Synthesis and Photocyclization of a Cyclodecadienone

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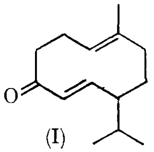
PHOTOCYCLIZATION[1] of the cyclodecadienone (I) could conceivably provide a novel synthetic route to an effective precursor [(II) or (III)] of copaene[2] or bourbonene[3] and might have biogenetic implications.† According to an empirical rule recently formulated,[4] photocyclization of (I) should yield (III) in preference to (II). To examine these questions, we have synthesized the model cyclodecadienone (IV) and now report its photo-chemical behaviour.

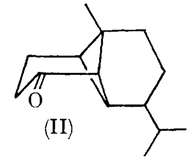
Acetalization of the known enone (V)[5] affords the acetal (VI) (m.p. 107·5—108·5°), which is oxidized by *m*-chloroperoxybenzoic acid in chloroform to yield a 1 : 1 mixture of the epoxides (VIIa) (m.p. 137—138°) and (VIIb) (m.p. 65·5—66·5°). Lithium aluminium hydride reduction of (VII) yields the diols (VIIIa) (m.p. 89—90°) and (VIIIb) (m.p. 106—107°); selective esterification of which with methanesulphonyl chloride in pyridine gives the monomethane sulphonates (IXa) (m.p. 104·5—105·5°) and (IXb) (m.p. 109—110°). Fragmentation of (IXa) or (IXb) with potassium t-butoxide in t-butyl alcohol[6] yields the cyclodecadienone monoacetal (X) (m.p. 50·5—51·5°), which is reduced by lithium aluminium hydride to give the alcohol (XI) (m.p. 46—46·5°).

Direct hydrolysis–dehydration of (XI) has not been accomplished, due to the propensity of (IV) to enter into acid-catalyzed transannular reactions. Effective acetal hydrolysis, without concomitant dehydration, occurs upon heating equal weights of (XI) and oxalic acid in aqueous acetone for 16 hr., to give the crystalline ketol (XII) (m.p. 41·5—43°). Treatment of the derived acetate (XIII) (m.p. 42—43°) with triethylamine at 50° yields a mixture, apparently containing the desired cyclodecadienone (IV) (λ_{max} 265 mμ, ν_{max} 1665) and its $\beta\gamma$-isomer (XIV) (ν_{max} 1695 cm.$^{-1}$).‡

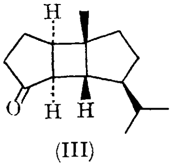
Irradiation of a 0·1% ether solution of the dienone mixture with a Hanovia 440 w high-pressure lamp through Corex, leads to a volatile photoproduct containing 22% of the ketone (XV),[7] 32% of the ketone (XVI), prepared independently by the photoaddition of 3-methylcyclopentenone



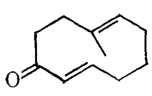
(I)



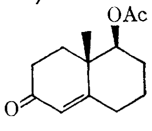
(II)



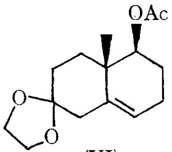
(III)



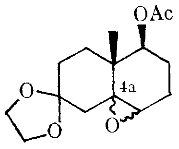
(IV)



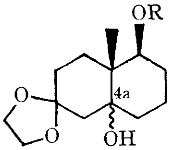
(V)



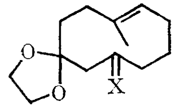
(VI)



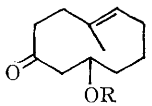
(VII)*



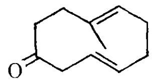
(VIII)* R=H
(IX)* $R=SO_2Me$



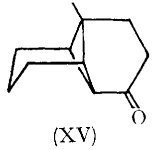
(X) X=O
(XI) X=H,OH



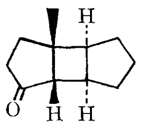
(XII) R=H
(XIII) R=Ac



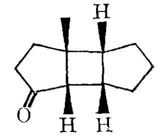
(XIV)



(XV)



(XVI)



(XVII)

* *a* series, 4aβ; *b* series, 4aα (steroid convention).

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† The suggestion has been made (R. A. Barnes, *Anais Acad. Brasil. Cienc.*, 1964, **36**, 238; M. Brown, *J. Org. Chem.*, 1968, **33**, 162) that copaene might arise *via* pigment-sensitised photocyclization of 10-isopropyl-3,7-dimethylcyclodeca-1,3,6-triene, which can be derived rationally from farnesyl pyrophosphate; an alternative cyclization mode would yield β-bourbonene.

‡ Both (IV) and (XIV) may be *cis–trans* mixtures at the C(2–3) or C(3–4) double bond. An effective means of rectifying the mixture has not been found. Attempted v.p.c. leads to the formation of several thermal products, whose structures are now being investigated.

onto cyclopentene, 18% of an unidentified ketone (ν_{max} 1705 cm.$^{-1}$), and several minor products.§

Thus, both major modes of photocyclization of the cyclodecadienone (IV) are realized. While Srinivasan's "Rule of Five"[4] correctly predicts the *predominant* product, the fact that both isomers are produced in substantial amounts indicates that such empirical formulations must be used with caution. The biogenetic connotations of the reaction are being pursued further.

This research was generously supported by P.H.S. Grant and the Alfred P. Sloan Foundation.

(*Received, September 16th,* 1968; *Com.* 1254.)

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§ Co-injection experiments (150 ft. × 0·01 in. Carbowax 20 M) suggest that one of the minor products (3% yield) is the *cis–syn–cis* tricyclic ketone (XVII), which is also formed in the photoaddition of 3-methylcyclopentenone and cyclopentene. This conclusion is tentative, since the material has not been isolated in the pure state.

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[3] J. Krepinsky, Z. Samek, F. Šorm, D. Lamparsky, P. Ochsner, and Y. R. Naves, *Tetrahedron*, 1966, **S. 8**, 53.

[4] R. Srinivasan, Abstracts, 156th National Meeting of the American Chemical Society, San Francisco, California, April, 1968, p. 89P.

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[7] C. H. Heathcock, R. A. Badger, and J. W. Patterson, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 4133.