Oxidative Bisdecarboxylation of αβ-Dicarboxylic Acids

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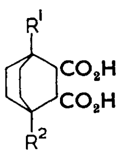
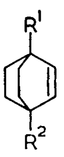
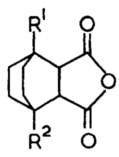
GROB and his co-workers[1,2] have described the oxidative bisdecarboxylation of αβ-dicarboxylic acids by the action of lead tetra-acetate and pyridine, in benzene or acetonitrile as solvent, at 50—60°. For 1-ethoxycarbonylbicyclo[2,2,2]octane-2,3-dicarboxylic acid (Ia), this procedure gives a 63% yield of the ester (IIa) and 12% yield of the anhydride (IIIa). Attempts to bisdecarboxylate a similar compound, 1,4-dimethoxycarbonyl bicyclo[2,2,2]octane-2,3-dicarboxylic acid (Ib), under these conditions have been reported to fail.[3,4] We find that both (Ia) and (Ib) undergo smooth oxidative bisdecarboxylation in dimethyl sulphoxide or dioxan as solvent at room temperature to give the esters (IIa) and (IIb) respectively, without formation of the corresponding anhydrides, (IIIa) and (IIIb). Compound (Ia) may also be similarly bisdecarboxylated in benzene at room temperature by using two moles of pyridine per mole of acid to give the ester (IIa) without the formation of the anhydride (IIIa). The experimental details are given in the table. Thus a new route for the synthesis of 1,4-disubstituted bicyclo[2,2,2]octane compounds is now available.



(I)



(II)



(III)

(a) $R^1 = CO_2Et$, $R^2 = H$

(b) $R^1 = R^2 = CO_2Me$

Table

Oxidative Bisdecarboxylation of the acid (Ib)

(Ib)	Pb(OAc)$_4$	Pyridine	Solvent	Temp.	Reaction time	Yield* of (IIb) (%)	Yield* of (IIIb) (%)	Recovery of (Ib) (%)
m moles								
74·6	82·0	111·5	Benzene (200 ml.)	50—70°	3 days	15	25	5
15·9	17·7	31·9	Acetonitrile (50 ml.)	50—70°	3—4 hr.	22	10	—
15·9	17·7	31·9	Dimethyl sulphoxide (50 ml.)	Room temp.	3—4 hr.	44	—	—
31·9	35·0	61·9	Dioxan (200 ml.)	Room temp.	2 days	45	—	15

Oxidative Bisdecarboxylation of the acid Ia

(Ia)	Pb(OAc)$_4$	Pyridine	Solvent	Temp.	Reaction time	Yield* of (IIa) (%)	Yield* of (IIIa) (%)
m moles							
66·7	70·0	100·1	Dimethyl sulphoxide (100 ml.)	Room temp.	3—4 hr.	44·7	—
66·7	70·0	133·3	Benzene (125 ml.)	Room temp.	2½ days	65	—

* Yields are based on the initial amount of dicarboxylic acid.

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