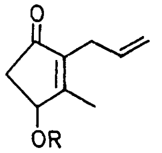
# Triplet Di-π-methane Rearrangement of a 'Free-rotor' 2-Prop-2-enylcyclopent-2-enone

By M. J. Bullivant and G. Pattenden*
(*Department of Chemistry, University College, Cathays Park, Cardiff* CF1 1XL)

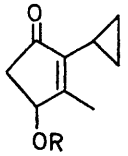
*Summary* The 2-prop-2-enylcyclopent-2-enone (**1**) undergoes an inefficient triplet di-π-methane rearrangement to give (**2**) whereas the side-chain substituted analogue (**4**), under similar conditions, undergoes only *Z–E*-isomerisation; the reactivity differences are rationalised on the basis of dissipation of triplet energy by 'free-rotor' effects.

There is considerable current interest in the relationship between molecular structure and the direction, multiplicity, and efficiency of the photochemical di-π-methane rearrangement.[1] Here we report some results on the photochemistry of substituted 2-prop-2-enylcyclopent-2-enones which have a significant bearing on this relationship.

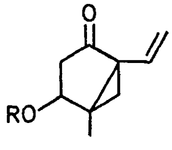
Direct photolysis of a 0·5% solution of cyclopentenone (**1a**)[2] in hexane, using a medium-pressure mercury arc and a Pyrex filter glass,† resulted in the slow formation (g.l.c. monitoring) of a photostationary equilibrium mixture of (**1a**) and a single monomeric photoproduct corresponding to *ca.* 83% conversion. Preparative g.l.c. purification gave a low melting (m.p. *ca.* 22°) compound‡ isomeric with (**1a**) whose spectroscopic properties showed that structural modifications had taken place in only the propenyl side-chain of (**1a**). In particular, the n.m.r. spectrum of the photoproduct showed total absence of absorption signals corresponding to olefinic and vinyl-methylene hydrogens, and instead displayed three groups of multiplets (ratio 1:2:2) centred at $\tau$ 8·57, 8·94, and 9·27, associated with cyclopropyl ring hydrogens; the i.r. spectrum of the photoproduct likewise revealed absence of olefinic C–H o.o.p. absorption bands, which corroborated the conclusions drawn from the n.m.r. spectrum. These, and other data were consistent with the cyclopropane formulation (**2a**) for the photoproduct. Similarly, direct irradiation of the corresponding acetate (**1b**) led to (**2b**), the structure of which was also apparent from its spectral properties. The rearrangement of (**1**) to (**2**) is a somewhat special example of the di-π-methane rearrangement.[3] The selective formation of only one of the two *a priori* possible di-π-methane rearrangement products [*i.e.* (**2**) and (**3**)] is interesting, and will be commented on further in the full report.



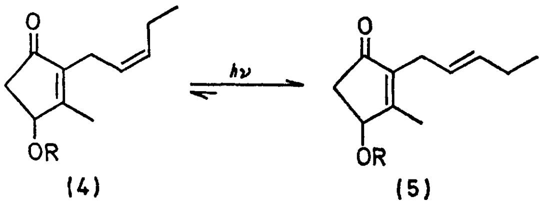
(1)



(2)



(3)



(4) (5)

a; R = Me b; R = Ac

In contrast, photolysis of the *Z*-isomers of the substituted 2-prop-2-enylcyclopent-2-enones (**4a**) and (**4b**) resulted solely in *Z–E*-isomerisation to produce (**5a**) and (**5b**), respectively. Both *Z–E*-isomerisations occurred with steady states of *ca.* 90% (**5**) and *ca.* 10% (**4**). Prolonged exposure

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† Similar results were obtained using quartz-filtered light. Precise quantum yields have not been determined but we estimate a figure < 0·01.

‡ Satisfactory analyses and spectral data were obtained for all new compounds described.

periods did not alter the $Z$–$E$- ratios or the amounts of (**4**) and (**5**) which could be recovered, and in neither case were we able to detect cyclopropane photoproducts analogous to (**2**) or (**3**). The configurations assigned to the $Z$–$E$-isomeric pairs (**4**) and (**5**) followed from their n.m.r. and i.r. spectral properties, and also from the method of synthesis.[4]

Recent studies on the relationship between structure and multiplicity in the di-$\pi$-methane rearrangement have led to the general conclusion that acyclic di-$\pi$-methane systems rearrange preferentially by way of their singlet excited states, whereas di-$\pi$-methane systems in a sterically constrained situation (*e.g.* in some bicyclic molecules) do so by way of their triplet states; for discussions on this difference see ref. 1 and *cf.* ref. 5. The di-$\pi$-methane system in (**1**) is a somewhat special type since it is neither acyclic nor is it particularly 'constrained'. The rearrangement to (**2**) was found to be completely quenched in the presence of 2,5-dimethylhexa-2,4-diene ($E_T$ *ca.* 58 kcal mol$^{-1}$) and could be sensitised by acetophenone ($E_T$ *ca.* 74 kcal mol$^{-1}$). These observations therefore suggested that the rearrangement occurs from a cyclopentenone triplet state.

The inefficiency† of the rearrangement (**1**) → (**2**), and the exclusive $Z$–$E$-isomerisation in the analogue (**4**) are consistent with the observed triplet path to (**2**), and the reactivity differences can be rationalised in terms of differential dissipation of triplet excitation energies in (**1**) and (**4**), by 'free-rotor' effects. In (**1**), the side-chain double-bond is able to dissipate triplet energy by free rotation (the 'free rotor' effect) and this process, as we observe, prevents an efficient triplet di-$\pi$-methane rearrangement taking place. In the analogue (**4**), where $Z$–$E$-isomerisation is possible, the di-$\pi$-methane rearrangement does not occur at all, and instead only $Z$–$E$-isomerisation is observed (this is true even after 3 weeks continuous irradiation!). It appears therefore that dissipation of triplet energy by the 'free-rotor' effect is very rapid and efficient in (**4**)—so much so that $Z$–$E$-isomerisation takes place to the complete exclusion of a triplet di-$\pi$-methane rearrangement.[6] Further studies to examine details of these 'free-rotor' effects in compounds related to (**1**) and (**4**) are in progress.

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[1] (a) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, 1970, **92**, 1411; (b) J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, p. 1406; (c) H. E. Zimmerman and A. C. Pratt, *ibid.*, p. 6259, 6267; (d) H. E. Zimmerman and A. A. Baum, *ibid.*, 1971, **93**, 3646.

[2] Y. Katsuda, T. Chikamoto, and Y. Inoue, *Bull. Agric. Chem. Soc., Japan*, 1959, **23**, 171.

[3] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, 1969, **91**, 1718.

[4] G. Pattenden and R. Storer, unpublished results; L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc.* (*C*), 1969, 1016.

[5] Z. Goldschmidt and A. S. Kende, *Tetrahedron Letters*, 1971, 4625.

[6] For contrastingly different results see refs 1(c), 6, T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Letters*, 1970, 3895; and P. S. Mariano and J. Ko, *J. Amer. Chem. Soc.*, 1972, **94**, 1766.