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Photochemistry of cyclic enones. Part 13[1]. Intermolecular addition of styrene and 1-phenylprop-1-enes with 3-phenylcyclopentenone and 3-phenylcyclohexenone

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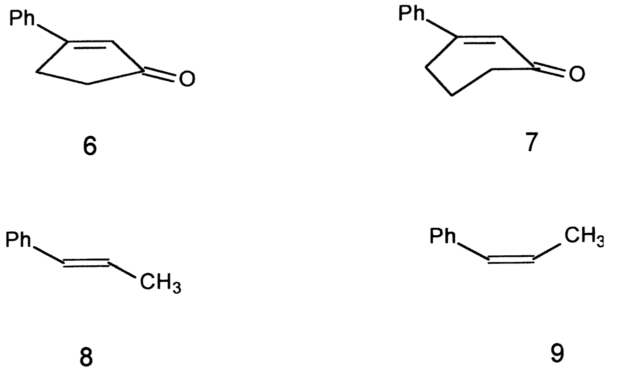
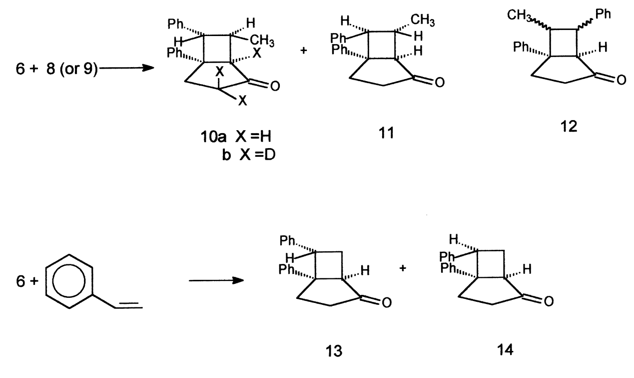
Arylalkenes undergo photochemical cycloaddition reactions with cyclic enones to give products with specific regiochemistry and controlled stereochemistry. The regio- and stereo-chemistries can be rationalised in terms of the stability of intermediate radicals.

Keywords: photochemistry, cyclic enones, regioselection, stereoselection, cycloaddition, bicycloalkanones

3-Phenylcyclopent-2-en-1-one (**6**) with either (*E*)- or (*Z*)-1-phenylprop-1-ene, **8** and **9** respectively, on photolysis affords a mixture of 7-*endo*-methyl-6-*exo*-methyl-5,6-*endo*-diphenylbicyclo[3.2.0]heptan-2-ones, **10a** and **11** respectively. 3-Phenylcyclohexenone affords only 8-*endo*-phenyl-5-methyl-6,7-*exo*-diphenylbicyclo[4.2.0]octan-2-one (**15a**).

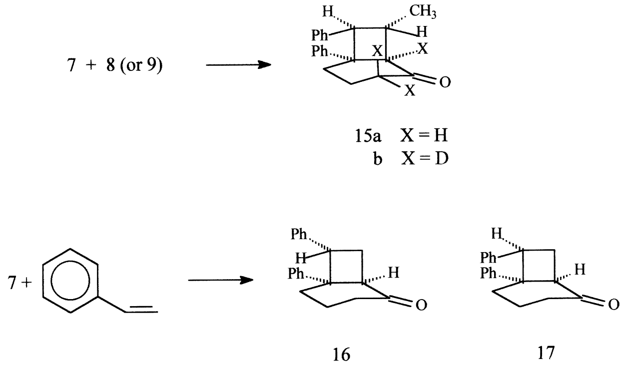


Structure 1



Structure 2
Reaction conditions: hv, benzene, pyrex filter

With styrene, the 3-phenylcylopentenone affords a mixture of 6-*exo*-and 6-*endo*-phenyl isomers, **13** and **14** respectively, and the 3-phenylcyclohexenone a mixture of two products, the 7-*exo*- and presumably 7-*endo*-phenyl isomers, **16** and **17** respectively.



Structure 3
Reaction conditions: hv, benzene, pyrex filter

We have already discussed the photophysical aspects of the reactions of the cyclopentenone **6** and cyclohexenone **7** with the two phenylpropenes.[1,11] In this paper we discuss the evidence for the structures of the products. We used the ^{1}H and ^{13}C NMR spectra, together with nOe measurements. The spectra of the photoadducts were simplified by carrying out, and isolating the products from, the photolysis reactions with deuterated starting materials.

The regio-and stereochemistry of the adducts are rationalised.[1,11]

Techniques used: ^{1}H and ^{13}C NMR, NMR, nOe measurements, IR.

References: 15

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