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A NEW REVERSIBLE SYNTHESIS OF VINYL PHOSPHATES FROM MERCURIALS

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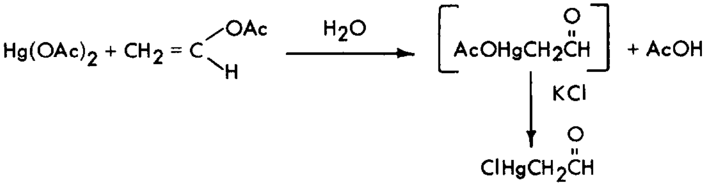
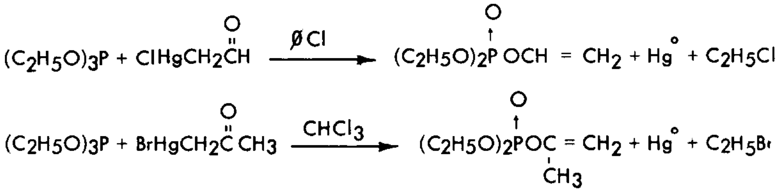
Halomercuri-aldehydes and ketones are easily prepared in high yield by aqueous mercuration of vinyl acetates(1).



$$Hg(OAc)_2 + CH_2=C\begin{matrix}OAc\\H\end{matrix} \xrightarrow{H_2O} \left[AcOHgCH_2\overset{O}{\overset{\|}{C}}H\right] + AcOH \xrightarrow{KCl} ClHgCH_2\overset{O}{\overset{\|}{C}}H$$

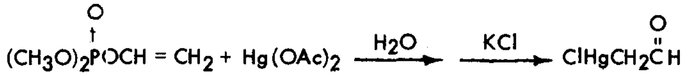
We report that the dry mercurials react smoothly with trialkyl phosphites in non-hydroxylic solvents to produce vinyl phosphates with liberation of free mercury.



$$(C_2H_5O)_3P + ClHgCH_2\overset{O}{\overset{\|}{C}}H \xrightarrow{\phi Cl} (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}OCH=CH_2 + Hg^{\circ} + C_2H_5Cl$$

$$(C_2H_5O)_3P + BrHgCH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{CHCl_3} (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}O\underset{CH_3}{C}=CH_2 + Hg^{\circ} + C_2H_5B$$

Of related interest is the observation of mercurial regeneration from vinyl phosphates, providing a cyclic process of intrinsic value. This is a useful extension of the Nesmeyanov mercurial synthesis as vinyl phosphates are often much more accessible

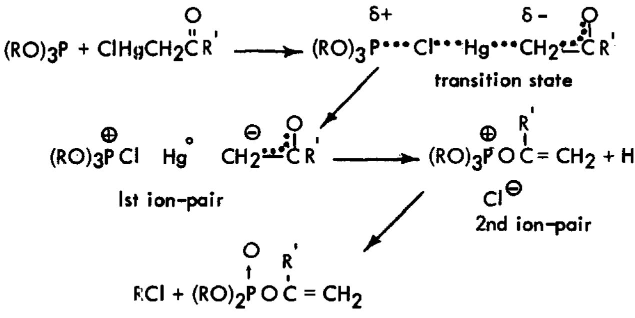


$$(CH_3O)_2\overset{O}{\overset{\uparrow}{P}}OCH = CH_2 + Hg(OAc)_2 \xrightarrow{H_2O} \xrightarrow{KCl} ClHgCH_2\overset{O}{\overset{\shortparallel}{C}}H$$

(via the Perkov reaction) than the corresponding vinyl acetates(2). It may be limited to simple alkyl and aryl substituted vinyl esters, however, as we were unable to convert dimethyl β,β-dichlorovinyl phosphate (DDVP) to its related mercurial. Halogens and other electronegative groups will, of course, reduce the nucleophilicity of the vinyl group toward Hg (II).

In many cases, the simple Perkov route to vinyl phosphates would be the method of choice over the mercurial route. The specific case of unsubstituted vinyl phosphates, however, has heretofore required the use of anhydrous chloroacetaldehyde, a hazardous and difficult chemical to acquire(3). With normal precautions against the presumed toxicity of chloromercuriacetaldehyde, large quantities of dialkyl vinyl phosphates can be made in a few hours from readily available vinyl acetate.

The recent work of Jensen and Ouellette(4) on solvolysis of RHgX tempts one to think in terms of a halomercuri leaving group with phosphite attack at the carbonyl center. Its obvious relation to the Perkov reaction, however, makes it more likely that a similar mechanism is operating. While the details of the Perkov are still in flux, the current thinking is sympathetic to phosphite attack at the halogen atom(5, 6). We suggest the following as likely in its grosser aspects:



It will be interesting to see if those cases which yield phosphonates (Arbuzov reaction) rather than vinyl phosphates, e.g., iodoacetone, will do so with the corresponding mercurial. Unlike the simple Perkov reaction, the first ion-pair is necessarily "non-intimate", being separated by a Hg° atom. In borderline cases, this may exert a significant influence on C- versus O- attack on the chlorophosphonium cation.

EXPERIMENTAL

Triethyl phosphite was refluxed with an equivalent of chloromercuriacetaldehyde in chlorobenzene for 1.2 hours. The finely divided mercury was separated as a gray solid and washed with benzene. Distillation gave a 60% yield of diethyl vinyl phosphate, b.p. 99 - 105°/20 - 25 mm.; calcd.: P, 17.19; found: P, 16.75. The bottoms plus column runback (30%) was identical in all major infrared peaks to the overhead product. A strong vinyl stretching appears at the same frequency (1645 cm^{-1}) as in an available authentic sample of <u>dimethyl</u> vinyl phosphate. The NMR spectrum is also fully consistent with structure.

An equivalent of triethyl phosphite was added dropwise to a stirred slurry of bromomercuriacetone in chloroform. The bulk of the mercurial entered solution with concomitant separation of finely divided mercury. After 20 minutes of reflux, Celite was added and the slurry filtered. During solvent stripping, more mercury separated, indicating that 20 minutes at 60° is insufficient. Final distillation gave diethyl isopropenyl phosphate boiling sharply at 50.5 - 51.5°/0.1 mm. in 72% yield; calcd.: P, 15.94; found: P, 15.25. The infrared spectrum is identical with that of an authentic sample prepared from triethyl phosphite and chloroacetone.

Dimethyl vinyl phosphate was shaken with an equivalent of mercuric acetate in water acidified with acetic acid. After 30 minutes, the solution was clarified with carbon and excess aqueous potassium chloride was added. The mercurial separated rapidly as a crystalline solid in 68% yield. It is identical with an authentic sample of chloromercuriacetaldehyde prepared from vinyl acetate (1).

REFERENCES

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(2) A wide variety of a-haloketones and aldehydes are available and conversion to the corresponding vinyl phosphates in high yield is experimentally simple.

(3) Chloroacetaldehyde can no longer be purchased. It was removed from the market because of severe problems in storage stability.

(4) F R. Jensen and R.J. Ouellette, *J. Am. Chem. Soc.* **85**, 363(1963), and references cited therein.

(5) A.J. Speziale and L.R. Smith, *J. Am. Chem. Soc.* **84**, 1868 (1962).

(6) H. Hoffman and H.J. Diehr, *Tetrahedron Letters* No. 13, 583 (1962).