cis-1,2-Dimethyl-5,7-di-*t*-butylspiro[2.5]octa-4,7-dien-6-one

Time (hrs.)	9:10 2.00	13:14 2.00
0.00	all 9	[13 and 14]
0.25	9.0	not clearly
0.50	4.5	[detectable]
1.00	1.6	2.3 ^b
2.00	0.9	2.6
3.00	[only 10]	2.0
4.00	[detectable]	1.7

- (a) The ratio determinations were sometimes complicated by overlapping resonances and should be considered to have only qualitative significance. Additionally, incident light intensity may not have been identical for all samples. Thermal reaction was excluded by the appropriate control.
- (b) This ratio may be inaccurate since the quinone methides are just beginning to be detectable by nmr.

The structural assignments of 13 and 14 rest on comparison of the infrared, ultraviolet, and nmr spectra of the product mixture with those of the authentic quinone methides prepared by the ferricyanide oxidation (4) of 2,6-di-t-butyl-4-isobutylphenol, 16, and 2,6-di-t-butyl-4-s-butylphenol, 17. Moreover, lithium aluminum hydride reduction of the product mixture yields a mixture of phenols 16 and 17 easily separable by glpc (ca. 150°C, 5' x 1/4" column of 15% carbowax 20M on chromosorb W treated with HMDS).

The demonstration that spiro[2.5]octadien-6-ones may be photolytically converted to quinone methides supports Schuster's invocation of 7 as an intermediate in the photochemistry of 1. Since both the cis-trans photoisomerization and the photorearrangement of the hindered spirodienones to quinone methides may be rationalized by either diradical or dipolar excited states, we prefer to postpone judgment on this issue. Indeed, it has not been established that these reactions involve common excited states or intermediates.

Continued irradiation of the mixture of quinone methides 13 and 14 causes their slow disappearance and leads to manifold products, the structures of which are yet unknown. Irradiation (16 2537A lamps, nitrogen swept quartz vessel, <20°C) of a thermally stable (at 23°) $4.5 \times 10^{-3}M$, cyclohexane solution of authentic 13 causes no detectable photoisomerization to 14 but does lead to slow disappearance of the quinone methide absorption at 302 mμ with concomitant appearance of a low intensity 280 mμ absorption band. Thin layer chromatography (silica gel, cyclohexane) of the crude photoproduct indicates the presence of at least ten components. The infrared spectrum of this mixture reveals carbonyl bands near 1640 and 1700 cm^{-1} but no hydroxyl absorption. That cyclohexane has been incorporated into some of the products is suggested by the appearance of an intense, broad multiplet between ca. τ 7.5-9.5 in the nmr spectrum of the mixture and is further supported by preliminary mass spectral data obtained from the total mixture. The observation of ions at m/e 452, 426, and 288 in the 11 ev mass spectrum seemingly indicates that loss of t-butyl groups as well as incorporation of cyclohexane has occurred on irradiation of 13. The observed average molecular weight (vapor pressure osmometer, cyclohexane solution) of the crude product is 457 which may indicate some polymer formation as well. Phenol 16, expected to arise via hydrogen atom abstraction from cyclohexane, could not be detected in the product mixture by glpc analysis. Evidence that quinone methides can undergo photoreduction in hydrogen donating solvents has recently been provided by Becker (5) who observed the photosensitized reduction of 3,5-di-t-butylfuchsons to the corresponding phenol upon irradiation in

isopropanol containing benzophenone or acetophenone, and by Schuster and Krull (6) who find that irradiation of ethereal solutions of quinone methide 18 leads to minor amounts of the corresponding phenol and to extensive solvent incorporation. Failure of quinone methide 13 to undergo photoreduction in cyclohexane may stem from the fact that this solvent is a less efficacious hydrogen donor than isopropanol or ether.

Work on the photochemistry of quinone methides is still in progress and will be reported in more detail at a later date.

Acknowledgement. This work was partially supported by an unrestricted research grant from the Rohm and Haas Company. We are grateful to Dr. D. I. Schuster for informing us of his work prior to its publication.

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