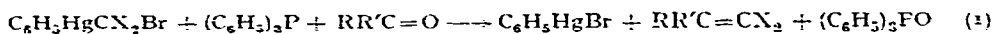


## SHORT COMMUNICATIONS

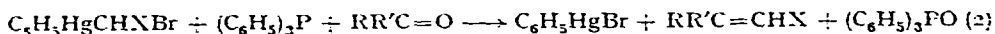
## Halomethyl-metal compounds

## III. The reaction of phenyl(trihalomethyl)- and phenyl(dihalomethyl)mercury compounds with trialkyl phosphites\*

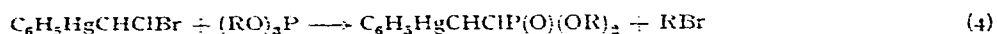
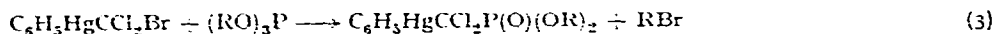
In a recent communication we reported the reaction of phenyl(trihalomethyl)- and phenyl(dihalomethyl)mercurials with triphenylphosphine in the presence of aldehydes and ketones<sup>2</sup>:



and



In an extension of this work we have examined the reactions of these mercurial reagents with trimethyl and triethyl phosphite. The results of this brief study may be summarized by equations (3) and (4).



Michaelis-Arbuzov reactions of polyhalomethanes have been reported previously and these have been shown to be radical processes<sup>3</sup>. Kamai<sup>4,5</sup> was not able to isolate  $\text{CBr}_3\text{P}(\text{O})(\text{OR})_2$  or  $\text{CHBr}_2\text{P}(\text{O})(\text{OR})_2$  from the reaction of carbon tetrabromide and bromoform respectively with trialkyl phosphites; alkyl bromide was formed, but most of the organophosphorus product was undistillable and possibly polymeric. In the present study we found that trimethyl phosphite and phenyl(dibromomethyl)-mercury react to give more than one mole of methyl bromide per mole of phosphite used. Here also the organophosphorus product appeared to be polymeric, as indicated by its undefined NMR spectrum. When a mixture of trimethyl phosphite and phenyl-(tribromomethyl)mercury was heated to 40°, an uncontrollable, exothermic reaction commenced. When these reactants were heated in benzene solution at 60–70°, more than one equivalent of methyl bromide was released. Removal of volatile materials left a viscous, brown residue. It would appear that the bromine atoms in initially formed  $\text{C}_6\text{H}_5\text{HgCHBrP}(\text{O})(\text{OCH}_3)_2$  and  $\text{C}_6\text{H}_5\text{HgCBr}_2\text{P}(\text{O})(\text{OCH}_3)_2$  are very reactive and that free radical Michaelis-Arbuzov reactions of these mercurials proceed under the reaction conditions to give materials of higher molecular weight.

The possibility that  $\text{C}_6\text{H}_5\text{HgCCl}_2\text{P}(\text{O})(\text{OR})_2$  and  $\text{C}_6\text{H}_5\text{HgCHClP}(\text{O})(\text{OR})_2$  might undergo  $\alpha$ -elimination of phenylmercuric chloride to give  $\text{ClCP}(\text{O})(\text{OR})_2$  and  $\text{HCP}(\text{O})(\text{OR})_2$  respectively was investigated. Such decomposition, however, did not occur. Thus the former mercurial decomposed slowly with gas evolution above 130°; no phenylmercuric chloride was formed. Apparently a radical Michaelis-Arbuzov

\* Part II: see ref. 1.

reaction occurred instead of the hoped-for  $\alpha$ -elimination reaction (which proved so valuable in the case of the  $C_6H_5HgCN_2Br^1$  and  $C_6H_5HgCHXBr^2$  compounds).

The structures of the phosphorus-containing mercurials were verified by their proton resonance spectra\*. In  $C_6H_5HgCCl_2P(O)(OCH_3)_2$  the methyl protons appeared as a doublet ( $J_{P-O-C-H} = 10.3$  cps) at 3.93 ppm, the phenyl protons at 7.28 ppm. The NMR spectrum of  $C_6H_5HgCHClP(O)(OCH_3)_2$  was of interest, since the asymmetric methylene carbon atom made the methoxy groups nonequivalent, resulting in two closely spaced doublets at 3.76 ppm and 3.78 ppm for the methoxy protons, with  $J_{P-O-C-H} = 10.8$  cps. The phenyl protons were observed at 7.28 ppm; the methylene proton was obscured by the methoxyl absorptions. In  $C_6H_5HgCHClP(O)(OC_2H_5)_2$  the  $CH_2$  protons of the ethoxy groups appeared as a quintet centered at 4.20 ppm, with further splitting of 2.5 cps due to the non-equivalence of the ethoxy groups. The methylene proton ( $-CHCl-$ ) was observed as a doublet ( $J_{P-C-H} = 10.2$  cps) at 3.70 ppm, the methyl protons as a triplet at 1.37 ppm and the phenyl protons as a singlet at 7.34 ppm.

### Experimental

*Preparation of  $C_6H_5HgCCl_2P(O)(OCH_3)_2$ .* Into a 100 ml, three-necked flask equipped with a magnetic stirrer and a condenser which led to a trap at  $-78^\circ$  was placed 0.2 mole of freshly distilled trimethyl phosphite and 0.025 mole of phenyl-(bromodichloromethyl)mercury<sup>6</sup> under an atmosphere of prepurified nitrogen. The contents were heated slowly to  $90^\circ$  with stirring. Bubbles of methyl bromide were given off constantly and condensed in the cold trap. Gas evolution ceased after about 1 h. The clear, homogeneous reaction mixture was stirred and heated for an additional hour. The excess trimethyl phosphite was removed by distillation *in vacuo*. The residual viscous liquid and solid were dissolved in 650 ml of hot *n*-hexane and the resulting solution was concentrated to 200 ml and chilled to  $0^\circ$ . Crude product, m.p.  $79-87^\circ$ , 10.25 g (88%), crystallized. Recrystallization from hexane gave 8.29 g (70.5%) of pure product, m.p.  $94-96^\circ$ . (Found: C, 22.54; H, 2.76; Cl, 14.95; Hg, 42.88.  $C_9H_{11}Cl_2HgO_2P$  calcd.: C, 23.02; H, 2.36; Cl, 15.10; Hg, 42.71%.) Infrared spectrum\*\* : 3040 (w), 2950 (w), 2830 (w), 1940 (w), 1820 (w), 1570 (w), 1470 (w), 1450 (w), 1425 (m), 1250 (s), 1185 (m), 1050 (s), 1000 (w), 890 (w), 835 (m), 755 (m), 726 (s), 687 (m), 655 (w), 610 (w), 588 (w), 545 (m), 525 (m), 450 (w).

The methyl bromide evolved was identified by comparison of its g.l.c. retention time and its infrared spectrum with those of an authentic sample.

$C_6H_5HgCCl_2P(O)(OCH_3)_2$  is very soluble in benzene, fairly soluble in carbon tetrachloride and slightly soluble in *n*-hexane. Recrystallization from *n*-hexane-chloroform or carbon tetrachloride was not successful, since the product seemed to react with these chlorinated solvents at their boiling points.

The following were prepared in essentially the same manner:

$C_6H_5HgCCl_2P(O)(OC_2H_5)_2$ , 88.5% yield, m.p.  $124-125^\circ$ . (Found: C, 26.10; H, 3.13; Cl, 14.26; Hg, 40.79.  $C_{11}H_{13}Cl_2HgO_3P$  calcd.: C, 26.54; H, 3.04; Cl, 14.25; Hg, 40.31%.)

\* Obtained in  $CDCl_3$  or  $CCl_4$  solution using a Varian Associates A60 high resolution NMR spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane.

\*\* IR spectra were obtained in KBr pellets using a Perkin Elmer Model 337 grating spectrometer.

$C_6H_5HgCHClP(O)(OCH_3)_2$ , 53% yield, m.p. 107–108° (from benzene–hexane). (Found: C, 24.46; H, 3.03; Cl, 8.28.  $C_9H_{12}ClHgO_3P$  calcd.: C, 24.82; H, 2.76; Cl, 8.16%.) Infrared spectrum: 3040 (w), 2940 (w), 2835 (w), 1470 (w), 1450 (w), 1415 (m), 1220 (s), 1185 (m), 1170 (m), 1075 (m), 1050 (s), 1025 (s), 1005 (s), 878 (s), 822 (s), 745 (m), 732 (s), 710 (m), 700 (m), 570 (m), 522 (m), 433 (w)  $cm^{-1}$ .

$C_6H_5HgCHClP(O)(OC_2H_5)_2$ , 60% yield, m.p. 74–76°. (Found: Hg, 43.22.  $C_{11}H_{16}ClHgO_3P$  calcd.: Hg, 43.29%.) Infrared spectrum: 3060 (w), 3040 (w), 2975 (m), 2920 (w), 2890 (w), 1945 (w), 1870 (w), 1810 (w), 1750 (w), 1630 (w), 1570 (w), 1475 (m), 1440 (w), 1420 (m), 1380 (m), 1360 (w), 1295 (w), 1220 (s), 1172 (m), 1098 (w), 1055 (s), 1030 (s), 998 (w), 960 (s), 860 (m), 790 (w), 734 (m), 702 (m), 575 (w), 522 (w), 450 (w)  $cm^{-1}$ .

*Reaction of phenyl(tribromomethyl)mercury with trimethyl phosphite.* The same procedure as had been used in the case of  $C_6H_5HgCCl_2Br$  was used in the reaction of  $C_6H_5HgCBr_3$  with trimethyl phosphite. (a) When a mixture of 0.025 mole of phenyl-(tribromomethyl)mercury and 30 ml of trimethyl phosphite was heated, an uncontrollable reaction commenced at about 40°, blowing the flask contents out of the reaction vessel. (b) Trimethyl phosphite (75 mmoles, diluted with an equal volume of benzene) was added slowly to a benzene solution of 25 mmoles of  $C_6H_5HgCBr_3$  at 60–70°. Methyl bromide was given off and collected in a cold trap. G.l.c. analysis of an ether solution of the evolved gases showed that 3.4 g of methyl bromide had been trapped (vs. 2.4 g of methyl bromide expected in a 1:1 reaction). The reaction mixture had turned dark brown by the time all of the phosphite ester had been added. Solvent and excess phosphite were removed by distillation at reduced pressure, leaving a viscous liquid which partially crystallized to a brown solid on standing. (c) The same reaction was carried out at 50° with phosphite and mercurial in 1:1 mole ratio, with a reaction time of 10 h. Again, a viscous, brown residue was obtained, which was very soluble in benzene and chloroform, but insoluble in ether, cyclohexane and *n*-hexane, slightly soluble in carbon tetrachloride. No pure, crystalline compounds could be isolated from these reaction mixtures.

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