MERCURATION OF DIALKYL BENZYLPHOSPHONATES

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Teruaki and Hirohiko² have studied the reaction of mercuric carboxylates with trivalent phosphorus compounds. They found that the mercuric and mercurous salts of carboxylic acids can be reduced by the trivalent phosphorus compounds under comparatively mild conditions to give mercury, the acid anhydride, and the corresponding pentacovalent oxyphosphorus compounds.

We are at present investigating the reactions of pentacovalent phosphorus compounds, in which the phosphorus atom is in a high oxidation state, and wish to report that instead of reduction of mercuric acetate decomposition of the phosphorus compound has occured. Thus a solution of $_{<\eta}$ 0.01 mole dialkyl benzylphosphonate in 10 ml hexane is added to a suspension of 0.01 mole mercuric acetate in 20 ml hexane, and the mixture is stirred at room temperature for two hr, then the precipitate is removed (from the reaction mixture) by filtration. Hexane is distilled from the filtrate whereby benzyl acetate is obtained. The latter gave the same i.r. spectrum as an authentic sample. The precipitate has been identified as dialkylphosphinyl mercuric acetate (2) by comparison with an authentic prepared by the method of Fox and Venezky³.

The mechanism proposed for this reaction is outlined in the following scheme (I).

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The last step (a) can be considered as an internal Arbuzov rearrangement.⁴ Analytical figures⁵ fit the structure proposed. NMR⁶ of (2) proved to be devoid of aromatic protons. The i.r. spectra of (2) showed bands at 1052 cm⁻¹ and 968 cm⁻¹ due to P-O-C (aliphatic).⁷ The phosphoryl band was found at 1300 cm⁻¹.

Compounds (2) are crystallised from polar media such as acetic acid. However, in benzene or toluene when the temperature is slightly raised they decompose to give mercury.

These compounds (2) react further with mercuric acetate in acetic acid at 100° C to give a dimercurated product (3) according to the following scheme (II).



The i.r. of (3) showed a strong depression in the intensity of the P-O-C (aliphatic) at 1052 cm⁻¹ and 986 cm⁻¹.

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- 6- NMR spectrum was carried out by Professor Dr. Friebolin at Heidelberg University, West Germany.
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