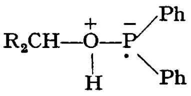
The Reaction of Diphenylphosphino-radicals with Alcohols

By R. S. DAVIDSON, R. A. SHELDON, and S. TRIPPETT
(*The University, Leicester*)

WE previously showed[1] that diphenylphosphinyl radicals, generated in the primary and secondary alcohols $R_2CH{\cdot}OH$ from tetraphenylbiphosphine either thermally or by irradiation, lead to the phosphinites $Ph_2PO{\cdot}CHR_2$, which may then rearrange to the phosphine oxides $Ph_2{\cdot}R_2CH{\cdot}PO$, or be partially oxidised to the phosphinates depending on the nature of the R_2CH group and on the conditions. The absence of products to be expected from the radical $R_2\dot{C}OH$ (except with diphenylmethanol which gives the stable radical $Ph_2\dot{C}OH$) led us to suggest that, in contrast with the behaviour of carbon radicals, the initial attack of the diphenylphosphino-radical on the alcohol is on the oxygen to give the intermediate (I) from which the hydrogen of the now relatively weak O–H bond is abstracted. Evidence in support of this is now presented from experiments using optically active octan-2-ol.



(I)

(+)-Octan-2-ol, $[\alpha]^{20}_{\mathrm{D}}$ +9·45°, on heating with tetraphenylbiphosphine to 180—200° for 4 hr. gave octan-2-yl diphenylphosphinite having $[\alpha]^{20}_{\mathrm{D}}$ + 26·9° (benzene), which on oxidation gave the phosphinate having $[\alpha]^{20}_{\mathrm{D}}$ + 1·9° (20% solution in CCl_4). Authentic phosphinite obtained from (+)-octan-2-ol and diphenylphosphinous chloride had $[\alpha]^{20}_{\mathrm{D}}$ + 28·1° (in benzene). Authentic phosphinate obtained from (+)-octan-2-ol and diphenylphosphinic chloride had $[\alpha]^{20}_{\mathrm{D}}$ + 1·85° (20% solution in CCl_4).

Irradiation[2] of a 40% solution of tetraphenylbiphosphine in (−)-octan-2-ol, $[\alpha]^{20}_{\mathrm{D}}$ −9·44°, at 100° (because of low solubility) gave a mixture of octan-2-yl diphenylphosphinite and the phosphinate, oxidation of which gave the phosphinate having $[\alpha]^{20}$ −4·98° (589 mμ), −5·22° (578 mμ), −5·80 (546 mμ), −9·30° (436 mμ), −12·9° (365 mμ in hexane). Authentic octan-2-yl diphenylphosphinate, obtained by oxidation of the phosphinite prepared from (−)-octan-2-ol and diphenylphosphinous dimethylamide at 125° for 15 hours, had $[\alpha]^{20}$ −5·63 (589 mμ), −5·91 (578 mμ), −6·64° (546 mμ), −10·51° (436 mμ), −14·44° (365 mμ in hexane).

The high degree of retention of configuration in both cases shows clearly that at no part in the reactions is the α-O–H bond broken, and supports the view that the initial attack by the diphenylphosphinyl radical is on the centre of highest electron density, *i.e.*, on the oxygen. This mode of attack is favoured (a) by the strength of the P–O bond formed and (b) by the ability of the phosphorus atom to accommodate an additional electron in a *d*-orbital.

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[1] R. S. Davidson, R. A. Sheldon and S. Trippett, *J. Chem. Soc.*, in the press. The substance of the paper was presented at the Autumn Meeting of the Chemical Society (Nottingham, September 1965).

[2] 450w. Hanovia medium-pressure mercury lamp.