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

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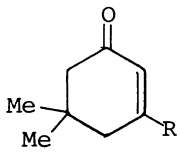
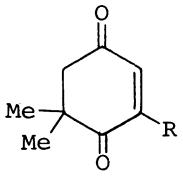
Treatment of 5,5-dimethyl-2-cyclohexen-1-one and isophorone with phosphomolybdic acid, potassium dichromate, cupric sulfate, and air gives 5,5-dimethyl- and 3,5,5-trimethyl-2-cyclohexene-1,4-dione, respectively. In the latter reaction treatment of the crude product with aqueous base leads to the formation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

Hosokawa et al.[1] 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.



1 R = H

2 R = Me



3 R = H

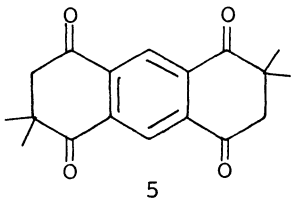
4 R = Me

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

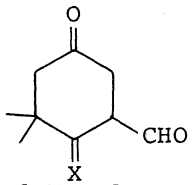
5,5-Dimethyl-2-cyclohexen-1-one (1)[4] (4.0 g, 0.032 mol) was added to phosphomolybdic acid (0.0148 g, 0.0089 mmol), $K_2Cr_2O_7$ (0.0018 g, 0.006 mmol), and $CuSO_4.5H_2O$ (0.0071 g, 0.045 mmol). The mixture was stirred and maintained at 100 °C while air was blown into it through a gas delivery frit 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 $MgSO_4$. 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.[5)]

In a run where the crude product from the oxidation of 2 was treated with aqueous base, an interesting by-product, $C_{18}H_{18}O_4$, was obtained to which we assign structure 5: IR (CCl_4) λ_{max} 5.87 μm; UV (MeOH) λ_{max} 238 (ε 58,000), 262 (ε 40,000), 324 (ε 3,000) nm; NMR ($CDCl_3$) δ 1.33 (s, 12H), 3.00 (s, 4H), 8.73 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 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 $FeCl_3$ catalyst [6)] and to both 4 and 7 by selenium dioxide in dioxane.[7)]



5



6 X = O

7 X = H_2

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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.

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