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DIVERGENT PHOTOREACTIVITY IN INTRAMOLECULAR CYCLOADDITIONS AMONGST PROP-2-ENYLCYCLOPENTENONES

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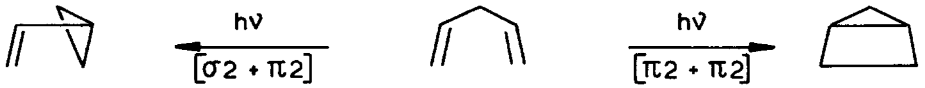
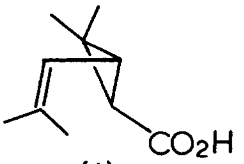
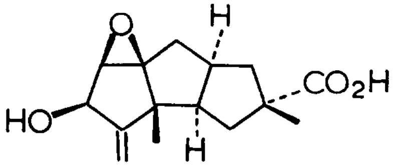
Summary Irradiation of the 1,4-diene(8) gave the corresponding geometrical isomer(10) whereas (5) produced the vinylcyclopropane(6), and (11a) and (11b) (in MeOH) led to the tricyclic adduct(14) and the isomeric cyclopentenone (15) respectively.

1,4-Dienes commonly undergo two types of competing intramolecular photocycloaddition reactions leading to either vinylcyclopropanes (the so-called 'di-π-methane' rearrangement)[1] or to bicyclo [2.1.0] pentanes (Scheme 1)[2]. In previous studies we have demonstrated the potential for both cycloadditions in syntheses of the vinylcyclopropane and the tricyclo $[6.3.0.0^{2,6}]$ undecane ring systems found in the natural terpenes chrysanthemic acid (1)[3] and hirsutic acid (2)[4] respectively. In continuation of our research on the scope of these intramolecular processes for the elaboration of natural carbocycles we have now examined the photochemistry of a number of related 2-prop-2-enylcycloalk-2-enone chromophores. In the accompanying Letter we report the development of the studies in a synthesis of the vinylcyclopropane ring system found in the natural sesquiterpene 'taylorione.'



Scheme 1


(1)


(2)

Irradiation of the prop-2-enyl substituted cyclopent-2-enones (3a,b,c) has been shown to lead to the vinylcyclopropanes (4a,b,c) respectively (50-80%) resulting from regiospecific di-π-methane rearrangement *via* the triplet manifold.[5] In a similar manner, irradiation of the gem-dimethyl substituted compound (5) in hexane or methanol through pyrex gave rise to the vinylcyclopropane (6)(66)%, ν_{max} 1690, 1640 cm^{-1}, τ7.96 (:CMe), 8.25 - 9.4 m (3H), 8.82 (Me), 9.16 (Me). By contrast, irradiation of the cyclopentenones (7) and (8) containing double bonds capable of undergoing Z - E isomerisation, instead led to only the corresponding geometrical isomers (9) and (10) respectively.[6] These latter observations are similar to those obtained earlier with related molecules,[5] and are rationalised in terms of preferential dissipation of the triplet excitation energy by 'free-rotor' effects about the double bonds; where this alternative is not possible, as in (3) and (5) the products of di-π-methane rearrangement are observed instead. Attempts to effect di-π-methane rearrangements in (7/9) and (8/10) by conducting the irradiations in the presence of triplet quenching reagents were not successful.

The cyclopentenones (11) containing cycloalk-1-enylmethyl substitution at C-2, are unable to dissipate excitation energy by 'free rotor' effects. Surprisingly, they neither undergo photochemical rearrangement to the corresponding vinycyclopropanes (12). Instead irradiation of (11*a*) in methanol, leads to intramolecular [π2 + π2] cycloaddition, followed by *in situ* addition of methanol to the presumed intermediate (13) producing the tricyclo [6.3.0.0.^{2,6}] undecane (14) in > 90% yield.[4] By contrast, the corresponding cyclohexene (11*b*) gives the isomeric cyclopentenone (15)(75%), ν_{max} 1690 cm^{-1} τ4.8 m (:CH), 7.2 - 7.9 m (8H), 8.0 (:CMe), 8.2 - 8.7 m (6H), resulting from 1,3-H migration, and the cyclohexenone (16) fails to produce any recognisable monomeric photoproducts.

Although the preparative value of the aforementioned photocycloadditions is unquestionable, like so many photo-processes they also demonstrate the remarkable effect of substitution on photo-reactivity amongst closely related molecules. A rational explanation as to the origin of the divergent photoreactivity in these chromophores is not immediately obvious. It does appear however, that when an opportunity presents itself the prop-2-enylcyclopentenones will undergo an alternative process to di-π-methane rearrangement (*cf* 8 → 10, 11*a* → 14, 11*b* → 15); in the cases of (11*a*) and (11*b*) it is probable that the differing rigidity and flexibility of the cyclopentene and cyclohexene rings contribute significantly to their divergent photoreactivity.

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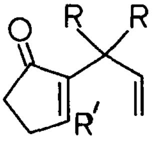
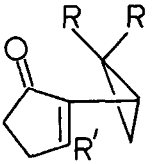


(3)

<u>a</u> $R = R' = H$

<u>b</u> $R = Me$, $R' = H$

<u>c</u> $R = H$, $R' = Me$



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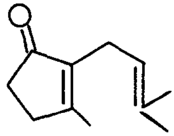
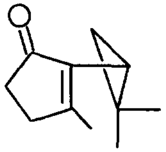
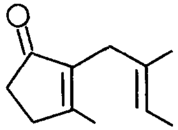


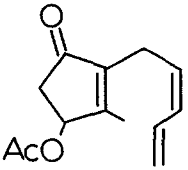
(5)



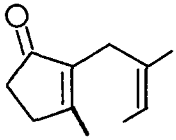
(6)



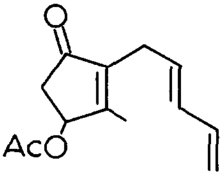
(7)



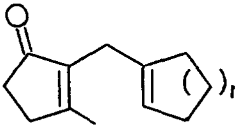
(8)



(9)



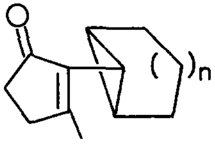
(10)



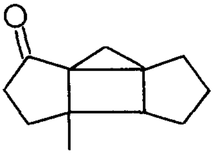
<u>a</u> $n = 1$

<u>b</u> $n = 2$

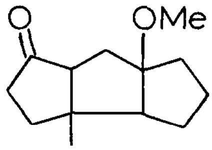
(11)



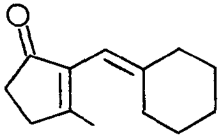
(12)



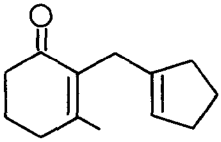
(13)



(14)



(15)



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1. S.S. Hixson, P.S. Mariano and H.E. Zimmerman, Chem.Rev. 73, 531 (1973); although the di-π-methane rearrangement is drawn here on paper as a $[\sigma 2 + \pi 2]$ mechanism, it is actually a $[\sigma 2 + \pi 2 + \pi 2]$ process.
2. M.J. Jorgenson, J.Amer.Chem.Soc., 88, 3463 (1966); H. Kristinsson and G.S. Hammond, ibid., 89, 5970 (1967).
3. M.J. Bullivant and G. Pattenden, J.C.S. Perkin I., 257 (1976).
4. J.S.H. Kueh, M. Mellor and G. Pattenden, J.C.S. Chem. Comm., 5 (1978).
5. M.J. Bullivant and G. Pattenden, J.C.S. Perkin I., 249 (1976).
6. A photostationary equilibrium mixture of Z- and E-isomers was obtained in each case.

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