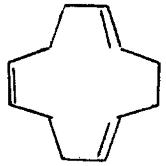
Tetrahedron Letters No.5, pp. 387-390. 1970. Pergamon Press. Printed in Great Britain.

# PHOTOLYSIS OF CYCLODODECA-1,5,9-TRIENE

C.J. Attridge and Miss S.J. Baker,
Imperial Chemical Industries Limited,
Petrochemical & Polymer Laboratory,
The Heath, Runcorn, Cheshire.

(Received in US 2 December 1969; accepted for publication 24 December 1969)

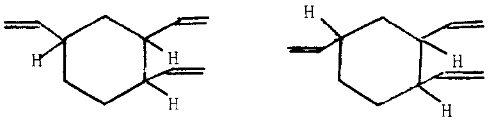
We have observed that ultraviolet photolysis of *cis*, *trans*, *trans*-cyclododeca-1,5,9-triene (I) yields, not only the previously reported[1] *cis*-*trans* double bond isomers, but at least two other significant products, one of which has been unambiguously identified as an isomeric mixture of 1,2,4-trivinylcyclohexanes (II,III):



I

(a) (b)

II



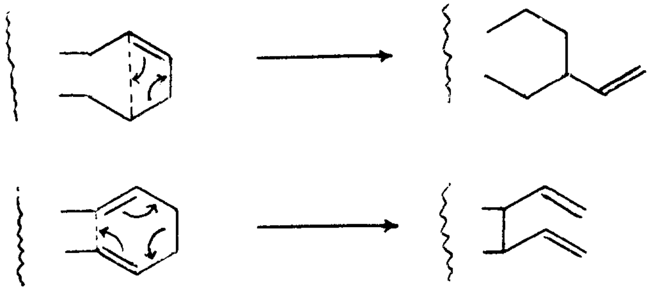
(a) (b)

III

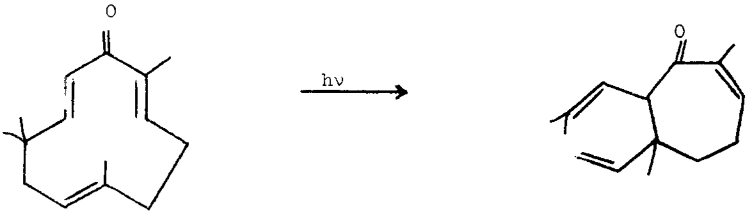
Irradiation of *cis*, *trans*, *trans*-cyclododeca-1,5,9-triene in ethereal solution with a 450 Watt medium pressure mercury lamp for 137 hours gave a 20% conversion to the following products; *trans*, *trans*, *trans*-(25%) and *cis*, *cis*, *trans*-(29%) - cyclododeca-1,5,9-triene, an isomeric mixture of 1,2,4-trivinylcyclohexanes (13%) and a further isomer of cyclododecatriene (24%) which has been tentatively identified as cyclododeca-1,4,7-triene or cyclododeca-1,4,8-triene. A g.l.c./mass spectrum of the product mixture gave molecular ions of m/e 162 and similar olefinic breakdown patterns for all the major products, confirming their isomeric nature. The cyclododeca-1,5,9-triene isomers were identified by comparison of their g.l.c. retention times and infrared spectra with those of standard samples. A specific study of this type of photo-induced *cis-trans* isomerisation has been reported by Nozaki and his coworkers,[1] who obtained similar results with regard to the formation of these products. G.l.c. of the product mixture showed two peaks of retention time approximately half that of the cyclododecatriene isomers (185°, 5M carbowax), which were identified as mixtures of *cis*, *trans*, *trans*-(IIa) and *cis*, *trans*, *cis*-(IIb) and *trans*, *trans*, *trans*-(IIIa) and *trans*, *trans*, *cis*-(IIIb) 1,2,4-trivinylcyclohexane by comparison of the infrared spectra and g.l.c. retention times of II and III with independently prepared samples. The proton n.m.r. and mass spectra of II were also consistent with this assignment. Pure samples of *ortho trans* (II) and *ortho cis* (III)-12,4,-trivinylcyclohexane were prepared, by the method of Rienäcker[2] and Wilke[3,4], by pyrolysis of *cis*, *trans*, *trans*-cyclododeca-1,5,9-triene at 450-500°; the product mixture was shown by g.l.c. to contain a mixture of *ortho trans* (II): *ortho cis* (III) in the ratio 35:65. The photochemical reaction was considerably more stereospecific in giving a ratio of *ortho cis*: *ortho trans* of 11:89. The additional isomer of cyclododecatriene was only partially resolved on g.l.c. from the cyclodeca-1,5,9-triene isomers, which made it difficult to trap a sample of high purity. However infrared, proton n.m.r. and ultraviolet spectra of mixtures containing about 60% of this component indicated the presence of both *cis* and *trans* double bonds, no vinyl groups and no conjugated species. It was therefore tentatively concluded that this material was probably cyclododeca-1,4,7-triene or cyclododeca-1,4,8-triene.

Attempts to increase the yield of 1,2,4-trivinylcyclohexane by adding cuprous chloride or organic sensitisers, such as acetophenone, were unsuccessful. Also the formation of 1,2,4-trivinylcyclohexane did not occur with irradiation from a 3 Watt low pressure mercury lamp for 200 hours.

It appears probable, as suggested by Rienäcker[4] for the thermal reaction, that two essentially independent processes occur in the formation of 1,2,4-trivinylcyclohexane; a ring contraction, involving one double bond, analogous to the known contraction of cycloocta-1,5-diene to 4-vinycyclohexane,[5] and a Cope rearrangement.



Orbital symmetry considerations[6] suggest that a concerted photochemical [3,3] Cope type migration, which would require the difficult suprafacial-antarafacial interaction of the allyl systems in the transition state, is unlikely and no clear cut example of this type of reaction is known. While the preliminary results presented here do not justify any firm conclusions, the failure of triplet sensitisers to promote the reaction and the stereospecific formation of the *ortho trans* isomer inclines us to suggest that a concerted photochemical [3,3] process may be involved, which occurs as a consequence of the unusual reactivity of *trans* double bonds in certain conformers of medium size rings.[7] The all *trans* medium ring zerumbone (IV) has recently been reported[11] to undergo a very similar photo-catalysed Cope type rearrangement to ψ-photozerumbone (V).



IV

V

## REFERENCES

1. H. Nozaki, Y. Nisikawa, M. Kawanisi and R. Noyori, Tetrahedron, 23, 2173, (1967).
2. We are indebted to Dr. R. Rienäcker of the Max-Planck-Institut für Kohlenforschung, Mulheim-Ruhr, for providing infrared spectra of the products from this reaction.
3. G. Wilke and R. Rienäcker, German Patent, 1,065,413; British patent, 848, 637.
4. R. Rienäcker, Doctoral dissertion, Bern, 1958; Brenstoff-Chem., 45, 206, (1964).
5. G.M. Whitesides, G.L. Goe and A.C. Cope, J. Amer. Chem. Soc., 91, 2608, (1969).
6. R.B. Woodward and R. Hoffman, J. Amer. Chem. Soc., 87, 2511, (1965).
7. e.g. Both *cis*, *trans*-cycloocta-1,5-diene[8] and the *trans* double bond of the 1:1 butadiene:benzene adduct[9] undergo 'disallowed' thermal (2+2) dimerisations. Also *trans*, *trans*-cyclodeca-1,5-diene undergoes a thermal Cope rearrangement[10] to 1,2-divinylcyclohexane at only 70°.
8. K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhom and J. Schneider, Annalen, 589, 122, (1954).
9. K. Kraft and C. Koltzenburg, Tet. Letters, 4357, (1967).
10. C.A. Grob, H. Link and P.W. Scheiss, Helv. Chim. Acta, 46, 483, (1963); C.A. Grob and P.N. Scheiss, Angew. Chem., 70, 502, (1958).
11. H.N. Subba Rao, N.P. Damodaran and S. Dev, Tet. Letters, 227, (1967).