The Oxidation of Pinacolone with Lead Dioxide in Toluene

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Summary Oxidation of pinacolone (3,3-dimethylbutan-2-one), but not other alkyl methyl ketones, with lead dioxide in toluene gives a cross-coupled product, 4,4-dimethyl-1-phenylpentan-3-one.

ALKYL METHYL KETONES of the type (I; R^1 or $R^2 \neq H$) undergo oxidative dimerization with lead dioxide to give 1,4-diketones of the type (II) by coupling at the α-carbon atom of the alkyl group.[1,2] These preparations can be performed advantageously in the presence of toluene as a diluent,[2] but we now report that when pinacolone (III) is oxidised by lead dioxide in the presence of toluene not only 2,2,7,7-tetramethyloctane-3,6-dione (IV)† but also a cross-coupled product, 4,4-dimethyl-1-phenylpentan-3-one (V)† and bibenzyl† are produced. Toluene is not oxidised to bibenzyl by lead dioxide in the absence of (III),[2] and acetone does not undergo an analogous reaction, probably because of its low b.p. Compounds (II) and (IV) presumably arise by the self-coupling of the radicals (VI) and (VII) formed in the heterogeneous oxidation of (I) and (III) by lead dioxide (*cf.* ref. 3) and bibenzyl and (V) by the self-coupling of benzyl radicals and the cross-coupling of benzyl radicals with (VII), respectively.

$MeCO{\cdot}CHR^1R^2$ (I) $MeCO{\cdot}CR^1R^2{\cdot}CR^1R^2{\cdot}COMe$ (II)

$MeCO{\cdot}Bu^t$ (III)

$MeCO{\cdot}\dot{C}R^1R^2$ (VI) $Bu^tCO{\cdot}CH_2{\cdot}CH_2{\cdot}COBu^t$ (IV)

${\cdot}CH_2{\cdot}CO{\cdot}Bu^t$ (VII) $Bu^tCO{\cdot}CH_2{\cdot}CH_2Ph$ (V)

Although no information seems to be available on the relative bond dissociation energies of the C–H bonds in the α-position to a ketonic carbonyl group, it seems likely that the value will be greater for a C–H bond in the methyl group in (III) than for the relevant C–H bond in (I; R^1 or $R^2 \neq H$) and that as a result only (VII) is capable of abstracting a hydrogen atom from the benzylic position in toluene. The relative extents to which alkyl methyl ketones undergo oxidation by lead dioxide in toluene and the proportions in which the products are formed will be discussed at greater length in the full paper.

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† The products were isolated by preparative g.l.c. and identified by conventional methods.

[1] A. Wolf, G. P. 876,237/1953 (*Chem. Abs.*, 1958, **52**, 9227); E. Wolthius, B. Bossenbroek, E. De Wall, E. Gellson, and A. Leegwater, *J. Org. Chem.*, 1963, **28**, 148; K. Schwetlick, J. Jentzsch, R. Karl, and D. Wolter, *J. prakt. Chem.*, 1964, **25**, 95.

[2] R. Brettle and B. Crowther, unpublished results.

[3] R. Brettle and D. Seddon, *Chem. Comm.*, 1968, 1546; *J. Chem. Soc.* (*C*), in the press.