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OXIDATIVE DIMERISATION OF 2-ALKENYLCYCLOPENT-2-ENE-1,4-DIONES BY MANGANESE DIOXIDE

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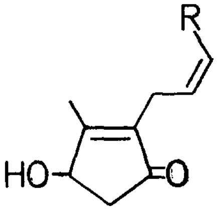
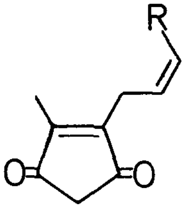
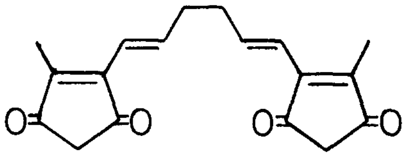
Cyclopentenolones of type (1) constitute the alcohol fragment of the natural rethrins. Knowledge of their oxidation reactions is of general interest in connection with the rapid and little understood deterioration of such insecticidal films. During a study of the reaction between manganese dioxide and the synthetic model compound (±)-allethrolone (1, R=H) we have found that, in addition to the expected dione (2, R=H), oxidative coupling occurs to give the novel tetraone (3).*



(I)



(2)



(3)

Shaking allethrolone (1, R=H) with finely ground manganese dioxide[1] in carbon tetrachloride at 25^{o}, rapidly produced the cyclopentenedione (2, R=H), b.p. $62-64^{o}/0.3$ mm., n_D^{20} 1.5170, $\lambda_{max.}$ (EtOH) 242 mμ (ε 12,600) $\nu_{max.}$ (film) 1745, 1705 (C=O, cyclopentenedione[2,3]), 1640, 1266, and 995, 925 (terminal vinyl) $cm.^{-1}$, τ 4.15 ddt (J 16,9,6)($-CH_2-\underline{CH}=CH_2$), 4.7-5.1 m ($-CH=\underline{CH_2}$), 6.77 d (J6)($-\underline{CH_2}-CH=$), 7.12 ($-COCH_2CO-$)(disappears on treatment D_2O/Na_2CO_3/T.H.F.), 7.94 ($=C.\underline{CH_3}$), $^m/e$ 150 , bis-2,4-dinitrophenylhydrazone m.p. 256^{o} (EtOH/$C_6H_5NO_2$). Quantitative study indicated that 0.53 g. of allethrolone required 4.4 g. (14.7 equivs.) of manganese dioxide (from the batch used) to convert it to (2, R=H)(60%) in 5 min., and longer periods of reaction did not diminish this yield.

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*This compound was isolated and investigated independently in our two laboratories.

Reactions with larger excess of reagent, and for longer periods, [especially in hot solvent ($CHCl_3$,C_6H_6)], gave a yellow crystalline solid (∿8%), m.p. 187-188°, for which elemental analysis and molecular weight [$^m/e$ 298.1208; $C_{18}H_{18}O_8$ requires 298. 1205] agree with a cyclopentenedione dimer structure. The same dimer (∿6%) is obtained by similar treatment (MnO_2/hot $CHCl_3$) of dione (2, R=H).

The dimer shows i.r. maxima at 1745, 1705 (C=O, cyclopentenedione [2,3]), 1640, 1590 (C=C, diene), and 980 $cm.^{-1}$ (<u>trans</u>-disubstituted double bond), and a u.v. maximum at 297 mμ (ε 25,700). The n.m.r. shows resonances at τ 7.92 (singlet, 6H, 2X=C.$C\underline{H}_3$), and τ 7.1 (singlet, 4H, disappears on treatment D_2O), similar to dione (2, R=H), and also resonances at τ 7.5 (multiplet, 4H, 2X =C.$C\underline{H}_2$-) 3.66 (doublet, $\underline{J}$ 16, 2H, 2X=C$\underline{H}$-, <u>trans</u>-disubstituted double bond), and 2.82 (doublet of multiplets, $\underline{J}$∿16, 2H, 2X=C$\underline{H}$-). Irradiation at the frequency (τ 2.82) due to one of the olefinic protons collapses both the multiplet at τ 7.5 (due to allylic-CH_2-) and the doublet centred at τ 3.66 (due to two olefinic protons) to singlet resonances. The data presented are thus consistent with formulation (3). Further support is found in the mass spectrum, where the base peak at $^m/e$ 149.0603[$C_9H_9O_2$ requires 149.06025] indicates the ease with which the molecule fragments into two identical parts to give a stabilised allylic ion. This ion then fragments further in a manner similar to the dione (2, R=H), dione (2, R=-CH=CH_2), and other 2-alkenylcyclopent-2-ene-1-ones.[4]

Oxidation of natural (+)-pyrethrolone (1, R=-CH=CH_2) with manganese dioxide in carbon tetrachloride, gives a distillable liquid dione (2, R=-CH=CH_2), identical to that obtained previously[3] using CrO_3/pyridine as oxidant, together with a non-distillable residue. Preliminary spectral examination of this residue indicates that it also contains a dimeric product similar to that obtained from allethrolone.

It seems reasonable that the dimerisations result from radical coupling, probably involving hydrogen abstraction by manganese dioxide[5] from the doubly-allylic methylene group in (2, R=H). The resulting bis-allylic radical couples preferentially at the primary terminus. Further investigations are in progress.

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