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THE PHOTOISOMERIZATION OF HOMOFULVENES

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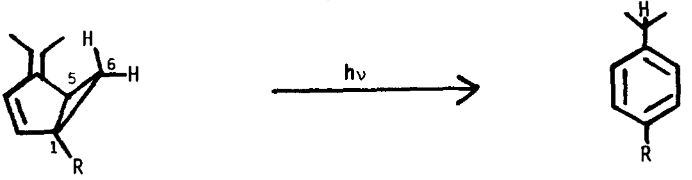
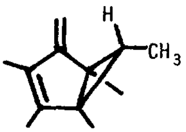
Although only two preliminary accounts [1,2] of the photochemistry of homofulvenes[3] have appeared, each reported novel and interesting chemistry. Irradiation of 1 (R=H, CH_3) in pentane at 2537 Å gave[1] the aromatic hydrocarbon 2 (R=H, CH_3), presumably by suprafacial transfer

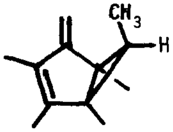


1 2

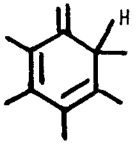
of the endo - C6 hydrogen.[4] In a parallel study,[2] it was found that 3a[5] photoisomerized (2537 Å, hexane) in high yield to hexamethylbenzene, whereas 3b, under similar conditions,



3a



3b

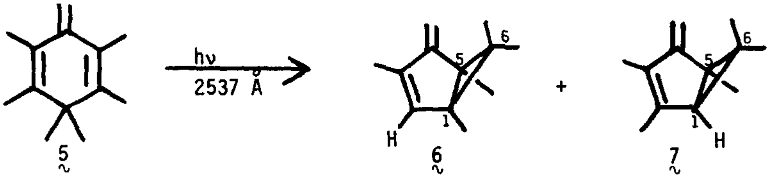


4

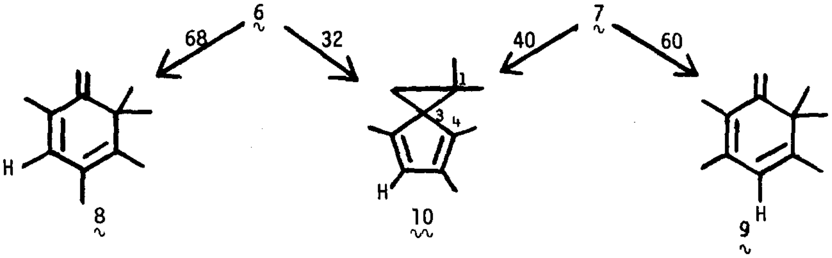
did so only to a trivial extent. Interestingly, an intermediate (4) was detected when the rearrangement of 3a was followed by uv. On separate irradiation, 4 gave not only hexamethylbenzene, but 3a and 3b.

We have studied the photoisomerization of two homofulvenes which have no hydrogen at C-6, and obtained not only conjugated trienes analogous to 4, but in addition a type of photoproduct not previously observed.

Irradiation of 5[6] ($\lambda_{max}^{Isooctane}$ 254 nm, ε 19,700) in ether at 2537 Å gave a mixture of homofulvenes 6 and 7[7], initially in the ratio 62:38.[8,9] After a short interval, three additional



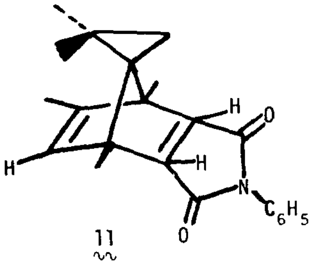
products began to form; the concentrations of **6** and **7** in the mixture reached maxima, then diminished. Separate irradiation at 2537 Å established that **6** (λ_{max}^{MeOH} 246 nm, ε 8140) was converted to **8** and **10**, whereas **7** (λ_{max}^{MeOH} 259 nm, ε 10,200) gave **9** and **10**.



The structures [7] of **8** and **9** were clear from their uv, ir, nmr and mass spectra. Also, **8** was synthesized by an unambiguous independent route.[10]

The nmr spectrum (CCl_4) of compound **10**[7] (1,1,4,5,7-pentamethylspiro[2.5]hepta-4,6-diene) had a poorly resolved quartet, J 1.4 Hz, at τ 4.14 (1H, vinyl) and multiplets at τ 8.20 (6H) and 8.30 (3H) for the three allylic methyls. Also present were singlets at τ 8.62 (6H, gem-dimethyl) and τ 8.65 (2H, methylene). Although the latter might appear low for cyclopropyl protons, it is well documented[11] that in spiro compounds of this type the cyclopropyl protons are deshielded by the π system.

The structural assignment for **10** is supported by its rapid reaction (CH_2Cl_2 solution, 0°, 4 hours) with N-phenylmaleimide to form adduct **11**, mp 125.5-126°.[7] The cyclopropyl methylene



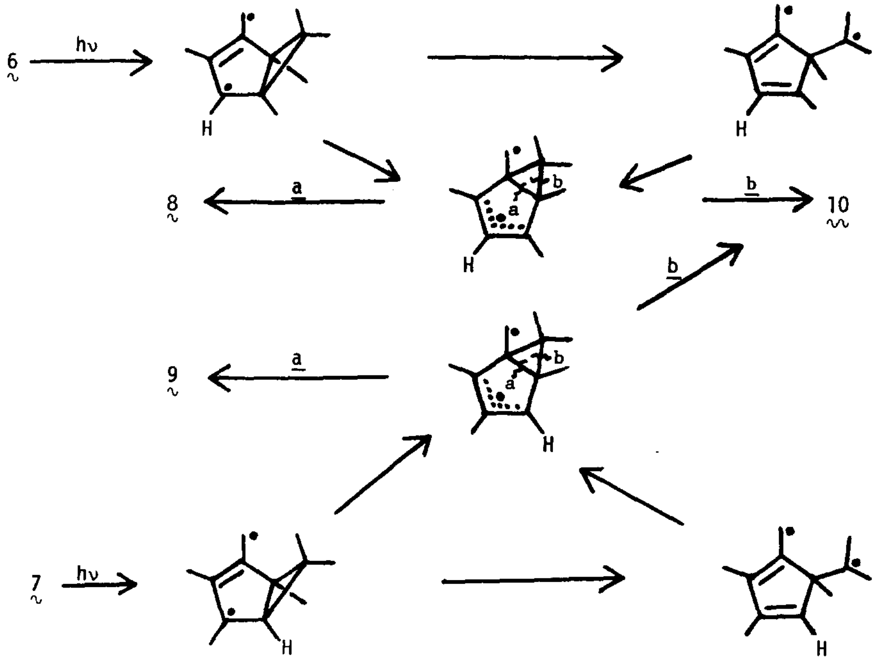
11

NMR τ	Assignment
9.65	CH_2
8.87, 8.85	gem-$(CH_3)_2$
8.60, 8.57	bridgehead CH_3's
8.25(d,J 1.8 Hz)	allylic CH_3
7.18	exo-H's
4.27(q,J, 1.8 Hz)	vinyl H
2.45-3.19	arom.

protons now appear at τ 9.65, as expected.[12]

The formation of a spiro[2.4]hepta-4,6-diene (**10**) by irradiation of a homofulvene is novel. Indeed two such spiro compounds have been shown to photoisomerize to fulvenes.[13] The reaction was sensitive to substituents, however, and with a gem-dimethyl at C-1 only slow photopolymerization was observed.

The products can be rationalized by a scheme in which excitation is followed by cleavage of the C1 - C6 bond in **6** or **7**. Some of these steps may be reversible, and the final concentrations of products should depend on the wavelength of light used.[14]



The photochemical behavior which we have observed for **6** and **7** may be quite general for homofulvenes with radical-stabilizing groups at C-6. Finally, attention is called to the difference between the photochemical and thermal reactions of these compounds.[1,4,15]

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2. H. Hüther and H. A. Brune, Z. Naturforsch., B, 23, 1612 (1968).
3. This trivial name has been used[1] to describe fulvenes in which one double bond in the 5-membered ring has been replaced by a cyclopropane ring.
4. Thermally, 1 and homofulvene itself gave[1] no alkylbenzenes, only polymer.
5. R. Criegee and H. Grüner, Angew. Chem., 80, 447 (1968); W. Schäfer and H. Hellmann, ibid., 79, 566 (1967).
6. H. Hart, P. M. Collins and A. J. Waring, J. Am. Chem. Soc., 88, 1005 (1966).
7. All new compounds gave satisfactory elemental analyses.
8. For an analogous reaction, see H. Hart, J. D. deVrieze, R. M. Lange and A. Sheller, Chem. Commun., 1650 (1968).
9. Compounds 6 and 7 can be separated by vpc under carefully controlled conditions, or by tlc on plates coated with silica gel impregnated with 20% $AgNO_3$. Caution must be exercised with vpc separation, because thermal rearrangement and decomposition occurs easily. Identification is based on elemental analysis, spectra, method of formation and the results of further irradiation. Details will be presented in a full paper, but the nmr spectra are as follows: 6 - τ 9.26 (3H, s, endo-C6 methyl), 8.95 (3H, s, exo-C6 methyl), 8.87 (6H, C1 and C5 methyls), 8.33 (3H, d, J 1.4 Hz, allylic methyl), 4.46 (1H, br m, C2 proton), 5.14 (1H, s) and 5.31 (1H, d, J 1.7 Hz), methylene protons. 7 - τ 9.35 (3H, s, endo-C6 methyl), 8.88 (3H, s, exo-C6 methyl), 8.73 (3H, s, C5 methyl), 8.63 (1H, br s, C1 proton), 8.43 and 8.28 (3H each, s, allylic methyls), 5.43 and 5.30 (1H each, s, methylene protons).
10. Hexamethyl-2,5-cyclohexadienone was reduced with $LiAlH_4$ and the resulting alcohol dehydrated to give 8. The initial experiments were done by Dr. A. Sheller. Experimental details and spectral data will be given in a full paper, but the uv spectrum of 8 in methanol had maxima at 314 nm (ε 5970) and 209 nm (ε 10,300). Compound 9 was similar, with maxima at 309 and 211 nm.
11. K. Bangert and V. Boekelheide, Tetrahedron Lett., 1119 (1963); R. A. Moss, Chem. Commun., 622 (1965); R. A. Moss, J. Org. Chem., 31, 3296 (1966); R. A. Moss and J. R. Przybyla, ibid., 33, 3816 (1968).
12. S. McLean and P. Haynes, Tetrahedron, 21, 2313 (1965).
13. P. H. Mazzocchi, Tetrahedron Lett., 989 (1969).
14. The question of reversibility is under study. It is also possible that certain of the steps may be concerted.
15. H. Hart and J. D. deVrieze, Chem. Commun., 1651 (1968).