Formation of 7-Substituted Norbornenes in the Photoaddition of Cyclohex-2-enones and Norbornadiene

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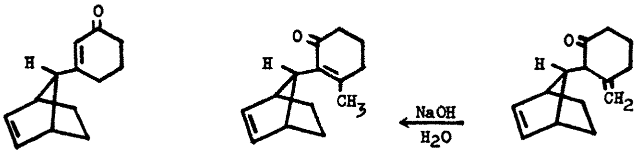
EARLIER we reported[1] that photolysis of cyclohex-2-enone and norbornadiene gave rise to 3-(3-nortricyclyl)cyclohex-2-enone (1) and 3-(norbornen-5-yl)cyclohex-2-enone (2). The former structure (1) was confirmed by synthesis.[1]

We now report that the product assigned structure (2) is in fact 3-(*anti*-bicyclo[2,2,1]hept-2-en-7-yl)cyclohex-2-enone (3); and that the photoaddition of 3-methylcyclohexenone and norbornadiene gives 3-methyl-2-(*anti*-bicyclo[2,2,1]-hept-2-en-7-yl)cyclohex-2-enone (4) and 3-methylene-2-(*anti*-bicyclo[2,2,1]-hept-2-en-7-yl)cyclohexanone (5).

The formation of 7-substituted norbornenes in this photoaddition† appears to be without precedent in enone photochemistry. Also, we have shown that the formation of (3) involves an intramolecular stereospecific hydrogen shift, and have suggested a mechanism consistent with this result.

The structures of photo-products (3), (4), and (6) were determined by a chemical degradation and n.m.r. spectroscopy.‡

First (4) and (5) were shown to be tautomers, since mild treatment of (5) with base resulted in clean isomerization to (4). Di-imide reduction[2] of (4) gave the corresponding norbornane in quantitative yield. Oxidation of the latter with aqueous permanganate–periodate[3] gave norbornane-7-carboxylic acid, m.p. and mixed m.p. 74—75° (lit.,[4] 75—76·5°).



(3) (4) (5)

SCHEME 1

The n.m.r. spectra of (3) and (4) (Figure) show that both compounds have the same arrangement of protons in the norbornene portion, and the spectra are in accord with the substituents being at C-7. The *exo*- and *endo*-pairs of

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† Irradiations were performed as described previously.[1] Products (4) and (5) constituted approximately 2% and 15% of the reaction mixture in the addition of 3-methylcyclohexenone and norbornadiene, the balance being mainly cyclobutanes (with 16% of homo-Diels–Alder adduct). Isolation and purification employed silica gel chromatography and gas chromatography.[1]

‡ N.m.r. spectra were measured at 100 Mc./sec. on a Varian HA-100 instrument. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

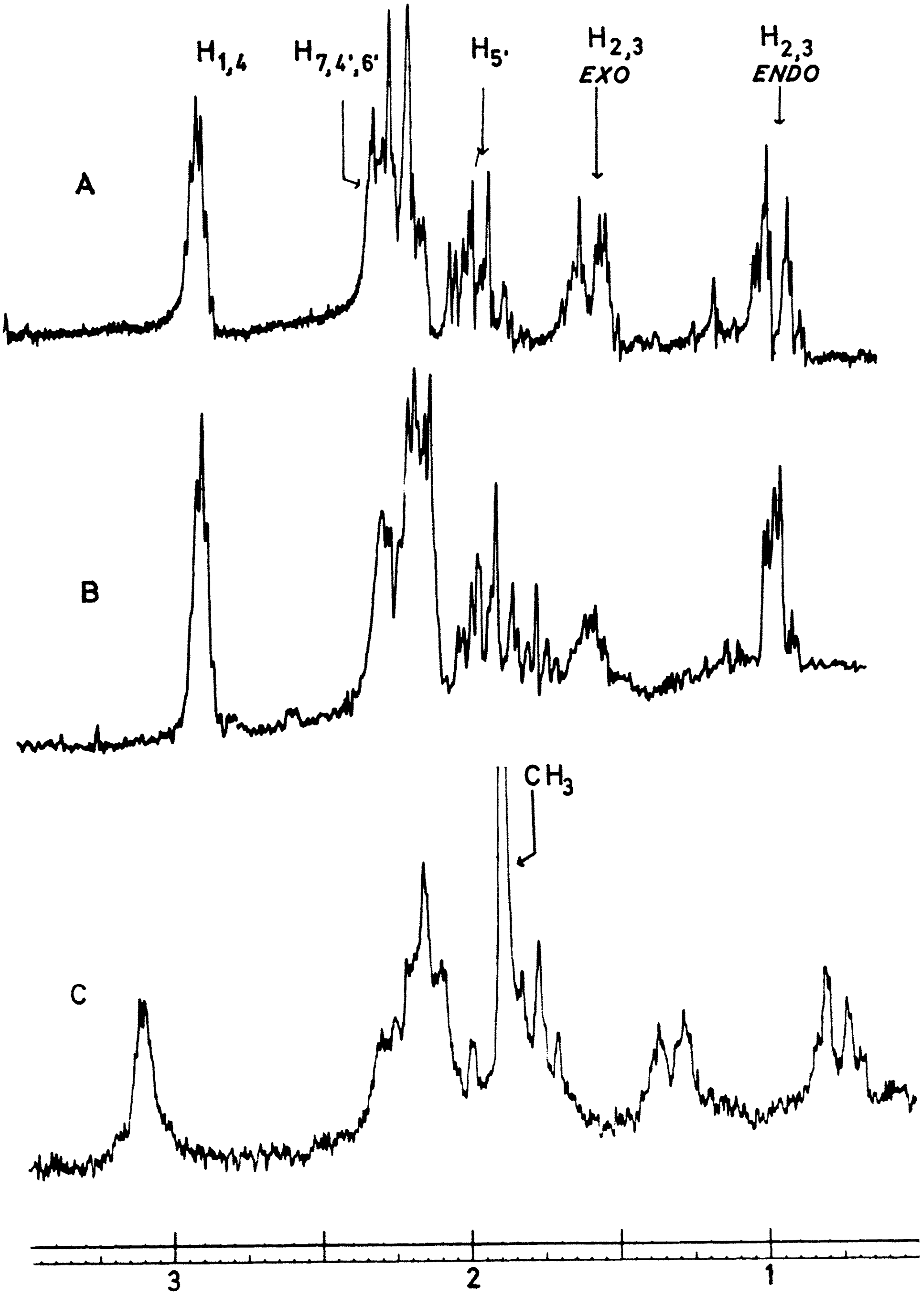

FIGURE. 100 Mc./sec. *n.m.r. spectra*: (A) *compound* (3); (B) *compound* (3) *showing one deuterium in the* exo-*position*; (C) *compound* (4).

protons shows as two pairs of multiplets of an AA'XX' system, the *endo*-multiplet being at higher field.[5]

Irradiation of the multiplet at 2·21, which includes the resonance of the allylic 7-proton, caused the *endo*-multiplet to collapse to a quartet. This shows that H-7 is coupled to the *endo*-protons and therefore must be *syn*[6] to the norbornene double bond. The assignments of the remaining non-vinylic protons are shown in the Figure.

The n.m.r. of (5) is different from the spectra of (3) and (4), showing resonances at 4·60 and 4·70 due to the exocyclic methylene group. This evidence, together with the ready isomerization to (4), leaves no doubt as to the structure of (5).

In order to obtain mechanistic evidence concerning the hydrogen shift which must occur in the formation of the enone products, the photoaddition of 3-deuteriocyclohexenone and norbornadiene was investigated. Deuterio-(3) was isolated, and the n.m.r. is shown in the Figure (B). The *endo* : *exo* peak ratio is 2 : 1, hence the deuterium initially at C-3 in the deuteriocyclohexenone has been transferred stereospecifically to the *exo*-side of the ethylene bridge in (3). A suggested mechanism is shown in Scheme 2.

The reaction can be considered to occur in three steps: (i) attack of an excited state of cyclohexenone from the *exo*-side of the norbornadiene; (ii) rearrangement of an intermediate, represented here as a diradical species, resulting in a formal Wagner–Meerwein shift; (iii) hydrogen transfer, regenerating the enone system and forming a stable molecule.

We have obtained evidence that a triplet state of the enone is involved.

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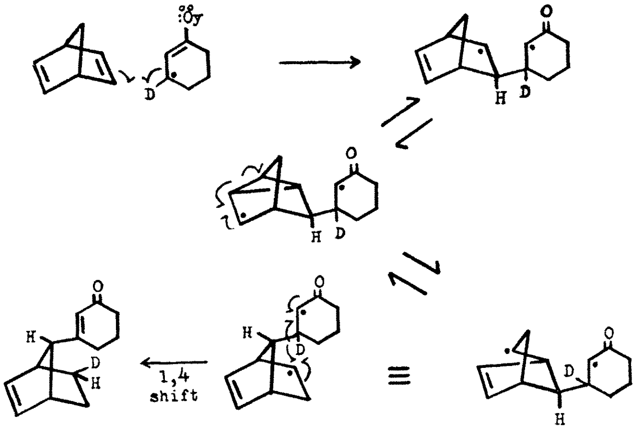

SCHEME 2

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