**Tetrahedron Letters No.26, pp. 1739-1742, 1964. Pergamon Press Ltd.
Printed in Great Britain.**

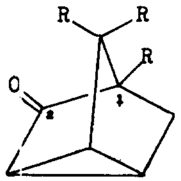
TWO PHOTOCHEMICAL REACTIONS
OF CYCLOCAMPHANONE

Peter Yates and Lindsay Kilmurry
Department of Chemistry, University of Toronto
Toronto 5, Ontario, Canada

(Received 8 May 1964)

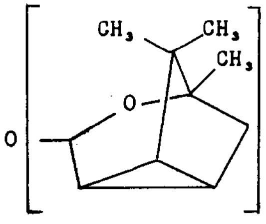
We report two novel reactions observed during studies of the photochemistry of d-cyclocamphanone (I). Irradiation of a 1% solution of I in methanol or ethanol under nitrogen with a 450-w. Hanovia high-pressure mercury-vapor lamp gives oils, whose infrared spectra differ, but in each case show only a very weak carbonyl-stretching band. These oils are each converted on standing exposed to the atmosphere for 48 hours to a colorless, crystalline solid, m.p. 152-154° (Found: C, 75.36; H, 9.49; M.W. (osm.) 309. $C_{20}H_{30}O_3$ requires: C, 75.43; H, 9.50; M.W. 318). The infrared spectrum (CCl_4) of this product, which shows no bands characteristic of hydroxyl, carbonyl or ethylenic groups, includes bands at 3.26, 7.25, 7.34, 9.74, 9.96, 10.13 and 10.52 (vs) μ; its ultraviolet spectrum shows no appreciable absorption $>$ 210 mμ. It is assigned structure II on the basis of these data, its conversion to the lactone III on oxidation with chromic acid, and its n.m.r. spectrum (CCl_4), which is interpreted as follows: $\delta = 5.33$ (doublet, $J \sim 1.5$ c./s.; acetal H coupled with adjacent cyclopropyl H), 1.65 - 2.1 (ABX system with $J_{AB} = 12$, $J_{AX} \sim 1.5$, $J_{BX} \sim 0$ c./s.; CH_2 with one H coupled with adjacent cyclopropyl H), 1.1 - 1.4

(complex group of signals; cyclopropyl H), 0.94 and 0.87 (intensity ratio ~2:1; CH_3).

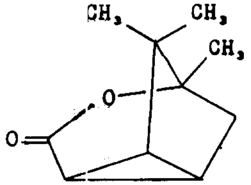


I, R = CH_3

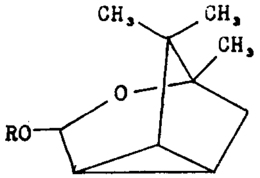
VIII, R = H



II



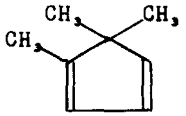
III



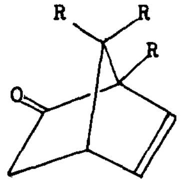
IV (R = CH_3 or C_2H_5)

The lactone III has m.p. 180-181° (sealed cap.), $\lambda_{max}^{CCl_4}$ 3.26, 5.74, 9.26, 9.37 μ, λ_{max}^{EtOH} 231 mμ (ε 41) (Found: C, 72.09; H, 8.53; M.W. (osm.) 178. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49; M.W. 166). Its n.m.r. spectrum (CCl_4) shows a complex group of signals at $\delta = 1.4 - 2.1$, attributed to overlap of multiplets due to CH_2 and cyclopropyl H's, the latter being shifted to lower field than in the case of II because of the adjacent carbonyl group (1), and two signals at $\delta = 1.07$ and 0.82 of relative intensity ~1:2, assigned to the CH_3 groups. It was shown to be identical with the product obtained by treatment of I with peracetic acid (2). Reduction of III with lithium aluminum hydride gives rise to II.

The bis acetal II is considered to be formed originally by hydrolysis of the acetals IV; the infrared and n.m.r. spectra of the oily photochemical products which give rise to II are in accord with their consisting mainly of anomers of IV. The formation of an aldehyde derivative on photolysis of I is reminiscent of the formation of α-campholenaldehyde on photolysis of camphor (3,4). It appears unlikely, however, that IV could arise from an analogous unsaturated aldehyde formed from I. We suggest that photolysis of I proceeds via cleavage of the 1-2 C—C bond followed by bond formation between C.1 and the oxygen atom of the carbonyl group, held in close propinquity by virtue of the geometry of the bicyclo[3.1.0]hexane system.



V



VI, R = H

VII, R = CH_3

A second, minor product was detected in the distillate obtained on removal of the solvent from the ethanol irradiation mixture, which showed strong ultraviolet absorption with λ_{max}^{EtOH} 255 mμ. This product was shown to be 1,5,5-trimethylcyclopentadiene (V) by isolation of its adduct with N-phenylmaleimide, m.p. 108-109° (Found: C, 76.34; H, 6.85; N, 4.88. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98), and comparison of this with an authentic sample.* The formation of a cyclopentadiene derivative in the photochemical reaction may be related to the observation (5,6) that cyclopentadiene is formed in high yield on photolysis of dehydronorcamphor (VI); it is possible that V arises in the present case *via* photoisomerization of I to VII.

Lemal and Shim (8)[†] have recently investigated the mercury-sensitized photolysis of the related nortricyclanone (VIII) in the vapor phase; here the reaction not unexpectedly follows a different course, with loss of carbon monoxide and formation of tricyclo$[2.2.0.0^{2,6}]$hexane and benzene.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for the support of this research.

REFERENCES

(1) *Cf*. P. Yates and C.D. Anderson, *J.Am.Chem.Soc*. **85**, 2937 (1963).

(2) *Cf*. R.R. Sauers, *Tetrahedron Letters*, 1015 (1962).

(3) R. Srinivasan, *J.Am.Chem.Soc*. **81**, 2604 (1959).

(4) *Cf*. P. de Mayo in "Advances in Organic Chemistry: Methods and Results", ed. R.A. Raphael, E.C. Taylor and H. Wynberg, Vol. II, Interscience, 1960, p. 367.

(5) G.O. Schenk and R. Steinmetz, *Chem.Ber*. **96**, 520 (1963).

(6) D.I. Schuster, M. Axelrod and J. Auerbach, *Tetrahedron Letters*, 1911 (1963).

(7) S. McLean and P. Haynes, to be published.

(8) D.M. Lemal and K.S. Shim, *J.Am.Chem.Soc*. **86**, 1550 (1964).

---

[*] We thank Professor S. McLean, University of Toronto, for generously providing us with this sample, obtained in the course of studies on the methylation of cyclopentadiene (7).

We thank Professor D.M. Lemal, University of Wisconsin, for informing us of his results prior to publication.