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THE REACTION OF TRIPHENYLPHOSPHINE WITH SOME ORGANOMETAL HALOACETATES

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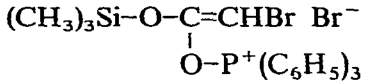
SUMMARY

The reaction of triphenylphosphine with some organometal haloacetates [$(CH_3)_3SiOCOCHBr_2$, $(CH_3)_3SiOCOCCl_3$, $(n\text{-}C_4H_9)_3SnOCOCCl_3$ and $(CH_3)_3Sb(OCOCCl_3)_2$] gave the corresponding organometal halides (ca. 80%) and $(C_6H_5)_3PO$ (ca. 90%), and in the presence of cyclopentadiene, cycloaddition products (ca. 30%). Evidence was obtained that the enolphosphonium salt,



$$(CH_3)_3Si{-}O{-}\underset{\displaystyle O{-}P^+(C_6H_5)_3}{\underset{|}{C}}{=}CHBr\ Br^-$$

is an intermediate in the reaction of $(C_6H_5)_3P$ with $(CH_3)_3SiOCOCHBr_2$.

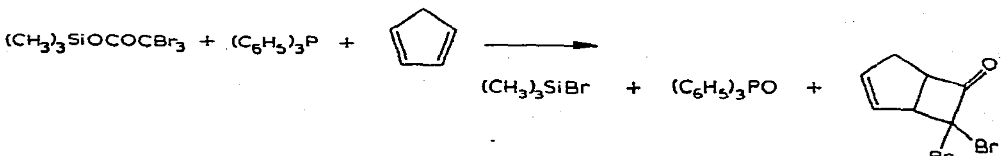
INTRODUCTION

Many studies of the reaction of triphenylphosphine with organic halogenated compounds have been reported. For instance, triphenylphosphine reacts with organic polyhalogenated esters, such as methyl trichloroacetate, to give Wittig reagents[1]. Triphenylphosphine shows a different behavior towards sodium chlorodifluoroacetate; this reaction gives triphenyl(difluoromethylene)phosphorane accompanied by decarboxylation[2].

$$CCl_3CO_2CH_3 + 2\,(C_6H_5)_3P \rightarrow (C_6H_5)_3P{=}CClCO_2CH_3 + (C_6H_5)_3PCl_2$$

$$NaOCOCF_2Cl + (C_6H_5)_3P \rightarrow NaCl + (C_6H_5)_3P{=}CF_2 + CO_2$$

We have reported already that triphenylphosphine reacted in a unique manner with $(n\text{-}C_4H_9)_3SnOCOCCl_3$[3] and $(CH_3)_3SiOCOCBr_3$[4], the latter reaction being remarkably effective as a source of dibromoketene, since when cyclopentadiene was present, the adduct, 7,7-dibromobicyclo[3.2.0]hept-2-ene-6-one, was obtained almost quantitatively.



In this paper, the reaction of triphenylphosphine with some other organometal haloacetates is described.

EXPERIMENTAL

Hexamethyldisilazane[5] and trimethylstibine sulfide[6] were synthesized by the standard methods described in the literature. Cyclopentadiene was prepared just before use by thermal cracking at about 160° of commercially available dicyclopentadiene. All solvents were dried and purified by distillation from P_2O_5 or lithium aluminum hydride. Triphenylphosphine, bis(tributyltin) oxide and all haloacetic acids were reagent-grade.

Preparation of organometal haloacetates

(*i*). *Trimethylsilyl haloacetates.* Trimethylsilyl haloacetates were prepared from hexamethyldisilazane and the corresponding haloacetic acids in a manner similar to the method reported[7].

$(CH_3)_3SiOCOCCl_3$: b.p. 74–75°/17.5 mmHg; yield 68%. (Found: Cl, 44.76. $C_5H_9Cl_3O_2Si$ calcd.: Cl, 45.15%.)

$(CH_3)_3SiOCOHBr_2$: b.p. 88–89°/16.5 mmHg; yield 62%. (Found: Br, 54.86. $C_5H_{10}Br_2O_2Si$ calcd.: Br, 55.10%.)

$(CH_3)_3SiOCOCH_2Br$: b.p. 68–69°/17 mmHg; yield 54%. (Found: Br, 37.92. $C_5H_{11}BrO_2Si$ calcd.: Br,37.85%.)

The preparation of $(CH_3)_3SiOCOCF_3$ (b.p. 85–87°) was carried out without solvent. The IR and NMR spectra of this compound agreed well with those of an authentic sample[8].

(*ii*). *Tributyltin trichloroacetate, $(n\text{-}C_4H_9)_3SnOCOCCl_3$.* A slight excess of bis(tributyltin) oxide (30 g) was added to trichloroacetic acid (16.0 g) in petroleum ether at room temperature. After the solvent was removed *in vacuo*, the residual solid was recrystallized from petroleum ether, giving $(n\text{-}C_4H_9)_3SnOCOCCl_3$[9] (36 g, 79%); m.p. 81.5–82.5°. (Found: C, 37.30; H, 6.01. $C_{14}H_{27}Cl_3O_2Sn$ calcd.: C, 37.17; H, 6.02%.)

(*iii*). *Trimethylantimony bis(trichloroacetate), $(CH_3)_3Sb(OCOCCl_3)_2$.* Trichloroacetic acid (8.2 g) in 20 ml methylene chloride was added dropwise with stirring to a solution of trimethylstibine sulfide (5 g) in 30 ml methylene chloride at room temperature. After stirring for 1 h, the solvent was removed *in vacuo*. The residual solid was recrystallized from methanol and petroleum ether, giving $(CH_3)_3Sb(OCOCCl_3)_2$ (11.5 g, 93%); m.p. 164–166°. (Found: C, 17.14; H, 1.85. $C_7H_9Cl_6O_4Sb$ calcd.: C, 17.10; H, 1.85%.)

Reaction of triphenylphosphine with organometal haloacetates

All procedures described below were carried out under an atmosphere of nitrogen. The reaction at an appropriate temperature with equivalent amounts of the two reagents in toluene with or without cyclopentadiene has been examined.

(*i*). *With $(CH_3)_3SiOCOCHBr_2$.* Triphenylphosphine (4.3 g, 0.016 mole) in 30 ml toluene was added with stirring over a period of about 5 h to a solution of trimethylsilyl dibromoacetate (4.8 g, 0.016 mole) and excess cyclopentadiene (10.9 g) in 15 ml toluene at 0°. The reaction mixture was kept overnight at room temperature.

The solvent, unreacted cyclopentadiene and trimethylsilyl bromide (2.1 g, 84%)* was removed *in vacuo*. To the residue was added 60 ml of n-hexane and the mixture was stirred for about 4 h. The black precipitate was filtered and purified by passing through an alumina column with benzene as solvent, to give triphenylphosphine oxide (4.4 g, 95%)**. Distillation of the filtrate gave the cycloaddition product (0.8 g, 26%). This adduct was identified as 7-bromobicyclo[3.2.0]hept-2-ene-6-one[10]; b.p. 63.5°/0.5 mmHg; IR (neat): ν(C=O) 1796 cm^{-1}; NMR (CCl_4) (δ): 2.6 (m, 2 H), 3.87 (m, 2 H), 5.16 (m, 1 H) and 5.78 (m, 2 H); mass spectrum (70 eV): *m/e* (rel. intensity) 188 (90, $M^+ + 2$) and 186 (100, M^+). (Found: C, 44.48; H, 3.72. C_7H_7BrO calcd.: C, 44.95; H, 3.77%.)

The reaction without cyclopentadiene under the same conditions gave a white precipitate which gradually disappeared. The reaction products were $(CH_3)_3SiBr$ and $(C_6H_5)_3PO$ in quantitative yield, together with a viscous resin.

This reaction in CH_3CN at room temperature was followed by NMR spectroscopy at appropriate time intervals, as shown in Fig. 1.

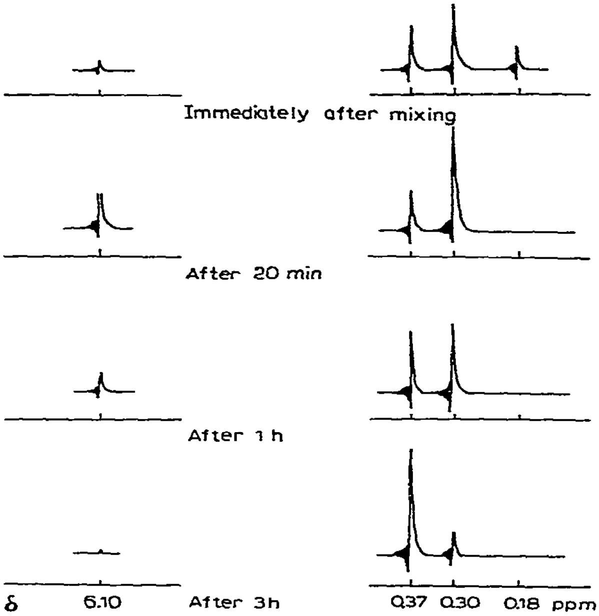


Fig. 1. NMR spectra of the reaction mixture of $(CH_3)_3SiOCOCHBr_2$ and $(C_6H_5)_3P$ in CH_3CN.

The resonance peaks at 0.18 ppm (s) and at 0.37 ppm (s) are assigned to $(CH_3)_3SiOCOCHBr_2$ and $(CH_3)_3SiBr$, respectively. The resonance peak at 6.10 ppm (d), which is in the vinyl proton region, is spaced in the ratio of 1/9 relative to that at 0.30 ppm (s). The $J(^{31}P\text{–}H)$ value of this peak is 0.68 Hz.

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* Trimethylsilyl bromide was identified by gas chromatography, and its yield was estimated by an NMR spectrum using cyclohexane as a reference.

** Triphenylphosphine oxide was identified by a mixed melting point with an authentic sample and by its IR spectrum.

(*ii*). *With* $(CH_3)_3SiOCOCH_2Br$. The reaction of triphenylphosphine (4.7 g) and $(CH_3)_3SiOCOCH_2Br$ (3.8 g) in 40 ml toluene gave a white precipitate which did not seem to change up to 110°. This precipitate was found to be an adduct, $(CH_3)_3SiOCOCH_2-P^+(C_6H_5)_3\ Br^-$(I); m.p. 150–151° (decomp.): IR (nujol mull): ν(C=O) 1708 cm^{-1}: NMR ($CHCl_3$) (δ): 0.1 (s, $SiCH_3$), 5.44 {d, [$J(^{31}P-H)$ 13.5 Hz], OCO-CH_2P} and 7.76 (m, PC_6H_5). (Found: C, 58.50; H, 5.55. $C_{23}H_{26}BrO_2PSi$ calcd.: C, 58.35: H, 5.54%.) This adduct was also obtained in the presence of cyclopentadiene.

(*iii*). *With organometal trichloroacetates in the presence of cyclopentadiene.*

$(CH_3)_3SiOCOCCl_3$. The reaction products were $(CH_3)_3SiCl$ (84%), $(C_6H_5)_3PO$ (87%) and an adduct (36.5%), 7.7-dichlorobicyclo[3.2.0]hept-2-ene-6-one[11]; b.p. 61.5°/0.5 mmHg; IR (neat): ν(C=O) 1806 cm^{-1}; NMR (CCl_4) (δ): 2.69 (m, 2 H), 4.10 (m, 2 H) and 5.89 (m, 2 H): mass spectrum (70 eV): *m/e* (rel. intensity) 180 (15, $M^+ +4$), 178 (66, $M^+ +2$) and 176 (100, M^+). (Found: C, 47.11; H, 3.48. $C_7H_6Cl_2O$ calcd.: C, 47.49; H, 3.42%.)

$(n\text{-}C_4H_9)_3SnOCOCCl_3$. $(C_6H_5)_3PO$ (92%) was precipitated by treatment of the reaction mixture with n-hexane. $(n\text{-}C_4H_9)_3SnCl$ (90%) and an adduct (30%) were obtained through successive vacuum distillations of the filtrate. The adduct was identified as 7,7-dichlorobicyclo[3.2.0]hept-2-ene-6-one.

$(CH_3)_3Sb(OCOCCl_3)_2$. $(CH_3)_3SbCl_2$* (79%) and $(C_6H_5)_3PO$ (92%) were precipitated by treatment with n-hexane. The adduct (33%) was identified as 7,7-dichlorobicyclo[3.2.0]hept-2-ene-6-one.

(*iv*). *With* $(CH_3)_3SiOCOCF_3$. A mixture of triphenylphosphine (1.8 g) and trimethylsilyl trifluoroacetate (1.3 g) in 8 ml toluene was heated at 80° for 3 h, however the $(CH_3)_3SiOCOCF_3$ remained unchanged**.

Physical measurements

The IR spectra were obtained using a Hitachi 225 spectrophotometer equipped with gratings. The NMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz, and mass spectra were recorded with a Hitachi Model RMU-6E mass spectrometer.

RESULTS AND DISCUSSION

The reaction of $(C_6H_5)_3P$ with organometal haloacetates such as $(CH_3)_3SiOCOCHBr_2$, $(CH_3)_3SiOCOCCl_3$, $(n\text{-}C_4H_9)_3SnOCOCCl_3$ and $(CH_3)_3Sb(OCOCCl_3)_2$ at room temperature gave the corresponding organometal halides and $(C_6H_5)_3PO$ in almost quantitative amounts together with a viscous resin, and in the presence of cyclopentadiene, an adduct (ca. 30%), 7-halo- or 7,7-dihalobicyclo[3.2.0]hept-2-ene-6-one. In the case of $(CH_3)_3SiOCOCH_2Br$, the ketophosphonium bromide (I), which is stable up to 110°, was obtained. The reaction with $(CH_3)_3SiOCOCF_3$ did not proceed even at 80° for 3 h.

The $J(^{31}P-H)$ value (0.68 Hz) of the resonance peak at 6.10 ppm shown in

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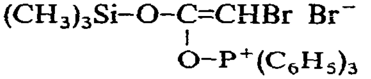
* The yield was estimated as trimethylantimony diacetate formed by reaction with sodium acetate in benzene.

** Trimethylsilyl trifluoroacetate was identified by means of IR and NMR spectra, and its yield was estimated by NMR.

Fig. 1 is comparable with that of the enolphosphonium salt, (2-bromo-1-phenylvinyloxy)triphenylphosphonium bromide [$J(^{31}P\text{–}H)$ 1.8 Hz][12]. The resonance peaks at 6.10 and 0.30 ppm may be interpreted as due to the enolphosphonium bromide (II), which is probably a



$$\begin{array}{l}\mathrm{(CH_3)_3Si{-}O{-}\underset{|}{C}{=}CHBr\ \ Br^-} \\ \qquad\qquad\quad \mathrm{O{-}P^+(C_6H_5)_3}\end{array}$$

(II)

precursor for bromoketene. It is reasonable to suggest that the reaction with the organometal trichloroacetates used in this study proceeds via intermediates similar to (II). Di- or tri-substitution at the α-carbon by bulky electron-withdrawing groups such as bromine and chlorine appears to be effective for the enolphosphonium formation. These results also parallel the suggestion by Borowitz *et al.*[12] that enolphosphonium is formed in the reaction of triphenylphosphine and organic α-haloketones.

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