Tetrahedron Letters No. 6, pp. 213-214, 1962. Pergamon Press Ltd. Printed in Great Britain.

THE STRUCTURE OF "BENZALYCYCLANONE PEROXIDES" OBTAINED BY AIR OXIDATION OF BENZALCYCLANONES

Alfred Hassner and Theodore C. Mead

Department of Chemistry, University of Colorado, Boulder, Colorado

(Received 14 February 1962, in revised form 2 March 1962)

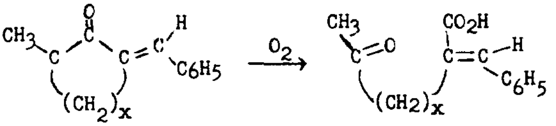
UPON prolonged exposure to air of 2-benzal-6-methylcyclohexanone (I), Cornubert and co-workers[1] were able to isolate a product, m.p. 122-123°, to which they assigned the structure of a peroxide of I on the basis of elemental analysis and a positive starch iodide test. With other cyclanones they were not able to isolate well defined products, but elemental analysis of the crude products after exposure to air indicated a certain percentage of oxygen uptake, and therefore they assumed that the mixture contained peroxides.

In connection with related work we re-examined the reaction of <u>trans</u>-2-benzal-6-methylcyclohexanone (I) with oxygen in the presence and absence of solvents and found that the compound, m.p. 122°, obtained in quantitative yield (based on consumed starting material) was actually a cleavage product, namely 2-benzal-6-oxoheptanoic acid (II) rather than a peroxide. In a typical run 20 g of I were heated on a steambath to a melt, a trace of benzoyl peroxide was added and dry air was bubbled through for 160 hr. The darkened and solidified melt was dissolved in ether and extracted with 5% sodium hydroxide. Starting ketone I (8.4 g) was recovered from the ether. The aqueous layer was acidified and worked up as usual to furnish 12.5 g of keto acid II, which upon recrystallization from benzene melted

---

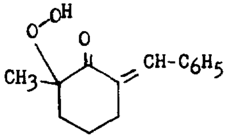
[1] R. Cornubert, M. Andre, M. de Demo, P. Louis and A. Strebel, <u>Bull. Soc. Chim. Fr.</u> [5], <u>5</u>, 544 (1938).

at 122°; neutr. equiv.: 232 (calc.: 232). Pure II, unlike crude II, did not give a positive starch-iodide test. The latter test must therefore be attributed to minor peroxide impurities. The structure of the keto acid (II) was evident from its infrared (2650 cm^{-1}, broad, CO_2H; 1700 cm^{-1}, CO_2H; 1665 cm^{-1}, conj. C = O; 1610 cm^{-1}) and ultraviolet spectra (λ_{max}^{MeOH} 264 mμ (ε 19,600), characteristic[2] of <u>trans</u> α-substituted cinnamic acids), its solubility in sodium bicarbonate, and a quantitative positive iodoform test accompanied by conversion to the known 2-benzaladipic acid,[3] m.p. 173°.



I x = 3 **II x = 3**

Ia x = 2 **IIa x = 2**



III

That the oxidation of I to II is probably a free radical reaction is indicated by the catalytic effect of benzoyl peroxide and of ultraviolet light in speeding up the reaction. It is mechanistically probable that a hydroperoxide of type III is an intermediate in the reaction, but efforts to isolate such an intermediate have been to no avail. In the case of 2-benzal-5-methylcyclopentanone (Ia) air oxidation led to 2-benzal-5-oxohexanoic acid IIa (81%), m.p. 138°, neutr. equiv.: 221 (calc. 218), λ_{max}^{MeOH} 262 mμ (ε 16,000), ν_{max}^{KBr} 2650 cm^{-1} (broad, CO_2H), 1700 cm^{-1} (CO_2H), 1670 cm^{-1} (conj. C = O), 1620 cm^{-1} (conj. C = C). We have observed analogous oxidative cleavages with the 2-benzal derivatives of 3,6-dimethylcyclohexanone and 5-ethylcyclopentanone but not with 2-benzal-6,6-dimethylcyclohexanone nor with the saturated 2-benzyl-6-methylcyclohexanone.

<u>Acknowledgement</u> - We are grateful to the National Institutes of Health for financial support of this work. (Grant CY-4474).

---

[2] H. Ley, <u>Ber. Dtsch. Chem. Ges.</u> 50, 243 (1917).

[3] R. Poggi and V. Guastalla, <u>Gazz. Chim. Ital.</u> 61, 405 (1931).