

SHORT  
COMMUNICATIONS

# Mercuration of Benzyltriphenylphosphonium Chloride with Mercury(II) Acetate and Trifluoroacetate and Some Transformations of the Products

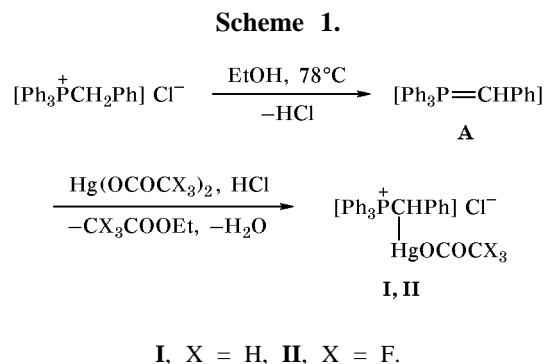
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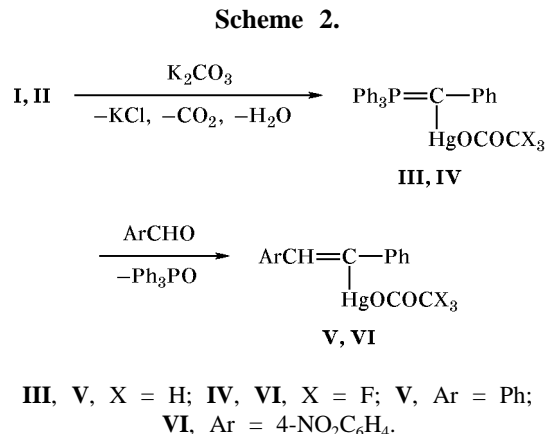
It is known [1] that compounds possessing labile hydrogen atom are readily mercured with mercury salts under appropriate conditions to give highly reactive organomercury derivatives [2] which are widely used in organic synthesis [3].

We have found that benzyltriphenylphosphonium chloride having an activated methylene group [4] readily reacts with mercury(II) acetate or trifluoroacetate on heating of equimolar amounts of the reactants in boiling anhydrous ethanol. As a result, products of hydrogen replacement by HgOCOCX<sub>3</sub> group (compounds **I** and **II**, Scheme 1) are formed in quantitative yield, and the corresponding carboxylic acids are released. The latter undergo esterification during the reaction to give ethyl esters (GLC data). Presumably, this process favors displacement of the mercuration equilibrium toward formation of products **I** and **II**. By analogy with other reactions with electrophilic reagents [5], we presumed that the mercuration begins with elimination of  $\alpha$ -hydrogen atom from phosphonium salt to form ylide **A**. The latter takes up mercury(II) salt, and exchange of CX<sub>3</sub>COO<sup>-</sup> ion by Cl<sup>-</sup> yields products **I** and **II** (Scheme 1).



The proposed mechanism is supported by the known data on addition of mercury(II) salts to stable [6, 7] and unstable [8, 9] alkylidenephosphoranes like **A** at room temperature.

The chemical properties of mercury-containing salts **I** and **II** turned out to be typical of such compounds [1, 5]. On heating in hydrochloric acid, they underwent protodemercuration with formation of initial benzyltriphenylphosphonium chloride and inorganic mercury(II) salt; treatment of the latter with hydrogen sulfide quantitatively yielded HgS. By the action of aqueous potassium carbonate on compounds **I** and **II** in acetonitrile at room temperature we obtained unexpectedly stable mercury-containing phosphorus ylides **III** and **IV** (Scheme 2). These compounds fairly smoothly reacted with benzaldehyde and 4-nitrobenzaldehyde (according to Wittig) on heating equimolar amounts of the reactants in boiling MeOH. As a result, we isolated 90–91% of mercured stilbenes **V** and **VI** as mixtures of *E* and *Z* isomers (<sup>1</sup>H NMR data) and triphenylphosphine oxide.



**$\alpha$ -(Acetoxymercurio)benzyltriphenylphosphonium chloride (I).** Mercury(II) acetate, 0.32 g (1 mmol), was added to a solution of 0.39 g (1 mmol) of benzyltriphenylphosphonium chloride [10] in 5 ml of anhydrous ethanol, and the mixture was stirred for 1 h under reflux. It was then cooled, 20 ml of diethyl ether was added, and the mixture was left to stand for 15 h in a refrigerator at 6–7°C. The tarry precipitate was ground with hexane until crystals were obtained. Yield 0.63 g (97%), mp 75–76°C. IR spectrum (mineral oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1662 (C=O), 1220 (C–O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 2.01 s (3H,  $\text{CH}_3$ ), 5.62 d (1H, CH,  $^2J_{\text{H,P}} = 16.2$ ,  $^2J_{\text{H,Hg}} = 252$  Hz), 7.68–7.92 m (5H,  $\text{C}_6\text{H}_5$ ), 8.02–8.94 m (15H,  $\text{Ph}_3\text{P}^+$ ). Found, %: C 49.63; H 3.61; Cl 5.23; Hg 30.71.  $\text{C}_{27}\text{H}_{24}\text{ClHgO}_2\text{P}$ . Calculated, %: C 49.41; H 3.70; Cl 5.46; Hg 30.86.

**Triphenyl- $\alpha$ -(trifluoroacetoxymercurio)benzylidenephosphonium chloride (II)** was synthesized in a similar way. Yield 96%, mp 66–67°C. IR spectrum (mineral oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1678 (C=O), 1218 (C–O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 5.72 d (1H, CH,  $^2J_{\text{H,P}} = 16.0$ ,  $^2J_{\text{H,Hg}} = 266$  Hz), 7.69–7.96 m (5H,  $\text{C}_6\text{H}_5$ ), 8.05–8.98 m (15H,  $\text{Ph}_3\text{P}^+$ ). Found, %: C 45.92; H 2.83; Hg 28.36.  $\text{C}_{27}\text{H}_{21}\text{ClF}_3\text{HgO}_2\text{P}$ . Calculated, %: C 46.24; H 2.99; Hg 28.59.

**Acetoxymercuriomethylenetriphenylphosphorane (III).** To a solution of 0.65 g (1 mmol) of phosphonium chloride I in 10 ml of acetonitrile we added 1.5 ml of 10% aqueous potassium carbonate, the mixture was stirred for 10 min at room temperature, 10 ml of water was added, and the precipitate was filtered off, washed with water, and recrystallized from methanol. Yield of III 0.32 g (52%), mp 185–186°C. IR spectrum (mineral oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1660 (C=O), 1218 (C–O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 1.98 s (3H,  $\text{CH}_3$ ), 7.38–7.69 m (5H,  $\text{C}_6\text{H}_5$ ), 7.83–8.24 m [15H,  $\text{P}(\text{C}_6\text{H}_5)_3$ ]. Found, %: C 53.29; H 3.68; Hg 33.02.  $\text{C}_{27}\text{H}_{23}\text{HgO}_2\text{P}$ . Calculated, %: C 53.09; H 3.77; Hg 32.83.

**Trifluoroacetoxymercuriomethylenetriphenylphosphorane (IV)** was synthesized in a similar way. Yield 90%, mp 152–153°C. IR spectrum (mineral oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1672 (C=O), 1218 (C–O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 7.36–7.87 m (5H,  $\text{C}_6\text{H}_5$ ), 7.93–8.28 m [15H,  $\text{P}(\text{C}_6\text{H}_5)_3$ ]. Found, %: C 48.57; H 2.88; Hg 29.80.  $\text{C}_{27}\text{H}_{20}\text{F}_3\text{HgO}_2\text{P}$ . Calculated, %: C 48.78; H 3.01; Hg 30.16.

**(*E,Z*)-1-Acetoxymercurio-1,2-diphenylethene (V).** Freshly distilled benzaldehyde, 0.11 g (1 mmol), was added to a solution of 0.62 g (1 mmol) of ylide

III in 5 ml of methanol, and the mixture was heated for 3 h under reflux. After cooling, the precipitate was filtered off, washed with 5 ml of cold methanol, and dried. Yield 0.40 g (91%), mp 204–206°C. IR spectrum (mineral oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1662 (C=O), 1612 (C=C), 1220 (C–O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 1.98 s (3H,  $\text{CH}_3$ ), 6.53 m (1H, =CH,  $^3J_{\text{H,Hg}} = 452$ , 182 Hz), 7.08–7.73 m (10H,  $2\text{C}_6\text{H}_5$ ). Found, %: C 43.62; H 3.12; Hg 46.03.  $\text{C}_{16}\text{H}_{14}\text{HgO}_2$ . Calculated, %: C 43.80; H 3.19; Hg 45.70.

The solvent was distilled off from the filtrate to isolate triphenylphosphine oxide, mp 154–156°C (from aqueous ethanol).

**(*E,Z*)-2-(4-Nitrophenyl)-1-phenyl-1-trifluoroacetoxymercurioethene (VI)** was synthesized in a similar way. Yield 90%, mp 208–210°C. IR spectrum (mineral oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1671 (C=O), 1618 (C=C), 1219 (C–O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 6.73 m (1H, =CH,  $^3J_{\text{H,Hg}} = 483$ , 196 Hz), 7.18–7.38 m (5H,  $\text{C}_6\text{H}_5$ ), 8.15 d and 8.48 d (2H each,  $\text{NO}_2\text{C}_6\text{H}_4$ ). Found, %: C 35.43; H 1.91; Hg 37.12; N 2.42.  $\text{C}_{16}\text{H}_{10}\text{F}_3\text{HgNO}_4$ . Calculated, %: C 35.74; H 1.86; Hg 37.29; N 2.60.

The IR spectra were obtained on an IKS-29 spectrometer. The  $^1\text{H}$  NMR spectra were recorded on a Bruker AM-300 instrument at 300.13 MHz using TMS as internal reference.

## REFERENCES

1. Makarova, L.G. and Nesmeyanov, A.N., *Metody elementoorganicheskoi khimii. Rtut'* (Methods of Organometallic Chemistry. Mercury), Moscow: Nauka, 1965, pp. 53–62.
2. Reutov, O.A., Beletskaya, I.P., and Sokolov, V.I., *Mekhanizmy reaktsii metalloorganicheskikh soedinenii* (Reactions Mechanisms of Organometallic Compounds), Moscow: Khimiya, 1972.
3. Larok, R.C., *Organomercury Compounds in Organic Synthesis*, Berlin: Springer, 1985, pp. 423–528.
4. Speziale, A.J. and Ratts, K.W., *J. Am. Chem. Soc.*, 1963, vol. 85, no. 10, p. 2790.
5. Erastov, O.A. and Nikonov, G.N., *Funktsional'noza-meshchennye fosfiny i ikh proizvodnye* (Functionally Substituted Phosphines and Their Derivatives), Moscow: Nauka, 1986, pp. 167–170.
6. Nesmeyanov, N.A. and Novikov, V.M., *Dokl. Akad. Nauk SSSR*, 1965, vol. 162, no. 2, pp. 350–353.
7. Nesmeyanov, N.A., Kalinin, A.V., and Reutov, O.A., *Dokl. Akad. Nauk SSSR*, 1970, vol. 195, no. 1, pp. 98–100.

8. Nesmeyanov, N.A., Novikov, V.M., and Reutov, O.A., *Zh. Org. Khim.*, 1966, vol. 2, no. 6, pp. 942–946.
9. Schmidbaur, H. and Rathlein, K.-H., *Chem. Ber.*, 1974, vol. 107, no. 1, pp. 102–111.
10. Tietze, L.-F. and Eicher, T., *Reactions and Syntheses in the Organic Chemistry Laboratory*, Mill Valley, California: University Science Books, 1989. Translated under the title *Preparativnaya organicheskaya khimiya*, Moscow: Mir, 1999, p. 215.