

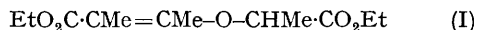
The Oxidation of Ethyl α -Methylacetoacetate by Lead Dioxide

By R. BRETTL* and D. SEDDON

(Department of Chemistry, The University, Sheffield, S3 7HF)

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



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.