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Abstract

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On the Reaction of Ketene with Mercury Salts

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Continuing the study of methods for the synthesis of esters of α-mercurated carboxylic acids and of their reactivity, we investigated the possibility of obtaining compounds of this type from ketene. Taking into account the high activity of ketene, it could be expected that mercury alcoholates (^{1}) would readily react with it to form esters of mercurated acetic acid. Indeed, when ketene is passed into a suspension of a mercury alcoholate in ether, a reaction readily occurs with evolution of heat and an organomercury compound is formed. In contrast to the known reactions of addition of mercury salts to a double and triple carbon-carbon bond (alkenes, dienes, enol esters), when salts of organomercury compounds, RHgX, are formed, in this case the reaction proceeds to the formation of the complete organomercury compound R_2Hg, which depends on the high reactivity of ketene:

$$\mathrm{Hg(OR)_2 + 2CH_2 = C = O \rightarrow Hg(CH_2COOR)_2}.$$

It was subsequently established that it is more convenient to carry out the reaction not starting from mercury alcoholates, which have been described only for the simplest alcohols (^{1}), but using solutions or suspensions of mercuric acetate in the corresponding alcohol:

$$\mathrm{Hg(OCOCH_3)_2 + 2ROH + 2CH_2 = C = O \rightarrow Hg(CH_2COOR)_2 + 2CH_3COOH}.$$

In carrying out the reaction, an excess of ketene should be passed through in order to convert completely the initially formed compound $\mathrm{CH_3COOHgCH_2COOR}$ into $\mathrm{Hg(CH_2COOR)_2}$, since in a number of cases it was not possible to separate the mixture of these compounds by crystallization. Finally, compounds of the type $\mathrm{Hg(CH_2COOR)_2}$ can also be obtained if mercuric oxide with a small addition of mercuric acetate is introduced into the reaction with ketene. Initially, mercuric acetate reacts with ketene, as described above. The acetic acid formed along with the organomercury compound dissolves mercuric oxide, regenerating the mercury salt that has entered into reaction with ketene. This variant of the reaction is the most convenient, since in this case a complete organomercury compound is formed, containing only traces of the organomercury salt $CH_3COOHgCH_2COOR$. The reaction of ketene with mercuric oxide in the presence of mercury acetate was studied in various alcohols: methyl, ethyl, normal and iso-propyl, butyl, and others. In all cases, in yields close to quantitative, compounds of the type $Hg(CH_2COOR)_2$ were obtained.

Esters of mercuribisacetic acid are crystalline compounds, readily soluble in ordinary organic solvents. Most esters of mercuribisacetic acid can be recrystallized from petroleum ether. The methyl ester of mercuribisacetic acid is readily soluble in water and can be isolated unchanged from aqueous solutions. The following compounds of the type $Hg(CH_2COOR)_2$ were obtained (R, melting point, Hg content in percent, found and calculated, are listed): CH_3, 100°, 57.99%, 58.05%, 57.85%; C_2H_5, 40°, 53.98%, 53.21%, 53.52%; n-C_3H_7, 46°, 49.86%, 49.61%, 49.80%;

iso-C_3H_7, 33°, 50.27%, 50.36%, 49.80%; n-C_4H_9, 38–39°, 46.95%, 46.98%, 46.55%; iso-C_4H_9, 72°, 47.15%, 46.97%, 46.55%; tert.-C_4H_9, 86°, 46.80%, 46.95%, 46.55%.

Esters of mercuriacetic acid readily enter into the reaction with sublimate that is the reverse of symmetrization, giving compounds of the type $ClHgCH_2COOR$ (listed are *R*, melting point, Hg content in percent: found and calculated for the compounds obtained; the substances marked with an asterisk had previously been obtained by another method (2)): CH_3, 83°, 65.02%, 65.06%, 64.88%; $C_2H_5^*$, 66°, –; $C_3H_7^*$, 57°, –; iso-C_3H_7, 59°, 59.29%, 59.28%, 59.49%; n-C_4H_9, 20–22°, 57.04%, 57.09%, 57.11%; iso-C_4H_9, 65°, 57.30%, 57.50%, 57.11%.

Experimental Part

Reaction of mercury methylate with ketene. A filtered solution of 16 g of mercury acetate in 160 ml of absolute methanol is added dropwise, with stirring, to a solution of sodium methylate (from 2.3 g of sodium and 40 ml of absolute methanol). After centrifugation and washing of the precipitate of mercury methylate with absolute methanol and ether, absolute ether is added, and ketene is introduced with vigorous stirring. The reaction proceeds with self-heating; the light-yellow precipitate of mercury methylate disappears, and crystals of methyl ester of mercuriacetic acid begin to separate from the warm solution. They are dissolved by adding ether, the solution is filtered, and after evaporation of the ether 13 g (75% of theory) of methyl ester of mercuriacetic acid is obtained. After recrystallization from a mixture of methanol with ether, m.p. 100°.

$C_6H_{10}O_4Hg$. Found %: C 20.52; 20.63; H 2.82; 2.71; Hg 57.99; 58.05;
Calculated %: C 20.78; H 2.91; Hg 57.85

Reaction of mercury acetate with ketene. A 3–4-fold excess of ketene is passed into a solution of 32 g of mercury acetate in 120 ml of absolute methanol. After filtration of the solution and evaporation in the vacuum of a water-jet pump, crystals and a small amount of oil remain (total weight 33 g, i.e., 95% of theory). Purification by two recrystallizations from methanol gives 18 g (52% of theory) of methyl ester of mercuriacetic acid with m.p. 98°; after a third recrystallization from a mixture of methanol with ether, m.p. 100°. A mixed sample with methyl ester of mercuriacetic acid gives no depression of the melting point.

Reaction of mercury oxide with ketene in the presence of mercury acetate. Into a suspension of 20 g of mercury oxide and 3 g of mercury acetate in 120 ml of absolute methanol, ketene is passed with vigorous stirring until the mercury oxide is completely dissolved. After filtration, the solution is evaporated in the cold, giving 34 g of methyl ester of mercuriacetic acid (96.5% of theory) with m.p. 96–98°. After recrystallization from methanol, m.p. 100°; a mixed sample with methyl ester of mercuriacetic acid gives no depression of the melting point.

Reaction of methyl ester of mercuriacetic acid with sublimate. A solution of 3.9 g of methyl ester of mercuriacetic acid and 3 g of sublimate in 13 ml of methanol was heated at 70° until the $HgCl_2$ disappeared (test with NaOH). After filtration, on cooling of the solution, 6 g of methyl ester of chloromercuriacetic acid precipitated (89% of theory), with m.p. 82–83°; after recrystallization from methanol, m.p. 83°.

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