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THE REACTION OF TRIPHENYLPHOSPHINE WITH TRI-n-BUTYLTIN TRICHLOROACETATE

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Triphenylphosphine reacts with methyl trichloroacetate1) or organic polyhalogen compounds2) to give Wittig reagents and in some cases to give olefins.3,4)

Triphenylphosphine has shown a different behavior towards triorganotin trichloroacetates from organic polyhalogen compounds. The reaction of triphenylphosphine with tri-n-butyltin trichloroacetate in molar ratio of 1:1 proceeds in benzene exothermally. The reaction mixture gives tri-n-butyltin chloride and triphenylphosphine oxide together with dark viscous resin, as shown in following equation.

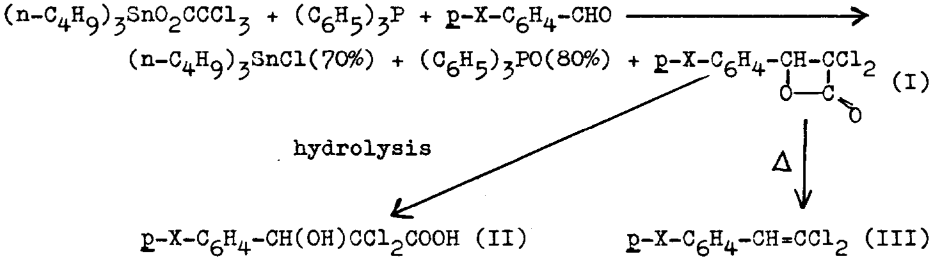
$$(n\text{-}C_4H_9)_3SnO_2CCCl_3 + (C_6H_5)_3P \longrightarrow (n\text{-}C_4H_9)_3SnCl(70\%) + (C_6H_5)_3PO(80\%) + \text{resin}$$

When the reaction was carried out in the presence of excess of benzaldehyde at 40°C in benzene, the reaction mixture showed a strong absorption band at $1860 cm^{-1}$ characteristic of β-lactones. Several attempts for the isolation of the product were unsuccessful but the distillation under a reduced pressure gave tri-n-butyltin chloride, unreacted benzaldehyde and triphenylphosphine oxide together with a small amount of β,β-dichlorostyrene which was identified by v.p.c. Usually in the similar reactions to give Wittig reagents1,2) benzalchloride has been produced by the reaction of benzaldehyde with triphenylphosphine dichloride. However, it was not detected in this case.

The hydrolysis of the reaction mixture by a 5% sodium bicarbonate solution gave a white crystalline compound (m.p., 167-168°C, Found: C,46.07; H,3.27; Cl,30.16%: M.W. in DMF by vapor pressure osmometer, 220) which was characterized as α,α-dichloro-β-hydroxy-β-phenyl propionic acid by comparing it to an authentic sample (m.p., 166-167°C, Found: C,46.21; H,3.55; Cl,30.23%: m.p., 171-172°C,[5] Calcd. for $C_9H_8O_3Cl_2$: C,45.99; H,3.43; Cl,30.16%: M.W., 235).

With other aromatic aldehydes the reaction mixture showed a similar band near 1860cm^{-1} and the hydrolysis gave analogous oxy-acids in 20-40% yield. With acetophenone or benzophenone, however, the reaction mixture showed no absorption band near 1860cm^{-1} and further treatments were abandoned.

These results obviously suggest the formation of α,α-dichloro-β-propiolactone derivatives (I) in the reaction mixture, which are hydrolyzed into oxy-acids (II) and also may be thermally decomposed into β,β-dichlorostyrenes(III).



X=	m.p.(°C)	Yield(%)
H	167-168	33
CH_3	148-149	20
Cl	149-149.5	42

Although the mechanism of this reaction is not clear, dichloroketene itself or its precursors probably exist as the reactive species in the course of the reaction. It is believed that this characteristic behavior results from the bilateral property of the Sn-O bond in triorganotin carboxylates.[6]

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