The Oxidation of Ethyl α-Methylacetoacetate by Lead Dioxide

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THE oxidation of aliphatic ketones with lead dioxide gives C–C-coupled dehydrogeno-dimers.[1] We now report that the oxidation of ethyl α-methylacetoacetate with lead dioxide gives the C–C-coupled dehydrogeno-dimer, but also a novel product derived from the C–C-coupled dehydrogeno-dimer.

Ethyl α-methylacetoacetate (0·5 mol.), heated in refluxing benzene for 61 hr., with commercial lead dioxide (1·0 mol.), gave the enol-ether (I) (18%†), b.p. 91—93°/0·04 mm., and the C–C coupled dehydrogeno-dimer (II) (33%†), b.p. 122–132°/0·05 mm. The structures were assigned on the basis of the

$$\mathrm{EtO_2C{\cdot}CMe{=}CMe{-}O{-}CHMe{\cdot}CO_2Et} \qquad \text{(I)}$$

$$\mathrm{MeCO{\cdot}CMe(CO_2Et){\cdot}CMe(CO_2Et)COMe} \qquad \text{(II)}$$

analytical data and n.m.r. spectra, and of the degradation of (I) with acid to ethyl lactate and ethyl α-methylacetoacetate. Compound, (I) was apparently a single geometrical isomer (n.m.r., g.l.c.) and was identical with material prepared by the action of ethyl sodiolactate with ethyl β-chloro-α-methyl-crotonate.[2]

The nature of the products suggests that this heterogeneous oxidation produces an enolate radical which undergoes both C–C and C–O coupling. The unexpected loss of an acetyl group in the formation of (I) presumably occurs by a subsequent retro-Claisen fission, but the nature of the base in this particular system is unclear.

No products analogous to (I) and (II) were formed from ethyl acetoacetate under similar conditions; in the absence of solvent a vigorous exothermic reaction caused rapid degradation to acetone and ethanol. We advise caution in the direct reaction of β-dicarbonyl compounds with lead dioxide; acetylacetone ignited under such circumstances.‡

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† Based on unrecovered starting material. The remainder of the material is accounted for by uncharacterised products removed with the lead-containing solid phase during the work-up.

‡ Experiment by B. Crowther.

[1] A. Wolf, W. G. P., 876,237/1953.

[2] D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 1960, 2349. The ethyl β-chloro-α-methylcrotonate is believed to be a single geometrical isomer, but the configuration has not been established.