Radical Ions in Photochemistry. Sensitised (Electron-transfer) Photochemical Reactions of Some 1-Phenylcycloalkenes in Polar, Nucleophilic Solvents

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Summary Irradiation of 1-phenylcyclopentene, 1-phenylcyclohexene, and 2-phenylnorbornene in methanol, acetic acid–dioxan, and aqueous acetonitrile solution, with methyl *p*-cyanobenzoate or 1-cyanonaphthalene as sensitiser (electron-transfer), gives fair to good yields of the product resulting from *anti*-Markovnikov addition of the nucleophilic solvent to the olefin.

Direct or triplet sensitised irradiation of phenyl cyclic olefins, 1-phenylcyclopentene (I), 1-phenylcyclohexene (II), and 2-phenylnorbornene (III), in polar nucleophilic solvents, can lead to mixtures of the reduced olefin, polymer, and the Markovnikov addition products.[1] In contrast we find electron-transfer photosensitised excitation of these olefins is a synthetically useful reaction for preparing the alcohol, ethers, and esters expected from *anti*-Markovnikov addition.

Irradiation (medium-pressure mercury vapour lamp, Pyrex filter, 10°) of an aqueous acetonitrile solution of (I) and 1-cyanonaphthalene (XV)† gave *cis*- (IV; 15%) and *trans*-2-phenylcyclopentanol (V; 27%).‡ From g.l.c. of the crude reaction mixture we estimated that <5% of any other adduct was present. When a similar irradiation was

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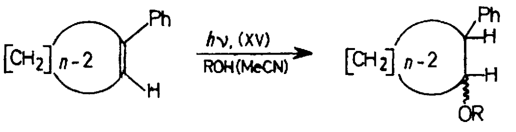
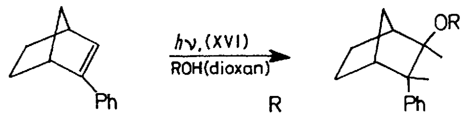
† The sensitiser was usually recovered; however, in some cases (XV) was partially consumed to give 1-cyano-3,4-dihydronaphthalene. This is an expected product from (XV)$^{\overline{\cdot}}$.

‡ New compounds (VI), (VII), (XIII), and XIV) gave satisfactory analysis or exact molecular weight for the parent-peak in the mass spectra. The structure of known compounds was confirmed by direct comparison (i.r.).

carried out in methanol–acetonitrile, *cis*- (VI) and *trans*-1-methoxy-2-phenylcyclopentane (VII) were formed. Insignificant amounts of isomeric products were detected. These results contrast with those obtained when (I) was irradiated, either directly or in the presence of a triplet sensitiser in methanol (acidic) or in acetic acid, where no monomeric adducts were obtained.[1a,c,d]



	R	*cis* (%)	*trans* (%)
(I), *n* = 5	H	(IV) (15)	(V) (27)
	Me	(VI) (12)	(VII) (19)
(II) *n* = 6	H	(VIII) (37)	(IX) (25)
	Me	(X) (29)	(XI) (18)



(III)

R		
H	(XII)	(38%)
Me	(XIII)	(63%)
Ac	(XIV)	(47%)

The electron-transfer sensitised excitation of (II) in aqueous acetonitrile affords *cis*- (VIII) and *trans*-2-phenylcyclohexanol (IX); in methanol *cis*-(X) and *trans*-1-methoxy-2-phenylcyclohexane (XI) are formed.

The direct and triplet sensitised excitation of (II) in methanol or acetic acid gives 1-methoxy-1-phenylcyclohexane or 1-phenylcyclohexyl acetate as the only isolated adducts. These are products expected from Markovnikov addition where the product determining step is protonation of the olefin in an excited state. Other products, indicative of a free-radical reaction, are also formed under these conditions.[1a,c–f].

The electron-transfer sensitised (methyl-*p*-cyanobenzoate, XVI) excitation of (III) in methanol, aqueous dioxan, or acetic acid–dioxan gave again the corresponding *anti*-Markovnikov addition products as the only adducts. The stereoisomeric alcohols have distinctive n.m.r. spectra;[2] direct comparison established the structure 3-*endo*-phenyl-2-*exo*-norbornanol (XII) for the product from aqueous dioxan. The ether (XIII) and acetate (XIV) have n.m.r. spectra similar to that of (XII) from which they were prepared.

Direct irradiation of (III) in methanol gave the Markovnikov addition product *exo*-2-methoxy-*endo*-2-phenylnorbornane as the only isolated adduct, together with *endo*- and *exo*-2-phenylnorbornane. No ether was obtained from (III) on triplet sensitisation.[1b]

The mechanism proposed[3] for these reactions is that of electron-transfer following excitation of the sensitiser. Subsequent formation of solvent-separated radical-ions may occur by sequential formation of an encounter complex, an exciplex, and/or a solvated radical-ion pair. The free-energy change for formation of the solvent-separated radical-ions can be calculated from the oxidation potential of the olefin, the reduction potential of the electron accepting sensitiser and the singlet excitation energy of the sensitiser using the equation proposed by Weller.[4] Since we assume that, in the polar solvents used here, complete separation of the ions has occurred, Coulombic attraction is negligible.

Using this equation we estimate that, with (XV) and (XVI) as acceptors, radical-ion formation will be spontaneous if the oxidation potential of the olefin is *ca.* 1·8 V. The oxidation potentials of (I)—(III) are not reported, but they are less than that of styrene, $E^{\frac{1}{2}}_{\text{ox}}$ 1·80 V.[5]

The direction and stereochemistry of the addition are consistent with the proposed mechanism. The configuration of (XII)—(XIV) indicates that both the nucleophile and proton source approach the norbornyl intermediates from the least hindered side. The ratio of isomers from (I) and (II) presumably reflects the relative rates of protonation from either side of the carbanion intermediate.

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