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THE PHOTOISOMERIZATION OF SPIRO[2.4]HEPTA-4,6-DIENE [1]

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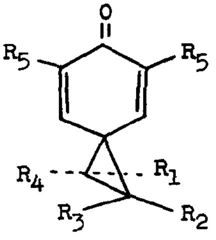
Although 1,2 hydrogen migration in ground state radicals are infrequent, there are several photochemical examples[2,3] in which the excited states are presumed to have "diradical" character. One of the first examples, reported by Schuster and Polowczyk,[3] was the photoisomerization of spirodienone 1a to 3a and is of particular interest since Pirkle and Koser[4] have shown that the reaction is quite general for substituted spirodienones 1b-e. Somewhat surprisingly 1d also affords a quinone methide 3d, a reaction which must take place with methyl migration.



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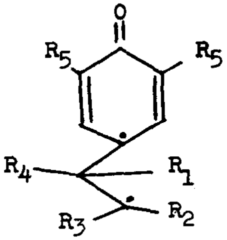

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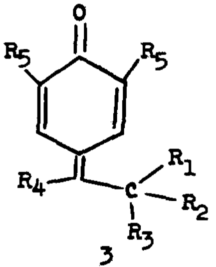
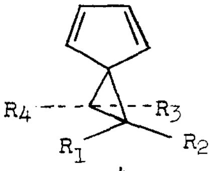


3

a, $R_1=R_2=R_3=R_4=R_5=H$.
b, $R_1=R_2=H$, $R_3=R_4=CH_3$, $R_5=C(CH_3)_3$.
c, $R_1=R_3=H$, $R_2=R_4=CH_3$, $R_5=C(CH_3)_3$.
d, $R_1=R_2=R_3=R_4=CH_3$, $R_5=C(CH_3)_3$.

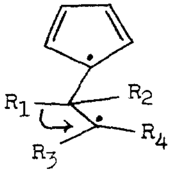
It was of interest to investigate the spiro[2.4]heptadiene system to see if the pattern of photochemical reactivity found in 1 was also exhibited by a hydrocarbon system.

Irradiation of a 1% pentane solution of 4a[5] proceeded with the appearance of a single new glpc peak. Product formation, which was initially rapid, continued until a 34% yield (75% based on unchanged starting material) resulted. After this point the reaction became inordinately slow presumably because the product was absorbing a significant portion of the incident radiation. Distillation of the bright yellow photolysate, followed by preparative glpc, afforded a product which was identified as 6-methylfulvene (6a) by comparison of its infrared and nmr spectra with those of an authentic sample.[6] Attempts to sensitize the reaction (benzophenone) were unsuccessful but triplet energy transfer was taking place as evidenced by the fact that 4a efficiently quenches the benzophenone-benzhydrol photoreduction.[7,8]



4

a, $R_1=R_2=R_3=R_4=H$.
b, $R_1=R_2=R_3=H$, $R_4=CH_3$.
c, $R_1=R_2=H$, $R_3=R_4=CH_3$.
d, $R_1=R_2=R_3=R_4=CH_3$.
e, $R_1=R_2=R_3=H$, $R_4=C_6H_5$.



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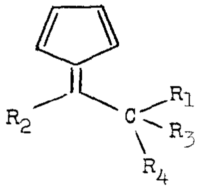

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Further investigation indicated that the reaction is quite specific and surprisingly sensitive to substitution on the cyclopropane ring in contrast to the results in the spirodienone series. Irradiation of 4b[9] afforded 6-ethylfulvene (6b)[10] whereas prolonged irradiation of 4c-e[9] proceeded with the slow disappearance (polymerization) of starting material and the appearance of no new components as evidenced by additional glpc peaks. A comparison of reactivity indicated that photoisomerization of 4a is much more efficient than that of 4b; in fact the ratio of yields in a parallel experiment was *ca* 0.3.[11]

An attractive mechanism for the isomerization to fulvenes, analogous to that suggested by Schuster, involves formation of excited state 5[12] followed by hydrogen migration to afford product. The photochemical *cis*⇋*trans* isomerization of 1-methyl-2-isopropylspiro[2.4]hepta-4,6-diene reported by Moss and Przybyla[14] provides evidence that the reversion of 5 to starting material is an efficient process.

Although comparisons of ground state and excited state chemistry are tenuous at best, a comparison of the thermal reactivity of the 4,5,6,7-tetrachlorospiro[2.4]hepta-4,6-dienes[15] with the photochemical reactivity of 4 might be fruitful. It has been demonstrated in a limited number of cases for the chlorinated spirodienes and quite conclusively for substituted cyclopropanes[16] that the rates of thermal isomerization to fulvenes and olefins, respectively, increase with substitution, i.e. as the stability of the incipient diradical increases, E_{act} decreases. Conversely, in the limited number of cases observed in the photochemical reaction, the least substituted compound appears to react most efficiently.

A rationale that explains the preceding is based on the assumption that the ground state energies of **4a**-d do not vary significantly. The apparent anomolous reactivity of **4** can then be explained by assuming that methyl substitution stabilizes the excited state of **4**(**5**) more than it stabilizes the transition state for hydrogen migration. The result is that with increasing substitution the energy gap between the excited state and transition state increases and, since product formation is only one of a number of non-radiative decay processes (including internal conversion to **4**), as the ease of hydrogen migration decreases other non-radiative processes dominate product formation.

The preceding arguments are clearly speculative, but experiments now in progress should further delineate the factors affecting product formation.

REFERENCES

1. The partial support of this work by the General Research Board of the University of Maryland is gratefully acknowledged.
2. H. Kristinsson and G.W. Griffin, *Tetrahedron Letters*, 3259 (1966).
3. D.I. Schuster and C.J. Polowczyk, *J. Am. Chem. Soc.*, **88**, 1722 (1966); **86**, 4502 (1964).
4. W.H. Pirkle and G.F. Koser, *Tetrahedron Letters*, 129 (1968).
5. C.F. Wilcox,Jr. and R.R. Craig, *J. Am. Chem. Soc.*, **83**, 4258 (1961).
6. J. Thiec and J. Wieman, *Bull. Soc. Chem. France*, 366 (1957).
7. W.M. Moore, G.S. Hammond and R.P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).
8. H.E. Zimmerman and G.E. Samuelson, *ibid.*, **89**, 5971 (1967).
9. Detailed procedures for the preparation of 4b and 4c were kindly supplied by Dr. S.W. Staley and Mr. J.J. Rocchio. Compounds 4d and 4c were prepared as previously described, R.A. Moss, *J. Org. Chem.*, **31**, 3296 (1966).

10. G. Albers-Schonberg, W. von Philipsborn, L.M. Jackman and H. Schmid, *Helv. Chim. Acta*, **45**, 1406 (1962).

11. Irradiations were carried out in vycor tubes on 1% solutions (100 mg/10ml) of diene in *n*-pentane with methylcyclohexane as an internal standard. Comparative yield studies were done using low pressure mercury lamps and a merry-go-round apparatus.

12. It has been predicted[13] that the excited states of vinylcyclopropanes should have a significant degree of charge transfer character; thus dipolar contributions to diradical **5** could be important.

13. R. Hoffmann, *Tetrahedron Letters*, 3819 (1965).

14. R.A. Moss and J.R. Przybyla, *J. Org. Chem.*, **33**, 3816 (1968).

15. E.T. McBee, J.A. Bosoms and C.J. Morton, *J. Org. Chem.*, **31**, 768 (1966).

16. H.M. Frey in "Advances in Physical Organic Chemistry, Vol. 4," V. Gold, Ed. Academic Press, New York, N.Y., 1966.