The Ring-size Effect in the Photoreaction of Phenylcycloalkenes

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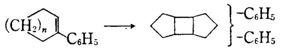
We have been studying the ring-size effect in the photoreaction of phenylcycloalkenes, in which the double bonds are a part of the chromophore. A recent publication by Nozaki *et al.*[1] reporting the photo-induced addition of acetic acid to phenylcyclohexene and phenylcycloheptene has now prompted us to report the results from our independent work.*1

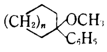
Methanolic solutions (0.1 M) of phenylcycloalkenes (I, II, III, and IV) containing a small amount (0.05% to methanol) of sulfuric acid were irradiated with a 100 W high pressure mercury lamp placed in a quartz cooling jacket for 6—24 hr (I, 10 hr; II, 6 hr; III, 7 hr: and I*X*, 24 hr). The reference solution was kept in the dark, and no change of phenylcycloalkenes was observed.

Phenylcyclopentene (I) gave a crystalline dimer, V-a (25%), mp 186°C, and an oily dimer V-b (12%) besides polymeric products. These two isomers were purified successively by alumina chromatography and preparative vapor-phase chromatography. The dimers have only phenyl-hydrogens and cycloparaffin-hydrogens in their NMR spectra. The mass spectrum of the V-a dimer has a strong peak at $m/e=144$ ($C_{11}H_{12}$) due to phenylcyclopentene, formed by the cleavage of the cyclobutane ring of the dimer upon electron impact, and no distinct peak over $m/e=144$. The V-b dimer has a molecular peak at $m/e=288$ ($C_{22}H_{24}$). Phenylcyclohexene (II) and phenylcycloheptene (III) gave methoxy-phenylcycloalkanes (VI, 54% and VII, 64%, after distillation) as the only isolable products besides the polymer. The structures of these adducts were characterized by a study of their mass spectra (M^+, $m/e=190$ for VI and 204 for VII) and by their NMR spectra, which have characteristic signals due to methoxy groups ($\delta=2.95$ for VI and 2.92 for VII in CCl_4). The irradiation of phenylcyclooctene (IV) gave phenylcyclooctane (VIII) (7%) and recovered phenylcyclooctene (15%) besides the polymer. The formation of the adduct between IV and methanol could be observed from the NMR spectrum of the crude product, but it was not present in an isolable amount.

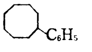


I: $n=1$, II: $n=2$
III: $n=3$, IV: $n=4$

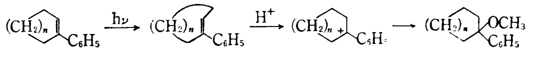
V-a, V-b



VI: $n=2$
VII: $n=3$



VIII



IX

Cyclohexene and cycloheptene give adducts with alcohol upon irradiation in the presence of benzene, but no photo-addition of alcohol to cyclopentene and cyclooctene occurs.[2] This difference in the reactivity of cycloalkenes with a variation in the ring-size is also seen in our experimental results on phenylcycloalkenes. This similarity in the reactivity between cycloalkenes and phenylcycloalkenes indicates that the addition of methanol to phenylcycloalkenes (II and III) may be the thermal addition of methanol to the *trans*-phenylcycloalkenes (IX, $n=2,3$) formed through the orthogonal excited states of II and III.

The protonation to these *trans*-phenylcycloalknes with high energy contents is obviously the rate-determining step of the addition reaction, since the reaction without an acid catalyst is much slower. The steric requirements do not allow the formation of *trans*-phenylcyclopentene (IX, $n=1$) from the excited state, and the dimerization of phenylcyclopentene (I) takes place preferentially on irradiation. The formation of *trans*-phenylcyclooctene (IX, $n=4$) can be expected without difficulty. The *trans*-isomer, however, does not suffer much ring strain and the enrgy content is not high enough for the facile addition of methanol. Phenylcyclooctene (IV) gives no dimer, but abstracts hydrogen radicals from the solvent to give phenylcyclooctane (VIII).*2

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1) S. Fujita, T. Nomi and H. Nozaki, *Tetrahedron Lett.*, **1969**, 3557.

*1 After the submission of our original manuscript, another paper dealing with the same subject has appeared: P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969).

2) a) P. J. Kropp, *J. Amer. Chem. Soc.*, **88**, 4091 (1966); **89**, 3651 (1967). b) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

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