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PHOTOLYSES OF TRICYCLO[4.2.2.$0^{3,5}$]DECA-7-EN-2-ONE SYSTEMS[1]

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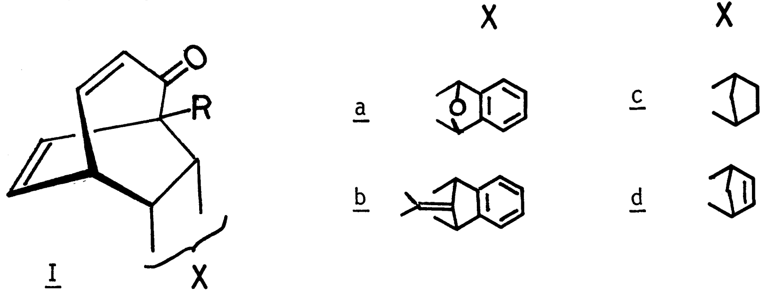
Photolyses (Pyrex, > 290 nm) of tricyclodecaenone derivatives (cyclopropylketone-π-methane moiety) gave the exclusive 1,3-acyl shift products in high yields.

Much interest has arisen in the photochemical rearrangement of the enone-π-methane moiety (bicyclo[3.2.2]nona-3,6-dien-2-one) (I).[2] In particular the influence of substituents on the photolyses of compound (I) has been evaluated by us;[3] compound (I) (R=H) undergoes a facile [3,3]-rearrangement to produce a ketene intermediate, trapped as the ester. The hydroxy-derivative (I) (R= OH) gave photolysis product as a result of 1,3-migration.



I

In the present communication, we report a photochemical transformation of the tricyclo[4.2.2.$0^{3,5}$]deca-7-en-2-ones (II) (cyclopropylketone-π-methane moiety).

Compounds IIa-d were prepared from the reactions of the endo,exo-[4+2]tropone adducts[3] Ia-d with trimethyl oxosulfonium iodide in the presence of 50% aqueous sodium hydroxide-benzene with triethylbenzylammonium chloride as a catalyst (the phase-transfer method)[4] at 35-40°C or from the cycloaddition reactions of 2,3-homotropone with dienophiles. The nmr spectra of IIa-d show the corresponding cyclopropane gem-proton signals at δ 0.7-1.5 as a multiplet.[5]

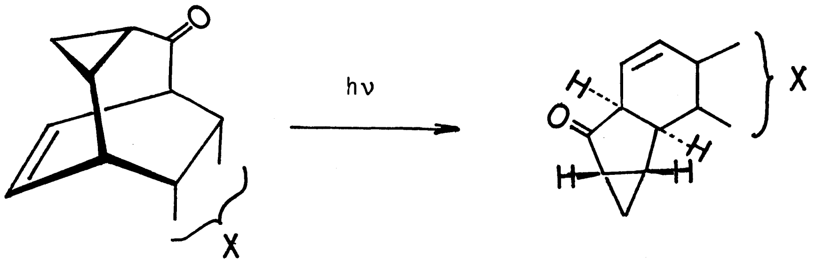
When compound (IIa) in a benzene or methanol solution was irradiated for 2 h with a high-pressure 100-W mercury lamp through a Pyrex filter under argon, only one product (IIIa) was isolated in 95% yield. No other products could be detected by tlc inspection.

Compound (IIIa) ($C_{18}H_{16}O_2$, mp 175-176°C)[5] exhibits aromatic protons(4H) at δ 7.17(m), olefinic protons(2H) at δ 5.95(m), oxygen bridgehead protons at δ 5.18 and 5.03 as each sharp singlet, allylic methine proton at δ 2.9(m), five methine protons at δ 1.5-2.65(complex multiplet), and cyclopropane gem-proton signals(2H) at δ 1.0-1.5 (m), The absence of appreciable coupling of the oxygen bridgehead protons indicated that the dihedral angles between the oxygen bridgehead protons and the vicinal methine protons are to be approximately 90°. Besides, significant appearance of the chemical shifts for the cyclopropane gem-protons indicates that the photochemical rearrangement reaction undergoes without cyclopropyl bond fission.

The ir spectrum of compound (IIIa) shows a carbonyl absorption at 1710 cm^{-1} instead of the original carbonyl one (IIa) at 1670 cm^{-1} indicating the presence of the strained five-membered carbonyl moiety.

Thus, the structure of compound (IIIa) was assigned a photoallowed suprafacial 1,3-acyl rearrangement product as depicted in Scheme 1.

Similar photolyses of compounds IIb-d under the above conditions afforded compounds IIIb-d in high yields respectively. Structural elucidation of these products IIIb-d was also accomplished by their ir (1715-1725 cm^{-1} (C=O)) and nmr (the cyclopropane gem-proton signals at δ 0.7-1.5). The spectral patterns of these products are grossly similar to that of compound(IIIa).^{5}



IIa-d IIIa-d

Scheme 1.

In contrast to the cyclopropane ring-fission in the photolysis of cyclopropyl ketones,^{6} the photoproducts IIIa-d arose from the exclusive 1,3-acyl shift, and the results provide a simple synthetic route to strained polycyclic hydrocarbons from a readily available precursor.

References and Notes

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