Tetrahedron Letters No.51, pp. 4679-4683, 1965. Pergamon Press Ltd.
Printed in Great Britain.

2-METHYLENE-[2:1:1]-BICYCLOHEXANE*

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(Received 15 October 1965)

The irradiation of acyclic conjugated dienes has been a subject which has attracted much attention recently. In particular two types of transformations have been studied in some detail. The first concerns the conversion of the dienes by direct irradiation into cyclobutenes[1,2] and bicyclobutanes.[2] The second concerns the photochemical behaviour of such dienes when excited by triplet-triplet energy transfer.[3,4]

The irradiation of the triene, 3-methylenehexa-1,5-diene (1) was thought to be of interest for several reasons.

First, it could provide support for the dichotomy of pathways mentioned [3,5]; and secondly the presence of the isolated double bond presented possibilities for internal cycloaddition which might proceed so as to give the chemically desirable 2,2,0- or the 2,1,1-bicyclohexane systems. The feasibility of such cycloaddition has already been demonstrated when

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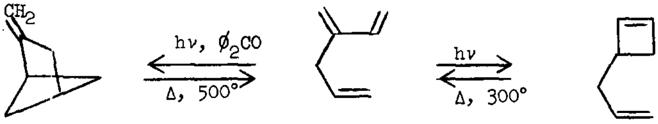
[*] This communication is Photochemical Syntheses, Part 12.

the chromophores are separated by two methylene groups.[1,5,6]

Irradiation of 1 in n- or cyclopentane solutions (0.3%) using a 450 W Hanovia mercury arc with a Corex filter gave, as far as could be discerned, a single monomeric product as indicated by gas-liquid chromatography. The product, isolated by such chromatography was attributed the structure (2) 1-(prop-2-enyl)-cyclobut-1-ene [Found: C, 89.59; H, 10.79%]. It showed absorption for the vinyl group in the infrared at 918, 996 and 3050 cm^{-1} and also absorption for the proton on the trisubstituted double bond at 855 cm^{-1}. The proton magnetic resonance spectrum showed the presence of four vinylic protons, two multiplets (at τ 4.83 and 5.07) being attributed to the terminal protons of the vinyl group. Pyrolysis of the hydrocarbon in the gas phase at 300° regenerated 1.[7]



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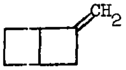

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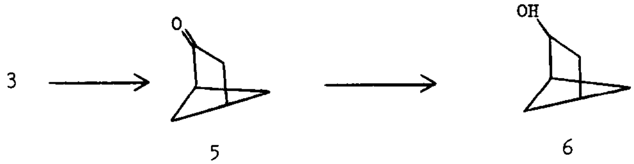
Irradiation of 1 in n-pentane (0.3%) containing 0.15% benzophenone with the 450 W arc, but using a pyrex filter gave in high yield (> 85%) a new substance which is attributed structure 3 2-methylene-[2:1:1]-bicyclohexane. The hydrocarbon [Found: C, 89.17; H, 10.59%] showed absorption in the infrared at 3084, 1670 and 870 cm^{-1} compatible with the presence of an exocyclic methylene group. This was confirmed by the presence in the proton resonance spectrum of two multiplets of one proton each centred at τ 5.35 and 5.05. There were no signals for other vinylic protons. Since the compound survived pyrolysis in the gas phase at 310°[7] the possibility that the substance might be attributed structure 4 could be dismissed.[8] At 500° the triene was regenerated.

Cleavage of the double bond by the permanganate-periodate method[9] gave a ketone (5) [Found: C, 74.58; H, 8.79%] the carbonyl frequency of which in the infrared, at 1755 cm^{-1}, was in agreement with expectation for 3, and constituted further evidence against 2.*

Reduction of the ketone in ethereal solution with lithium aluminium hydride gave a single crystalline alcohol isolated by g.l.c. on a 20% Carbowax-AgNO$_3$ on Chromosorb P column. A comparison of this substance with an alcohol having the structure (6)[10] indicated identity.** It was shown that no rearrangement had taken place during the reduction by re-oxidation (sodium dichromate in acetic acid) of the alcohol to the ketone.



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* This ketone has also been prepared by Professor F. T. Bond (Oregon State Univ.) as described in the accompanying communication.

** The substances had identical infrared spectra and retention times on g.l.c. We are very grateful to Professor Meinwald for establishing this identity. Very recently[13] the preparation of *exo* [2:2:0]bicyclohexanol has been reported.

In view of the readily availability of the triene **1**[11] this represents one of the simplest routes presently at hand for the preparation of many derivatives of the 2,2,1-bicyclohexane series.[12] The evidence here presented also supports the suggestion made by Srinivasan that cyclobutene formation involves the singlet (cf. Ref. 3, and earlier papers). Since excited cyclobutene, however, should be of considerably higher energy than the butadiene first excited singlet some intermediate stage involving electron demotion, and leading to the ground state cyclobutene must be involved.

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