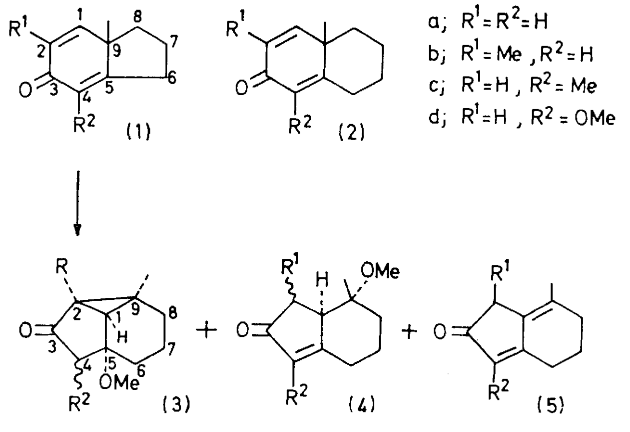
Photochemical Rearrangements of 6/5-Fused Cross-conjugated Cyclohexadienones in Protic Solvents

By Drury Caine,* John T. Gupton iii, Ko Ming, and William J. Powers iii
(*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia* 30332)

Summary Irradiation of the ring A unsubstituted 6/5-fused cross-conjugated cyclohexadienone (**1a**) and its 2-methyl derivative (**1b**) in methanolic acetic acid yields, in addition to other products, novel tricyclononane derivatives which have been assigned the structures (**3a**) and (**3b**).

The photochemical behaviour of the 6/5-fused dienones (**1a**—**c**) in dioxan[1] and of the 4-methyl (**1c**) and 4-methoxy (**1d**) compounds in protic solvents[1,2] has been shown to be similar to that of the related 6/6-fused compounds (**2**) which have been widely studied.[3] However, we have now found that the unsubstituted dienone (**1a**) and the 2-methyl derivative (**1b**) undergo novel photochemical rearrangements when irradiated in protic solvents.

Irradiation of (**1a**) for 1·5 h in 45% methanolic acetic acid or in methanol alone† yielded the tricyclic methoxy ketone (**3a**), the 5/6-fused methoxy ketone (**4a**), and the known 5/6-fused dienone (**5a**)[1] in a *ca.* 3:3:2 ratio.‡ Under similar conditions photolysis of (**1b**) gave (**3b**) and (**4b**) (as a *ca.* 9:1 mixture of C-2 epimers) in a 5:8 ratio. Evidence to support the α assignments of the methyl groups in (**3a**) and (**3b**) was obtained by converting these ketones into the 5/6-fused enones (**6a**) and (**6b**) by treatment with lithium in liquid ammonia followed by sodium hydride in dimethoxyethane. The predominance of inversion of configuration at C-9 in the reductive cyclopropane ring openings is consistent with the results of recent studies on the stereochemistry of this process.[4,5]



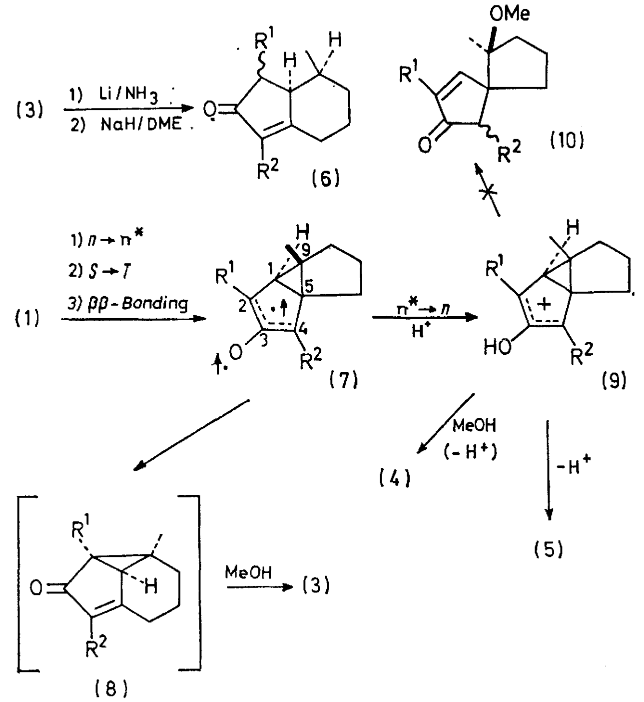
The photochemical results can best be explained by assuming that there is competition between rearrangement and electron demotion in diradical cyclopropyl intermediates

---

† Irradiations were carried out with a 450 W Hanovia lamp in a Pyrex probe.

‡ The photoproducts were isolated by column chromatography on silica gel followed in some cases by preparative gas chromatography. All new compounds exhibited the expected u.v., i.r., and n.m.r. spectral properties and gave correct combustion analysis or exact mass data.

such as (**7**) produced by excitation of the dienone systems. A symmetry allowed 1,4-sigmatropic rearrangement of (**7**) with retention of configuration at C-9[6,7] could lead to strained tricyclic enones such as (**8**) which could undergo thermal or photochemical 1,4-addition of methanol to yield tricyclic products (**3**). By electron demotion and protonation (**7**) could be converted into the mesoionic species (**9**).[3] Spiro[4,4]nonane derivatives, *e.g.* (**10**), were not formed in the above irradiations. Particularly, in the case (**9b**), derived from (**1b**), the electronic influence of the 2-methyl group would be expected to favour cleavage of the 1,9-bond.[3] However, the five-membered B ring apparently introduces sufficient strain to make the 5,9-bond more susceptible to cleavage.



Tricyclic products of the type (**3**), perhaps derived from rearrangement of excited state intermediates, have not been encountered in previous studies on methyl and unsubstituted 6/6-fused dienones (**2a**—**c**).[3] Thus it is possible that the strain in (**7**) resulting from the presence of the five-membered B ring allows a sigmatropic rearrangement to compete with the usually more efficient electron demotion step. However, products apparently derived from rearrangement of ground state dipolar intermediates were formed when (**1a**—**c**) were irradiated in dioxan[1] and 5/6-fused products of the type (**4**) were obtained exclusively on irradiation of (**1c**) and (**1d**) in protic solvents.[1,2] Thus it is clear that the solvent and the presence and location of substituents can have a profound effect on the photochemistry of 6/5-fused dienones.

Financial support from Public Health Service Research grants from the National Institute of General Medicine and from the National Cancer Institute is acknowledged.

(*Received* 3*rd April* 1973; *Com.* 471.)

---

[1] D. Caine, A. M. Alejandre, K. Ming, and W. J. Powers III, *J. Org. Chem.*, 1972, **37**, 706.

[2] D. Caine and F. N. Tuller, *J. Amer. Chem. Soc.*, 1971, **93**, 6311.

[3] For reviews see P. J. Kropp, *Org. Photochem.*, 1967, **1**, 1; K. Schaffner, *Adv. Photochem.*, 1966, **4**, 81.

[4] E. Piers and P. N. Worster, *J. Amer. Chem. Soc.*, 1972, **94**, 2895.

[5] Highly strained *trans*-bicyclo[4,1,0]heptanes would result if the configuration at C-9 were inverted in systems of the type (**3**). The preparation of *trans*-bicyclo[4,1,0]heptanes has been recently reported (see J. V. Paukstelis and J. Kas, *J. Amer. Chem. Soc.*, 1972, **94**, 4783). However, in the present case a *trans* fusion of the three- and six-membered rings would lead to a severe interaction between the C-9 methyl and C-4 methylene groups.

[6] R. B. Woodward and R. Hoffman, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781; H. E. Zimmerman, D. S. Crumine, D. Dopp, and Huyffer, *J. Amer. Chem. Soc.*, 1969, **91**, 434.

[7] K. Ogura and T. Matsuura, *Bull. Chem. Soc. Japan*, **43**, 2891; D. I. Schuster, K. V. Prabhu, S. Adcock, J. van der Veen, and H. Fujiwara, *J. Amer. Chem. Soc.*, 1971, **93**, 1557.