Photoisomerisation Reactions of Cyclohepta-2,4-dienone and 2-Methylcyclohepta-2,4-dienone

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Summary In non-polar solvents cyclohepta-2,4-dienone and 2-methylcyclohepta-2,4-dienone give upon irradiation the corresponding bicyclo[3,2,0]hepta-6-en-2-ones, where as in polar acidic solvents, including FSO_3H, norbornen-7-ones are formed.

DESPITE several publications describing the photochemistry of eucarvone (**1**) there has been no report on the photochemical behaviour of the parent dienone (**2**).[1] In order to understand better the role the methyl substituents play in the complex series of isomerisations of (**1**) we have investigated the photochemistry of (**2**) and its 2-methyl derivative (**3**).[2]

Irradiation (3500 Å) of a CH_2Cl_2 solution of (**2**) gave the bicyclo[3,2,0]heptenone (**4**), the only product detectable by g.l.c., which was identified by comparison of its properties with those published for authentic (**4**).[3] Similarly irradiation of (**3**) in CH_2Cl_2 under the same conditions gave (**5**) and (**6**). The photoproduct (**6**) was shown to arise from subsequent photoisomerisation of the primary product (**5**), as has been shown for the production of (**8**) from (**7**).[1a] These new ketones, (**5**) and (**6**), were fully characterised with satisfactory elemental analyses and by comparison of their spectral properties with those of (**4**)[3], (**7**), and (**8**).[1a]

When the irradiations were carried out in more polar solvents, additional products were detected. Thus (**2**), irradiated in 50% aqueous acetic acid gave (**4**) (99·5%) together with an additional product (0·5%), which was identified as norbornen-7-one (**9**).[4] The change in product distribution was much more marked with (**3**), 14% of the corresponding norbornenone (**10**) being formed in 50% aqueous acetic acid. (**10**) had satisfactory elemental analyses and spectroscopic properties. Decoupling of its n.m.r. spectrum (100 MHz) clearly indicated that the methyl group was in the 1 position. The results of competitive irradiations (3500 Å) of (**3**) in a variety of solvents are given in the Table. As has been demonstrated for eucarvone, there is a marked increase in the relative quantum efficiency with increase in solvent polarity and acidity.[1c] This enhanced efficiency is accompanied by a corresponding increase in the relative amount of (**10**) produced.

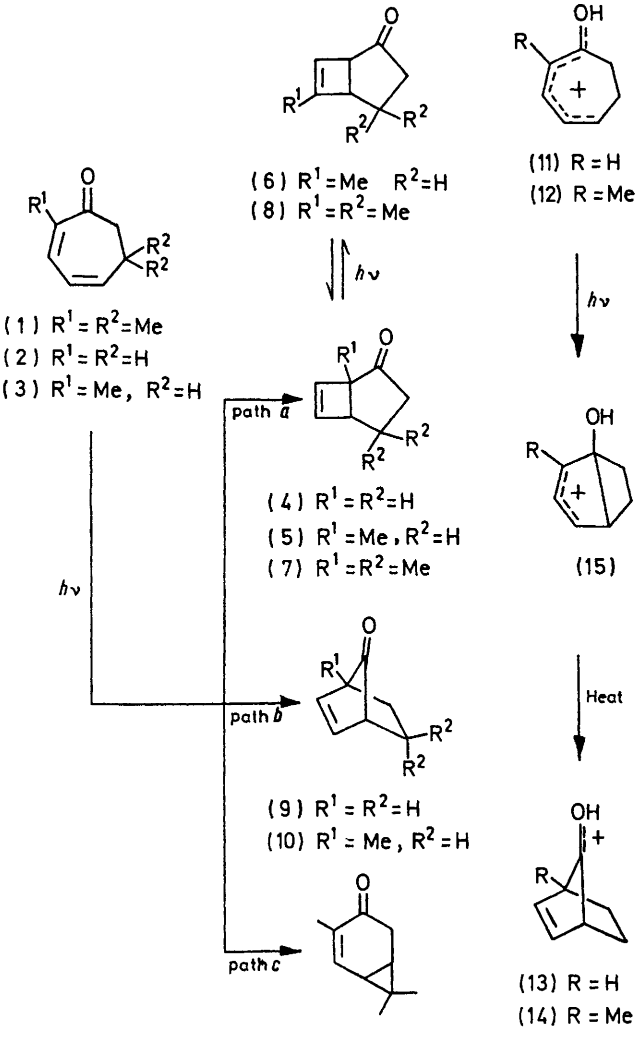
Protonation of (**2**) and (**3**) with FSO_3H gave stable solutions of the hydroxy cations (**11**) and (**12**) respectively.[2] Irradiation of (**11**) and (**12**) at −60° in FSO_3H (500 Watt lamp) resulted in isomerisation of these protonated ketones to (**13**) and (**14**) respectively.[5] No other products could be detected in the n.m.r. spectra of the acid solutions, nor products other than (**9**) and (**10**) when the FSO_3H solutions were quenched at −45° in a suspension of excess of $NaHCO_3$ in Et_2O. The formation of these protonated norbornen-7-ones can be thought of in terms of a photochemically allowed closure between C(1) and C(5) to give the bicyclic cation (**15**), followed by a thermal 1,2 alkyl shift.

TABLE

Product composition obtained upon irradiation of (**3**)

Solvent	Conversion (%)	Product composition (5) + (6) (%)	(10) (%)
Ether	1	100	—
Methanol	20	100	—
Acetic acid	47	99·8	0·2
50% Aqueous acetic acid	80	86	14

It has been shown that there are three primary products obtained upon irradiation of eucarvone, (**1**), which can arise by the three paths *a*, *b*, and *c*.[1e] The observed solvent dependence of the photoisomerization of (**2**) and (**3**) is similar in many respects to that observed for (**1**) except that there is no evidence for the formation of products by path *c*. For (**1**), path *c* becomes increasingly important with increasing solvent polarity and is dominant in FSO_3H where 95% of the reaction products arise by this route. Clearly the 6,6-dimethyl grouping is necessary for the effective operation of path *c* in these systems and this strongly supports the suggestion that considerable positive charge is developed at C(6) during one of the steps involved in this pathway.[1e,f]



The formation of (**13**) and (**14**) must involve π–π* state or states of the protonated ketones (**11**) and (**12**). As (**9**) and (**10**) are formed in significant quantities from (**2**) and (**3**) only when polar acidic solvents are employed, it is conceivable that the same type of intermediates are involved in these reactions.[1e,f,6]

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