References and Notes

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(13) We are grateful to Mr. Norman Nitzberg for construction of this apparatus.

An Unusual Oxidation–Reduction Reaction of Benzylbis(α-hydroxybenzyl)phosphine Oxide[1a]

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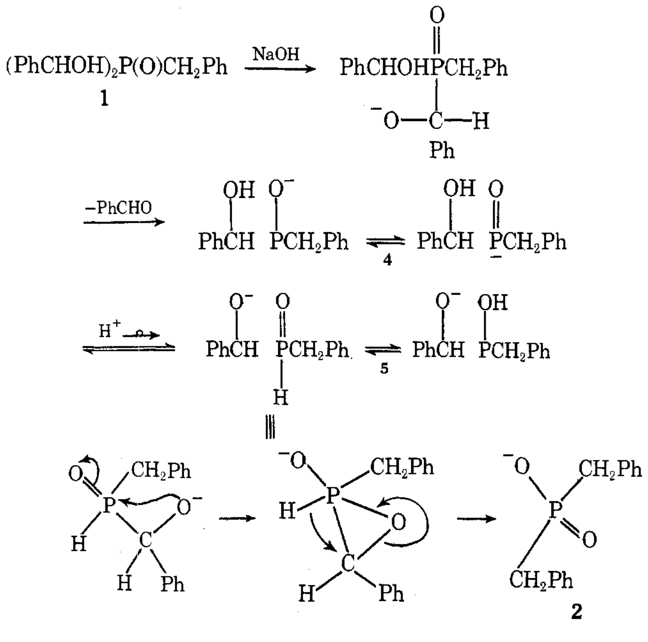
Received February 24, 1976

In previous publications[2–4] we have discussed the tendency of benzylbis(α-hydroxybenzyl)phosphine oxide (1) to undergo decomposition through the loss of benzaldehyde. Similar decompositions have been reported by other researchers.[5–7] In this work we wish to report an unusual oxidation–reduction reaction which was found to occur when 1 was treated with an equimolar amount of sodium hydroxide in refluxing benzene.

The product of this reaction (93% yield) was identified as the sodium salt of dibenzylphosphinic acid, 2, from the NMR spectrum and elemental analysis.

$$\underset{1}{(PhCHOH)_2P(O)CH_2Ph} \xrightarrow[\text{benzene}]{\text{NaOH}} \underset{2}{(PhCH_2)_2P(O)O^-Na^+} + PhCHO$$



Acidification of 2 with HCl caused precipitation of a white solid which was identified as dibenzylphosphinic acid (3) by the melting point, ir, and NMR spectra.

Our previous work[2–4] showed that 1 would react with base to eliminate benzaldehyde and form the anion of the secondary phosphine oxide 4. A proton shift yields 5, which can rearrange by hydride transfer from phosphorus to carbon by an intramolecular process (as shown, or a similar rearrangement, involving two molecules, which has a six-membered ring intermediate) to yield the dibenzyl phosphinate anion, 2.

This apparent hydride transfer from phosphorus to carbon is, to our knowledge, the first of its kind in α-hydroxyalkylphosphorus compounds. Hydride transfers from phosphorus to carbon are known, however, to occur during the alkaline hydrolysis of chloromethyl phosphinates.[8] Reductions of hydroxy groups in α-hydroxyalkylphosphorus compounds have been shown to occur but these involve reducing conditions,[9] disproportionations,[10,11] or transfer of hydrogen from oxygen to carbon.[12]

Experimental Section

Reagent grade chemicals and solvents were used without further purification. The ir spectra were taken on a Perkin-Elmer 137[1d] with NaCl optics. Solid samples were run as KBr pellets, using about 1% of the sample. The NMR spectra were taken on a Varian A-60A.[1d] Elemental analyses were performed by Enviro Analytical Laboratory, Knoxville, Tenn. All melting points are uncorrected.

Benzylbis(α-hydroxybenzyl)phosphine oxide (1) was prepared as described in an earlier publication.[2]

Reaction of 1 with Sodium Hydroxide. A mixture of 5 mmol of 1, 5 mmol of sodium hydroxide, and 300 ml of benzene was refluxed for 48 h. On cooling to room temperature, the solid which formed was collected (1.25 g) and washed with ether to remove benzaldehyde, the odor of which was quite noticeable above the reaction mixture. The solid was identified as the sodium salt of dibenzylphosphinic acid (2, 93% conversion) from the NMR spectrum and elemental analysis: NMR (D_2O) δ 2.97 (d, J = 16 Hz, 4 H, PCH_2Ph), 7.33 (m, 10 H, aromatics).

Anal. Calcd for $C_{14}H_{14}NaO_2P$: C, 62.69; H, 5.26; P, 11.55. Found: C, 62.45; H, 5.51; P, 11.36.

Acidification of an aqueous solution of 2 with HCl caused precipitation of a white solid which had mp 185–188 °C. Recrystallization from an ethanol (20 ml)–water (5 ml) mixture gave white platelets, 3, with mp 190–191 °C (lit.[13] 191°C); ir (KBr) 2.88 (OH), 3.28 (aromatic C–H), 3.65–4.8 (broad strong P–OH), 8.5 μ (P=O): NMR (Me_2SO-d_6) δ 3.0 (d, J = 16 Hz, 4 H, PCH_2Ph), 7.22 (m, 10 H, aromatics).

Registry No.—1, 36871-68-8; 2, 13422-04-3; 3, 7369-51-9; NaOH, 1310-73-2.

References and Notes

(1) (a) Decomposition Reactions of Hydroxyalkylphosphorus Compounds. 4. For parts 1, 2, and 3 see ref 2, 3, and 4. (b) One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture. (c) Formerly Louisiana State University in New Orleans. (d) Mention of companies or commercial products does not imply recommendations or endorsement by the U.S. Department of Agriculture over others not mentioned.
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