Tetrahedron Letters No.9, pp. 779-780, 1967. Pergamon Press Ltd. Printed in Great Britain.

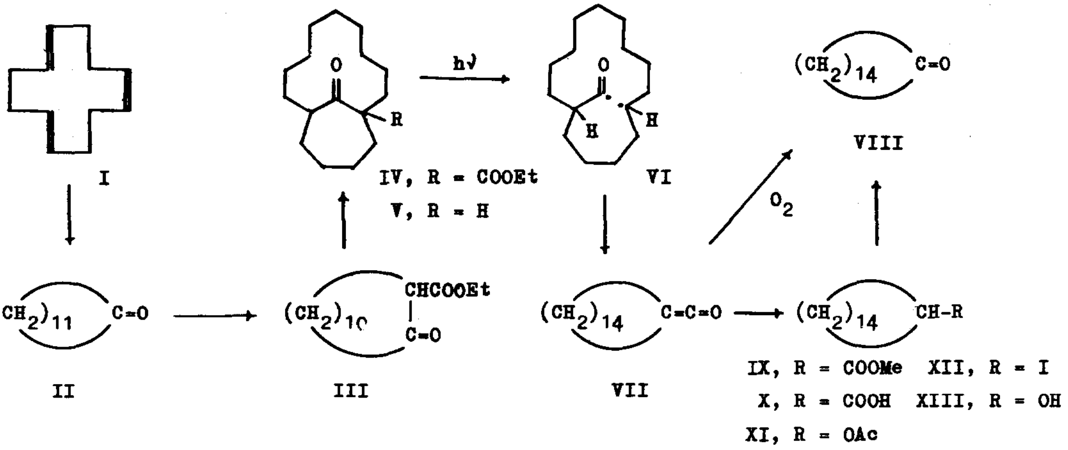
A NOVEL SYNTHESIS OF CYCLOPENTADECANONE FROM CYCLODODECANONE

H. Nozaki, T. Mori and R. Noyori

Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

(Received 6 December 1966)

We wish to report photochemical cleavage of a bicyclic ketone V yielding cyclopentadecanone (Exaltone) (VIII) or its precursor IX. The ketone V has been obtained from cyclododecanone (II) (1), hence this constitutes the first practical preparation of VIII from 1,5,9-cyclododecatriene (I), a readily available cyclotrimer of butadiene (2).



Condensation of 2-carbethoxycyclododecanone (III) (3) with 1,4-dibromobutane in the presence of sodium hydride yielded 1-carbethoxybicyclo[9.4.1]hexadecan-16-one (IV) as a crude oil. The corresponding carboxylic acid (4) melted at 141-142° (dec). Hydrolysis of IV followed by decarboxylation gave 65-72% yields (based on III) of bicyclo[9.4.1]-hexadecan-16-one (V) (4), m.p. 86-87°, $\nu_{C=O}$ (CCl_4) 1700 cm^{-1}. The ketone V did not give any carbonyl derivatives and the stereochemistry will be discussed in the full paper.

Photochemical reaction of V was effected by irradiating its carbon tetrachloride solution with a high pressure mercury arc lamp under streaming oxygen to afford 20-30% yields of VIII (5), m.p. and mixed m.p. 60-61°, along with considerable amount of hydrocarbon(s) and tarry materials.

Irradiation of a solution of V in carbon tetrachloride and methanol (6:1 mixture) gave a 73% yield of methyl cyclopentadecanecarboxylate (IX), b.p. 105-110°/0.15 mm, IR (neat) 1740, 1200 and 1165 cm^{-1} (4). Hydrolysis yielded cyclopentadecanecarboxylic acid (X) (4), m.p. 65-66°, in 95% yield. Irradiation of a benzene solution of X in the presence of iodine and mercuric acetate (6) gave a mixture of cyclopentadecyl acetate (XI) and iodocyclopentadecane (XII), which was converted into pure XI (7), b.p. 105-108°/0.14 mm, by acetolysis (74% yield based on X). Hydrolysis of XI and the subsequent oxidation (8) yielded VIII in 40-50% overall yields with respect to V.

In accord with the finding by Gutsche *et al.* (9) the photolysis of the bicyclic ketone V would probably proceed *via* α-fission intermediate VI and the corresponding ketene VII. The presence of VII among the photolysis products in cyclohexane was proven by IR absorption $\nu_{C=C=O}$ (cyclohexane) at 2140 cm^{-1}, but attempted isolation failed to success. This ketene is then transformed into VIII or IX depending on the reaction conditions used. Attempts of improving the yields as well as analogous preparation of muscone are in progress.

REFERENCES

1. (a) H. Nozaki and R. Noyori, *J. Org. Chem.* **30**, 1652 (1965); (b) E. P. Zinkevich, A. D. Treboganov, B. I. Mitsner, A. A. Kraevskii, I. K. Sarycheva and N. A. Preobrazhenskii, *Zh. Organ. Khim.* **1**, 1587 (1965); *Chem. Abstr.* **64**, 611 (1966).
2. G. Wilke, *Angew. Chem.* **75**, 10 (1963).
3. S. J. Rhoads, J. C. Gilbert, A. W. Decora, T. R. Garland, R. J. Spangler and M. J. Urbigkit, *Tetrahedron* **19**, 1625 (1963).
4. All novel compounds gave correct C,H-analyses.
5. L. Ruzicka, M. Stoll and H. Schinz, *Helv. Chim. Acta* **9**, 249 (1926).
6. This procedure was carried out according to the method of D. H. R. Barton, H. P. Faro, E. P. Serebryakov and N. F. Woolsey, *J. Chem. Soc.* 2438 (1965).
7. M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta* **32**, 256 (1949).
8. P. G. Stevens and J. L. E. Erickson, *J. Amer. Chem. Soc.* **64**, 144 (1942).
9. (a) C. D. Gutsche and C. W. Armbruster, *Tetrahedron Letters* 1297 (1962); (b) C. D. Gutsche and J. W. Baum, *Ibid.* 2301 (1965).

Acknowledgement. The authors are grateful to Prof. K. Sisido for help and encouragement.