Tetrahedron Letters No.25, pp. 2415-2417, 1967. Pergamon Press Ltd. Printed in Great Britain.

PHOTOCHEMICAL VALENCE ISOMERIZATION OF OXOBICYCLIC ANALOGS OF NORBORNADIENE

E. Payo, L. Cortés, J. Mantecón, C. Rivas and G. de Pinto

Department of Chemistry, Instituto Venezolano de Investigaciones
Científicas, Apartado 1827, Caracas, Venezuela

(Received 20 March 1967)

The photochemical valence isomerization of norbornadiene and its derivatives to quadricyclene and its derivatives by direct and triplet sensitized photolysis has been studied by several workers.[1,2,3] The reaction is characterized by an electronic reorganization in which two π bonds are broken with the subsequent formation of two new σ bonds.

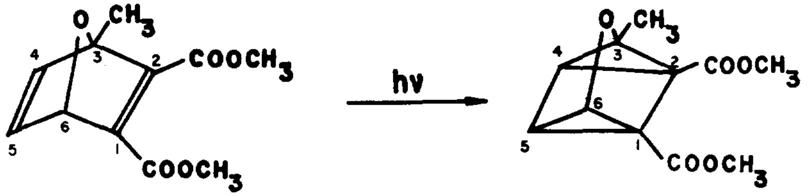
We now wish to report the photolysis of the first one of a series of oxobicyclic compounds obtained by Diels-Alder reaction between methyl-substituted furans and dimethyl acetylenedicarboxylate.

Irradiation of a 4% solution of 3,6-endoxo-3-methyl-$\Delta^{1,4}$-dihydrophthalic acid dimethyl ester (I) in carbon tetrachloride in a nitrogen atmosphere, after 16 hours exposure to U.V. light, resulted in an 80% conversion to the oxoquadricyclene derivative II.*

The product was identified by its nmr spectrum which allows the unequivocal assignment of the quadricyclene structure II. The features of the nmr spectrum are given in Table I.[4]

---

* The irradiations were carried out in a pyrex vessel fitted with a quartz immersion well cooled at -10°C using a Hanovia 450-W lamp.



I

II

TABLE I

Nmr Spectral Data on the Oxoquadricyclene II

Protons	Chemical shift,[a] ppm	Integral protons	Multiplicity[b]	Coupling constant, cps
C-4,5	2.60	2	m(AB)	$J_{4,5} = 2.8$ $J_{5,6} = 4.0$
C-6	4.80	1	d	$J_{5,6} = 4.0$
$3\text{-}CH_3$	1.60	3	s	

[a] TMS as internal standard in CCl_4 solution. The two $-COOCH_3$ signals appear at ~3.6 ppm. [b] m, multiplet; d, doublet; s, singlet.

The characteristic bands in the nmr spectrum of the product are those of the tertiary hydrogen atoms on the cyclopropane ring.[2,3] Protons at C-4 and C-5 form an AB spectrum at high field ($\delta = 2.60$ ppm) while the proton at C-6 appears at low field ($\delta = 4.80$ ppm) due to the action of the neighboring oxygen. The coupling between protons at C-5 and C-6 appears very neatly (Fig.1). The difference between the nmr spectra of the starting material and that of the product are very marked. In the former, protons at C-4 and C-5 also exhibit an AB type spectrum out at $\delta = 7.00$ ppm and the coupling constant $J_{5,6}$ is only 2 cps. On the other hand, the proton at C-6 appears also at lower field ($\delta = 5.5$ ppm) than in the quadricyclenic product.

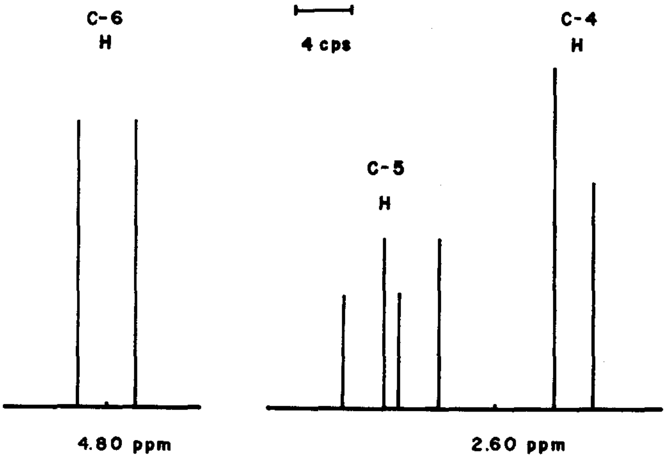


Fig. 1 Nmr spectrum of compound II

The choice of compound I to carry out this attempt was justified by the presence of the methyl group at the C-3 position which would facilitate the interpretation of the nmr spectrum of the expected oxoquadricyclene product.

REFERENCES

1. S. J. Cristol and R. L. Snell, J. Am. Chem. Soc., 80, 1950 (1958).
2. G. S. Hammond, N. J. Turro, and A. Fischer, J. Am. Chem. Soc., 83, 4674 (1961).
3. P. G. Gassman, D. H. Aue, and D. S. Patton, J. Am. Chem. Soc., 86, 4211 (1964).
4. Elemental analysis of a sample of II fully agrees with the proposed structure.