

Photochemical Reactions of Stereoisomeric 7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-ones

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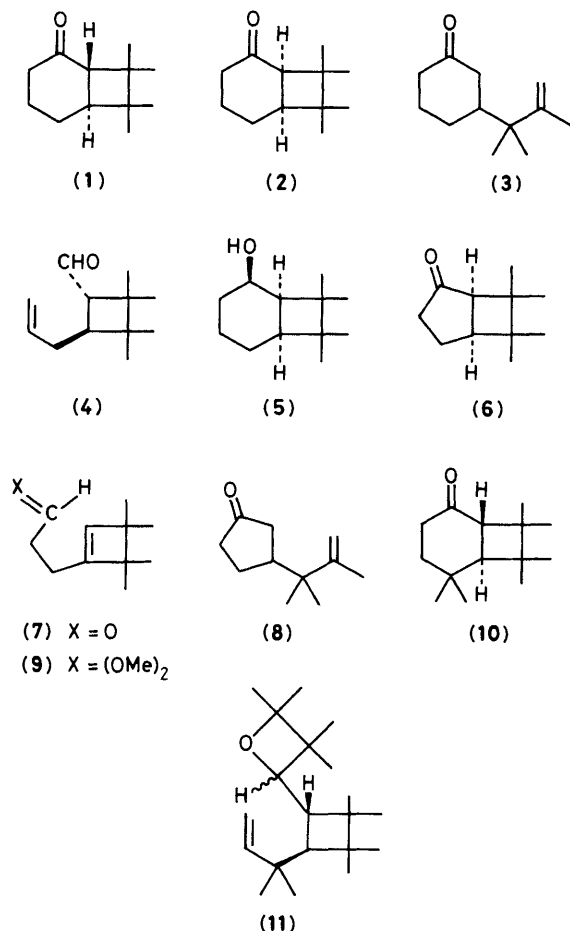
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Photochemical reaction of the *trans*-fused bicyclic ketone (**1**) in solution gave the unsaturated aldehyde (**4**), whereas irradiation of the *cis*-fused isomer (**2**) in methanol led to inefficient photoreduction.

It has been reported that u.v. irradiation of a mixture of bicyclic ketones (**1**) and (**2**) gave a Norrish type II reaction to yield the unsaturated cyclohexanone (**3**) in 85% yield.¹ Several examples of photochemical [2 + 2] cycloaddition, followed by selective cyclobutane cleavage, have been used by other groups as an approach to spirosesquiterpenes.^{2,3} In our

studies of intramolecular hydrogen abstraction,⁴ we have had reason to examine the photochemistry of the individual isomers (**1**) and (**2**), and report substantially different results from those of Fetizon and co-workers.¹

Photocycloaddition of cyclohexenone to 2,3-dimethylbut-2-ene gave the bicyclic adducts (**1**) and (**2**) and the unsaturated



ketone (3) in the ratios 3 : 2 : 1, which did not vary significantly with time during the first 30% of reaction.⁵ The product distribution is typical of cyclohexenone-alkene photoadditions,⁶ and the *trans*-fused geometry of the major adduct was assigned on the basis of the easy isomerisation of (1) on contact with basic alumina to the more stable *cis*-fused (2).⁷ The photoproducts were separated by repeated column chromatography and preparative g.l.c., and their structures assigned by ¹H and ¹³C n.m.r.⁸ and i.r. spectra, and elemental analysis.

Irradiation of the *trans*-adduct (1) in solution under a variety of conditions† gave the unsaturated aldehyde (4) (14–18% isolated yield) as the only detected volatile product. In particular, no significant amount of unsaturated ketone (3) was found. It is known that ketene intermediates in photochemical reactions can be trapped by methanol,⁹ but irradiation of (1) in methanol gave no evidence for additional products.

The *cis*-adduct (2) was considerably more photostable than (1). Prolonged irradiation in acetonitrile or dichloromethane solution led only to polymeric material, and no discrete products could be isolated. The unsaturated ketone (3) could not be detected at any stage during the irradiation. However, upon u.v. irradiation of (2) in methanol, the photoreduced bicyclic alcohol (5) was formed (14%).‡

We have also investigated the photochemical reactions of the corresponding *cis*-fused bicyclo[3.2.0]heptanone (6).

† (a) MeCN, quartz, 20 °C; (b) MeCN, quartz, –30 °C; (c) CH₂Cl₂, Pyrex, 0 °C; (d) CH₂Cl₂, quartz, 0 °C; (e) MeOH, quartz, –50 °C.

‡ This compound has identical spectra to that prepared by lithium aluminium hydride reduction of (2).

Irradiation of (6) in acetonitrile led to the cyclobutenyl aldehyde (7) as the major photoproduct (42%). The unsaturated ketone (8) which could arise by Norrish type II reaction of (6) in methanol was not detected in this example, either. Irradiation of (6) in methanol gave the acetal (9) (22%) derived from the aldehyde (7); such photochemically induced additions of methanol to carbonyl compounds have precedent.¹⁰

The contrast between the photochemical reactions of the bicyclic ketones (1), (2), and (6) is notable. The *cis*-fused bicyclo[4.2.0] ketone (2) is evidently sufficiently inert towards Norrish type I and type II reactions that the slow process of photoreduction from methanol can compete.¹¹ For the *trans*-fused compound (1), Norrish type I reaction does occur, but in the ‘abnormal’ mode;¹² the reduced stability of the cyclobutyl radical has been advanced to explain this type of selective bond breaking between the carbonyl group and the less-substituted α -carbon atom. Interestingly, Chapman and co-workers¹³ were unable to isolate the aldehyde analogous to (4) from irradiation of the bicyclic ketone (10), although they did provide evidence for it by photochemical trapping with 2,3-dimethylbut-2-ene to yield oxetanes (11). In contrast, the cyclopentanone ring of the bicyclo[3.2.0]heptanone (6) encourages much more rapid α -cleavage than for the cyclohexanones, to generate a biradical which eventually leads to the cyclobutenyl aldehyde or its acetal.¹⁴

In conclusion, it is unlikely that subtle differences in irradiation conditions are responsible for this major divergence from the earlier report on the photochemistry of (1) and (2).§

We thank Professor Fetizon for exchange of information and n.m.r. spectra.

Received, 8th May 1985; Com. 615

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§ It would appear that the yield reported in the earlier work relates only to the relative percentage of products detected by h.p.l.c., and that the unsaturated ketone (3) may be more photostable than the bicyclic ketones (1) and (2); on prolonged irradiation, compound (3) therefore appears to become dominant in the detected products.