# Organo-mercury-(I) and -(II) Ketenide Derivatives

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*Summary* Reactions of certain mercury-(I) and -(II) salts with keten or acetic anhydride yield organometallic ketenide derivatives of mercury-(I) and -(II) respectively: the former represent the first examples of stable organomercury(I) compounds to be characterised.

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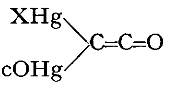
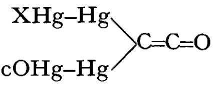
Lutsenko *et al.* have reported that mercury(II) acetate and mercury(II) oxide react with keten in various alcohols to form the corresponding esters of mercuribisacetic acid, $Hg(CH_2CO_2R)_2$.[1] A later paper described the formation of chloromercuricacetyl chloride, $ClHgCH_2COCl$, by reaction of mercury(II) chloride with keten in diethyl ether at −30 °C.[2] Although a mercury(II) ketenide, *e.g.* ClHg-CH=C=O, might well have been an intermediate in such reactions, the authors did not isolate or refer to such a species. We now report the preparation and isolation of mercury(II) and mercury(I) ketenides, (**1**) and (**2**) respectively, where X = –OAc, $–NO_3$, or $–ClO_4$. The mercury(II) ketenides (**1**) have been prepared by several different procedures, the simplest of which is to warm a solution of a suitable mercury(II) salt, such as the acetate, nitrate, or perchlorate (but not the halides or tetrafluoroborate) in an aprotic solvent such as acetonitrile, with acetic anhydride. The insoluble white ketenides separate out within a few minutes (60—80% yields) [reaction (1)].



(**1**) **a**, X = OAc
**b**, $X = NO_3$
**c**, $X = ClO_4$



(**2**) **a**, X = OAc
**b**, $X = NO_3$
**c**, $X = ClO_4$

$$2HgX_2 + Ac_2O \xrightarrow{60\,°C} (\mathbf{1}) + 3HX \qquad (1)$$

An attempted preparation of (**1b**) using acetic anhydride in pyridine gave the corresponding mono-pyridinate. A reaction of mercury(II) acetate with acetic anhydride has been previously reported, although the work-up procedure used would have decomposed any ketenide produced.[3]

Direct reaction of keten with solutions of the mercury(II) salts in acetonitrile at room temperature initially gives the same products (**1**), but continued treatment with ketene causes decomposition to mercury metal.

Interestingly, reactions of mercury(II) nitrate and perchlorate dihydrates with isopropenyl acetate or vinyl acetate instead of acetic anhydride give the same products [*e.g.* reaction (2)].

$$2Hg(NO_3)_2{\cdot}2H_2O + 5CH_2{=}C(Me)OAc \rightarrow (\mathbf{1}) + 3AcOH + 5Me_2CO + 3HNO_3 \qquad (2)$$

Reaction (1) occurs more rapidly in the presence of traces of strong acids such as sulphuric or perchloric acid, but the yields are not significantly increased.

Mercury(I) ketenides are less readily prepared, the most satisfactory preparation (60—80% yields) being *via* reaction of mercury(I) acetate, nitrate, or perchlorate with acetic anhydride in the presence of a trace of concentrated sulphuric acid [reaction (3)]. The exclusive presence of mercury(I) is unambiguously established by the quantitative formation of mercury(I) chloride on treatment with dilute hydrochloric acid. Acetic acid was the only organic product detected.

$$2Hg_2(OAc)_2 + Ac_2O \rightarrow (AcOHg_2)_2C{=}C{=}O + 3AcOH \qquad (3)$$

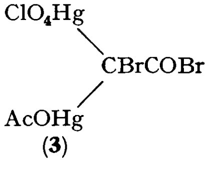
The mercury-(I) and -(II) ketenides, like the copper,[4] silver,[5] and gold[6] analogues, are involatile infusible solids, insoluble in all common solvents. These properties suggest strongly associated structures [*cf.* $(Ag_2C_2O)_n$[4]], although the structures are here depicted as monomeric for convenience. Unlike the group IB metal ketenides,[4–6] they are not explosive, except for those containing perchlorate ion, *which are dangerously so.* They are stable in dry air for several weeks at room temperature. The poor crystallinity has precluded *X*-ray structural studies.

The principal feature of the i.r. spectra of all the mercury ketenides is an intense band at *ca.* 2070 $cm^{-1}$ (ν CCO), the position of which varies slightly with the nature of the associated anions and the valence state of mercury. The only other bands, apart from those of the associated anions, are at 276 m (ν Hg–C) and 620 w (δ CCO) $cm^{-1}$. Very similar bands are present in the i.r. spectra of group IB metal ketenides.[4–6]

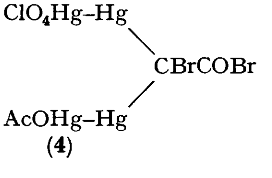
Attempts to corroborate the presence of an Hg–Hg bond in (**2a**) by Raman spectroscopy failed owing to intense fluorescence of the samples in the laser beam. The peaks of highest *m/e* in the mass spectrum of (**2a**) showed the characteristic isotope pattern of mercury around *m/e* 200, suggesting that complete thermal decomposition of involatile (**2**) had occurred on the heated probe. Mercury(I) acetate likewise gave peaks corresponding to Hg, not $Hg_2$.

The mercury(II) ketenides dissolve in dilute hydrochloric acid to form $Hg^{2+}$ totally free from mercury(I) products [*cf.* the mercury(I) ketenide species]; acetic acid is the only organic product. The mercury-(I) and -(II) ketenide species all react with hydrogen chloride gas to give keten and acetyl chloride. Rapid thermal decomposition of all these ketenides under argon gives carbon suboxide as a major gaseous product (i.r. spectrum), as with group IB metal ketenides.[4–6]

It is interesting that reaction of (**1c**) and (**2c**) with bromine in carbon tetrachloride did not rupture the C–Hg bonds, but gave the novel organomercury species (**3**) and (**4**). Reaction of (**4**) with hydrochloric acid gave a quantitative yield of mercury(I) chloride. Reaction of (**3**) with methanol gave the corresponding bromoester which on



(**3**)



(**4**)

demercuration with sodium borohydride gave methyl bromoacetate; compound (**4**) behaved similarly, although the corresponding intermediate was not isolated.

The formation of organomercury(I) species is of special interest, as organomercury(I) compounds are virtually unknown. Although Casanova *et al.* claimed the preparation of di-n-hexyldimercury by electrochemical reduction of 1,6-dibromohexane at a mercury cathode,[7] Avaca *et al.* subsequently obtained polymeric $Hg^{II}$ products from reactions of this type, and doubted whether $Hg^{I}$ was present.[8] Moreover, Butin *et al.* have reported that RHgHgR species formed at a mercury surface during electrochemical reduction have short lifetimes.[9] Thus the species (**2**) and (**4**) appear to represent the first clear examples of stable organomercury(I) compounds. Good analytical data have been obtained for all the new compounds mentioned.

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[1] I. F. Lutsenko, V. L. Foss, and I. L. Ivanova, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 5, 1708.

[2] M. A. Kazankova, I. G. Trostyanskaya, T. Ya Satina, and I. F. Lutsenko, *Zhur. obshchei Khim.*, 1976, **46**, 1412.

[3] J. Sand and F. Singer, *Ber.*, 1903, **36**, 3707.

[4] E. T. Blues, D. Bryce-Smith, H. Hirsch, and M. J. Simons, *Chem. Comm.*, 1970, 699; D. Bryce-Smith, *Chem. and Ind.*, 1975, 154.

[5] E. T. Blues, D. Bryce-Smith, B. Kettlewell, and M. Roy, *J.C.S. Chem. Comm.*, 1973, 921.

[6] E. T. Blues, D. Bryce-Smith, I. W. Lawston, and G. D. Wall, *J.C.S. Chem. Comm.*, 1974, 513; E. T. Blues, D. Bryce-Smith, and I. W. Lawston, *Gold Bulletin*, 1976, **9**, 88.

[7] J. Casanova and H. R. Rogers, *J. Amer. Chem. Soc.*, 1974, **96**, 1942.

[8] L. A. Avaca, F. R. Gonzalez, and N. R. Stradiotto, *Electrochim. Acta*, 1977, **22**, 225.

[9] K. P. Butin, A. B. Ershler, V. V. Strelets, A. N. Kashin, I. P. Beletskaya, O. A. Reutov, and K. Marcuskova, *J. Organometallic Chem.*, 1974, **64**, 171.