

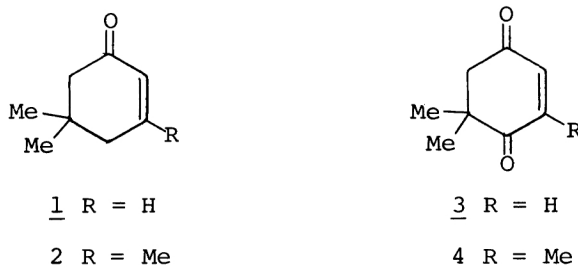
## THE OXIDATION OF 2-CYCLOHEXEN-1-ONES TO 2-CYCLOHEXENE-1,4-DIONES

Vernon J. FREER and Peter YATES\*

Lash Miller Chemical Laboratories, University of Toronto, Toronto  
Ontario, Canada M5S 1A1

Treatment of 5,5-dimethyl-2-cyclohexen-1-one and isophorone with phosphomolybdic acid, potassium dichromate, cupric sulfate, and air gives 5,5-dimethyl- and 3,5,5-trimethyl-2-cyclohexene-1,4-dione, respectively. In the latter reaction treatment of the crude product with aqueous base leads to the formation of 2,3,6,7-tetrahydro-2,2,6,6,-tetramethylantracene-1,4,5,8-tetrone.

Hosokawa et al.<sup>1)</sup> have recently reported the direct oxidation of 5,5-dimethyl-2-cyclohexen-1-one (1) and isophorone (2) with *t*-BuOOH and Pd(II) catalysts to the enediones 3 (32% yield) and 4 (49-55% yield (GLC)), respectively.

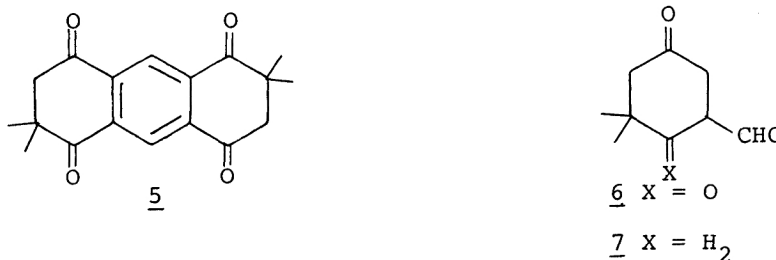


The conversion of 2 to 4 has previously been reported by a multi-step sequence<sup>2)</sup> and, in the patent literature, by direct oxidation.<sup>3)</sup> We have found that the method of choice for the preparation of 3 and 4 is that detailed below, based on the patent literature.<sup>3)</sup> This gives each in 60% yield (isolated).

5,5-Dimethyl-2-cyclohexen-1-one (1)<sup>4)</sup> (4.0 g, 0.032 mol) was added to phosphomolybdic acid (0.0148 g, 0.0089 mmol), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.0018 g, 0.006 mmol), and CuSO<sub>4</sub>·5H<sub>2</sub>O (0.0071 g, 0.045 mmol). The mixture was stirred and maintained at 100 °C while air was blown into it through a gas delivery frit at a flow rate of 300 mL/

min. Consumption of starting material was complete after 84 hours. The viscous black mixture was extracted with diethyl ether (100 mL) and the extract was washed with distilled water (4 x 50 mL) and saturated brine (2 x 50 mL) and dried over  $\text{MgSO}_4$ . Removal of the solvent gave a dark brown oil, which was distilled (0.5 mmHg, 90 °C) to give 3 as a clear yellow oil which crystallized upon addition of hexanes and cooling with ice; the yield was 2.24 g (60%); mp 39.0–39.5 °C.<sup>5)</sup>

In a run where the crude product from the oxidation of 2 was treated with aqueous base, an interesting by-product,  $\text{C}_{18}\text{H}_{18}\text{O}_4$ , was obtained to which we assign structure 5: IR ( $\text{CCl}_4$ )  $\lambda_{\text{max}}$  5.87  $\mu\text{m}$ ; UV (MeOH)  $\lambda_{\text{max}}$  238 ( $\epsilon$  58,000), 262 ( $\epsilon$  40,000), 324 ( $\epsilon$  3,000) nm; NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (s, 12H), 3.00 (s, 4H), 8.73 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.5 (q), 45.8 (s), 51.8 (t), 126.8 (d), 137.1 (s), 138.6 (s), 194.4 (s), 199.5 (s). This is considered to arise via base-catalyzed condensation of 4 with 6, formed by over-oxidation of 2, followed by air oxidation of the resulting dihydrobenzene derivative. Oxidation of the methyl group of 2 finds analogy in the oxidation of 2 to 7 by molecular oxygen in the presence of  $\text{FeCl}_3$  catalyst<sup>6)</sup> and to both 4 and 7 by selenium dioxide in dioxane.<sup>7)</sup>



We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

#### References

- 1) T. Hosokawa, S. Inui, and S.-I. Murahashi, *Chem. Lett.*, 1983, 1081.
- 2) J.N. Marx and F. Sondheimer, *Tetrahedron, Suppl.* 8, Part I, 1 (1966).
- 3) M. Seuret and E. Widmer, *Belg. Patent* 830 723 (1975); *Chem. Abstr.*, 84, 164269e (1976); *cf.* H.G.W. Leuenberger, W. Boguth, E. Widmer, and R. Zell, *Helv. Chim. Acta*, 59, 1832 (1976).
- 4) G.A. Hiegel and P. Burk, *J. Org. Chem.*, 38, 3637 (1973).
- 5) In the case of 4 100 hours were required for complete consumption of 2.
- 6) S. Ito and M. Matsumoto, quoted in Ref. 1.
- 7) D.J. Burnell, R. Grewal, and P. Yates, unpublished results.

(Received August 20, 1984)