Intramolecular Photocyclisation of 1,5,5-Trimethyl-8-methylenecyclodeca-6,10-diene

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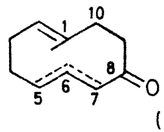
Summary U.v. irradiation of 1,5,5-trimethylcyclodeca-1,6-dien-8-one resulted in the formation of a photofission product, whereas the corresponding 8-methylene compound gave an intramolecularly cross-cyclised product.

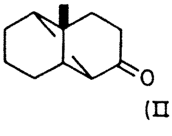
Some synthetic approaches have been reported for sesquiterpenoids containing a fused cyclobutane ring, such as copaene, ylangene, bourbonene, *etc.* Intramolecular photocyclisation of cyclodecadiene derivatives provides a promising route for the synthesis of such natural products and has also been suggested as a possible biogenetic pathway for these sesquiterpenoids.[1] Heathcock and Badger reported that irradiation of the cyclodecadienone mixture (Ia and Ib) gave two photocyclised ketones (II and III) as the major products.[2]



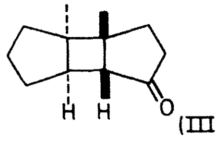
(I)

(a) $\Delta^{5(6)}$

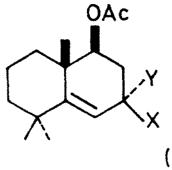
(b) $\Delta^{6(7)}$



(II)



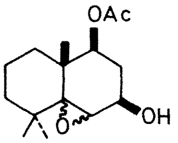
(III)



(IV)

(a) X, Y = O

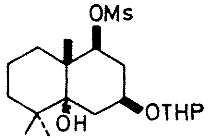
(b) X = OH, Y = H



(V)

(a) β-epoxide

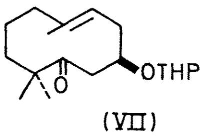
(b) α-epoxide



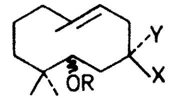
(VI)

(a) β-OH

(b) α-OH



(VII)

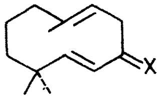


(VIII)

(a) R = H, X = OTHP, Y = H

(b) R = Ac, X = OH, Y = H

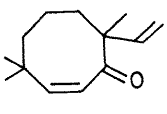
(c) R = Ac, X, Y = O



(IX)

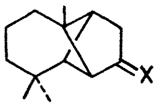
(a) X = O

(b) X = CH$_2$



(X)

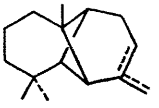
(XI)



(XII)

(a) X = CH$_2$

(b) X = O


(XIII)

We report the synthesis and the photolysis of 1,5,5-trimethylcyclodeca-6,10-dien-8-one (IXa) and 1,5,5-trimethyl-8-methylenecyclodeca-6,10-diene (IXb).

The acetoxy-octalone[3] (IVa) gave the acetoxy-octalol (IVb; 79% yield), m.p. 75—76°, upon sodium borohydride reduction. The alcohol was treated with *m*-chloroperbenzoic acid (0·13 M in methylene chloride) affording a mixture of the *cis*-epoxide (Va; 78%), m.p. 173—177°, and the *trans*-epoxide (Vb), an oil, in a ratio of 88 : 12 (g.l.c.).[4] The use of higher concentrations of the oxidant resulted in an increase in the proportion of the *trans*-isomer formed. The *cis*-isomer (Va) was transformed into the mesylate (VIa) *via* the following steps; protection of the hydroxy-group of (Va) with dihydropyran, lithium aluminium hydride reduction of the resulting tetrahydropyranyl ether, and selective mesylation of the secondary hydroxy-group of the diol thus formed. The mesylate (VIa; 70% overall yield from Va) consisted of two diastereomers, m.p. 105·5—106·5° (decomp.) and m.p. 92·5—94°, which could be separated by fractional recrystallisation. A similar treatment of the *trans*-epoxide (Vb) gave the mesylate (VIb).

The *cis*-mesylate (VIa) was submitted to a fragmentation reaction. Treatment of the mesylate with sodium hydride in tetrahydrofuran gave the unstable cyclodecenone (VII; 83%), ν_{max} 1695 cm^{-1}, whereas attempted fragmentation was unsuccessful for the *trans*-isomer (VIb). Subsequent reduction of (VII) with lithium aluminium hydride in dimethoxyethane yielded the cyclodecenol (VIIIa; 90%). Reduction of the mesylate (VIa) with lithium aluminium hydride in dimethoxyethane[5] gave (VIIIa) quantitatively. The fragmentation product (VIIIa) was acetylated (74%), and the product was treated with toluene-*p*-sulphonic acid in aqueous methanol. The resulting hydroxy-acetate (VIIIb) was oxidised with the Collins reagent and gave the acetoxy-ketone (VIIIc; 82%), m.p. 51—52°, ν_{max} 1726 and 1710 cm^{-1}, δ 1·97 (3H, s), 4·86 (1H, d, J 9·0 Hz), and 5·56 (1H, t, J 8·3 Hz). Passage of (VIIIc) through an active alumina column formed the unstable cyclodecadienone (IXa; almost quantitative yield), λ_{max} 255 nm (sh.; ϵ 1630), ν_{max} 1679 cm^{-1}, δ 5·23, 6·05 (2H, q, J 18 Hz, AB-type), and 5·56 (1H, t, J 9 Hz).

Irradiation of an ethereal solution (0·2%) of (IXa) in a quartz vessel with a 400w high-pressure mercury lamp at 0° under nitrogen for 1 h resulted in the formation of the cyclo-octene (X; 13%). Since no formation of intramolecularly cyclised product was observed, photofission probably proceeds *via* production of the keten radical (XI).†

1,5,5-Trimethyl-8-methylenecyclodeca-6,10-diene (IXb), λ_{max} 213 (ϵ 10,700) and 245 nm (3750), was obtained from

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† The crude photolysis product showed absorptions, assignable to a keten carbonyl and a vinyl group, at 2120 and 917 cm^{-1}. Detailed analysis of the product is now being undertaken.

the cyclodecadienone (IXa) in 70% yield by reaction with methylenetriphenylphosphorane in dimethyl sulphoxide. Photolysis of the former (0.1% solution, 400 w high-pressure mercury lamp, Pyrex filter, 5—10°, 19 h), sensitised with β-acetonaphthone led to the cross-cyclised product (XIIa, 75%), ν_{max} 1670 and 869 cm^{-1}, δ 0.76 (3H, s), 0.91 (6H, s), 4.59, and 4.82 (1H, br. s each), and an unidentified product (10%). Upon osmic acid oxidation, followed by treatment with periodic acid, (XIIa) afforded the cyclopentanone (XIIb) ν_{max} 1755 cm^{-1}, in high yield.

The compounds (XIIa and XIIb) thus obtained may be potential intermediates for the synthesis of longipinenes[6] (XIII).

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[1] M. Brown, *J. Org. Chem.*, 1968, **33**, 162.
[2] C. H. Heathcock and R. A. Badger, *Chem. Comm.*, 1968, 1510.
[3] P. Beak and B. M. Monroe, *J. Org. Chem.*, 1967, **32**, 2778.
[4] For the directive effect of hydroxy-group in peroxy-acid oxidation, see H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1957, 1958; H. B. Henbest, *Proc. Chem. Soc.*, 1963, 159.
[5] J. A. Marshall and C. J. V. Scanio, *J. Org. Chem.*, 1965, **30**, 3019.
[6] The α-isomer has been isolated from the essential oil of *Pinus silvestris*. L. Westfelt, *Acta Chem. Scand.*, 1967, **21**, 159.