Photolysis of Cyclohexadiene Imides: *N*-Substituent Effects and Bicyclo[2,2,0]hexene Formation[1]

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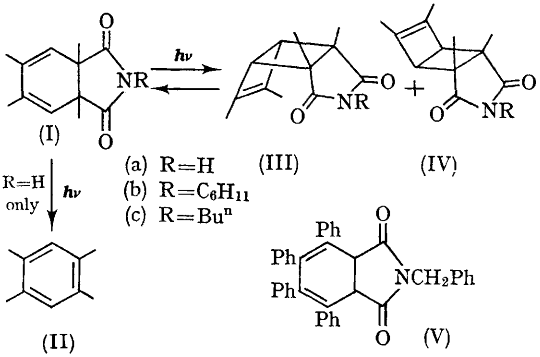
VAN TAMELEN'S observation[2] on the photolysis of cyclohexa-3,5-diene-*cis*-1,2-dicarboxylic anhydride, which selectively formed[3] *anti*-bicyclo[2,2,0]hex-5-ene-*cis*-2,3-dicarboxylic anhydride, appeared to offer a simple route to other bicyclo[2,2,0]hexene derivatives.[4] However, as we,[5,6] and subsequently others,[7] reported, photolysis of poly-substituted cyclohexadiene anhydrides gave mainly the aromatic hydrocarbon by fragmentation of the anhydride group. In an attempt to suppress this aromatization reaction in favour of bicyclo[2,2,0]-hexene formation, and yet retain the potential functionality of an anhydride group, a number of related cyclohexadiene imides (Ia–c, V) were prepared and photolysed.†,‡

The photolytic behaviour of the unsubstituted imide (Ia)† closely paralleled that of the corresponding anhydride.[6] Thus fragmentation of (Ia) to durene (II) was observed, as well as the formation of mixture of (IIIa) and (IVa). However, in the case of the *N*-cyclohexyl imide (Ib)† the formation of durene was completely suppressed in favour of the valence-bond isomerisation (4-centre) to the bicyclo[2,2,0]hexene isomers (IIIb, IVb). While this mixture was difficult to separate, repeated chromatography on silica gel did yield the *syn*-isomer (IIIb) in pure form, m.p. 104—105° (*M*, by mass spectra, 287). Thermolysis at 210° converted (IIIb) back into the starting material, cyclohexa-1,3-diene (Ib) and is consistent with the assigned structure. The stereochemical assignment is based on the ^{1}H n.m.r. spectra [methyl proton resonances at τ 8·73, 8·42 (*syn*-isomer) and τ 8·83, 8·23 (*anti*-isomer) superimposed in each case on a broad methylene proton resonance τ 8·90 to 8·20, methine proton resonance at τ 7·11 (singlet, *syn*-isomer) and τ 7·03 (singlet, *anti*-isomer) together with a broad resonance at τ 6·00 (cyclohexyl proton adjacent to nitrogen in each isomer)]. These structures (IIIb, IVb) are further supported by conversion into the known[5] *syn*- and *anti*-2,3,5,6-tetramethylbicyclo-[2,2,0]hex-5-ene-2,3-dicarboxylic anhydrides, upon vigorous hydrolysis followed by cyclisation of the initially generated dicarboxylic acids. Similar results were obtained on photolysis of the *N*-n-butyl imide (Ic)† and the *N*-benzyl imide (V),‡ where again no aromatic hydrocarbon was observed.



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† For compounds (Ia, Ib, and Ic): photolyses were carried out in dilute ether solution under argon; Hanovia U.V.S.500, medium pressure Hg lamp, water cooled quartz probe with Vycor filter. Compound (Ia) was prepared from the related anhydride (ref. 5) by refluxing with urea in ethylene glycol, m.p. 135—137°. Compounds (Ib), m.p. 92°, and (Ic), a liquid, were formed from the anhydride by heating (100°) with a solution of the appropriate amine in 2-methoxyethanol.

‡ Compound (V), m.p. *ca.* 180° resolidifies m.p. 210°, was prepared by decarbonylation of the Diels–Alder adduct of tetracyclone and *N*-benzylmalemide. The photolysis was run in dilute benzene solution at 30° under argon, with a Pyrex filter; Hanovia U.V.S. 500 Hg lamp.

[1] Considered as a part of the series, "Excited State Reactions of Imides and Anhydrides".
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