Photochemical Intramolecular [2 + 2] Cycloaddition of 5-(1- and 2-Naphthylmethyl)-3-phenylcyclopent-2-enones

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Photolysis of 5-(1- and 2-naphthylmethyl)-3-phenylcyclopent-2-enones affords [2 + 2] cycloaddition products, the 7,8- and 5,6-benzo-fused 10-phenyltetracyclo[7.2.1.0^{3,10}.0^{4,9}]dodec-5- and -7-en-2-ones respectively, in a mixture with the starting enones; the photoproducts revert to the respective enones on acid treatment, or pyrolysis, and to the photostationary-state mixture on photolysis.

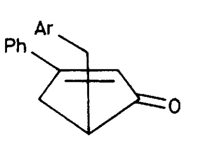
While there are many examples of the photoaddition of electron-deficient alkenes to substituted naphthalenes,[1] there are no examples reported of the addition of enones to naphthalene, or substituted naphthalenes. We report here examples of the photochemical intramolecular [2 + 2] cycloaddition of enone and naphthalene ring systems.

We have shown that when 5-(1-naphthylmethyl)-3-phenylcyclopentenone (**1a**)† was irradiated in benzene (Pyrex filter, 460 W medium-pressure Hg lamp), a photostationary state was set up between (**1a**) and the cycloaddition product (**2a**). Isolation of (**2a**) (22% yield) was achieved by chromatography over basic alumina, as it is labile to acid, even silica, reverting to the starting enone (**1a**). Pyrolysis of (**2a**) also leads to (**1a**), and photolysis of (**2a**) in benzene gives a mixture of (**1a**) and (**2a**).

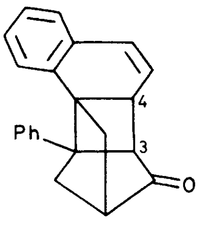
Similar behaviour is found with the 2-naphthyl analogue (**1b**),† the photoproduct (**2b**) being isolated in 15% yield from the photostationary state.

Both forward photoreactions are regiospecific, and proceed in the same manner. This follows from the i.r. spectra.† The latter showed a carbonyl peak at 1740 cm^{-1} characteristic of a carbonyl located at a position common to a 5- and a 6-membered ring, rather than at a position common to two 5-membered rings ($\nu_{max.}$ 1750 cm^{-1}), as would be expected from a product with the opposite regiospecificity. The n.m.r. spectra also support this assignment. It is expected that the electron density at the 1- and 2- positions would not be greatly affected by alkyl substituents at these positions. If this is true, the regioselectivity is not controlled by electron density considerations at the 1- and 2- positions of the aromatic nucleus.

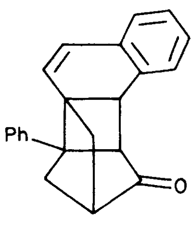
The mode of ring closure can be accounted for by the 'rule of five,[2] and the M.O. treatment to explain this rule.[3] We can treat the molecule as a 1,6-diene, using either two naphthalene carbons, the naphthylmethyl carbon, and the 5-, 4-, 3-, and 2-carbons of the cyclopentenone ring, or the two naphthalene,



(**1**)



(**2a**)



(**2b**)

a; Ar = 1-naphthyl
b; Ar = 2-naphthyl
c; Ar = Ph

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† All the starting materials were synthesised by routine methods to be described in the full paper, as will the spectroscopic properties of the enones and photoproducts.

the naphthylmethyl, and the 5-, 1-, 2-, and 3-carbons. In the former, the terminals of the system lie on the naphthalene ring and the 2-carbon; in the latter, on the naphthalene ring and the 3-carbon atom. In the cases presently studied, the former pathway is followed. The same regioselectivity was shown in the 5-allylcyclopentenones studied by us before,[4] and by others.[5] The only exceptions to this mode in 5-allylcyclopentenones appear in some, but not all, cases where there is an electron-donating group in the 3-position.[5,6]

The reverse reaction formally involves β-cleavage involving the 3,4-bond. We believe that this does not happen directly, but that there is energy transfer from the triplet excited state of the carbonyl group to the styryl chromophore, which promotes the 3,4-bond cleavage.

Not surprisingly, we were unable to isolate or detect any monomeric photoproduct from the photolysis of the 5-benzyl analogue† (**1c**), but rather we obtained a mixture of photodimers, which we have not examined further.

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