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Abstract

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PREPARATION OF METALLIC DERIVATIVES OF VINYL ALCOHOL

The most interesting feature of α-monomercurated carbonyl compounds is their capacity for dual (at C and at O) reaction and for the formation of two series of derivatives. In the first case, reaction products corresponding to direct replacement of the mercury atom are formed; in the second case the reaction proceeds with transfer of the reaction center of the molecule, owing to the strongly pronounced conjugation of the Hg—C and C—O bonds (σ—π conjugation) ($^{1-4}$).

In the present article we report on a new group of reactions of monomercurated carbonyl compounds studied by us, which likewise proceed with transfer of the reaction center. The reactions described below make it possible to effect an easy transition from C-metallic derivatives of carbonyl compounds to their O-metallic derivatives and, in particular, to obtain, in high yields, metallic derivatives of the simplest enol—vinyl alcohol.

Some of these results were reported by us in 1955 in Zurich at the 14th International Congress of Theoretical and Applied Chemistry.

To obtain lithium and sodium vinylates we carried out experiments on the cleavage of monomercurated acetaldehyde with metallic lithium and sodium in benzene and toluene. These attempts were not successful, since even upon many hours of boiling no cleavage of the Hg—C bond was observed.

Lithium and sodium vinylates in the individual state were isolated by us upon cleavage of the Hg—C bond of mercury derivatives of aldehydes and ketones by solutions of alkali metals in liquid ammonia:

$$\mathrm{Hg(CH_2CHO)_2 + Li/NH_3 \rightarrow Li/Hg + 2CH_2 = CHOLi.}$$

The compounds obtained are colorless crystalline substances. Lithium vinylate is soluble in ether and benzene; sodium vinylate is insoluble in both ether and benzene.

The composition and structure of the compounds obtained were demonstrated by analyses, titration of a weighed sample with acid, and hydrolysis to acetaldehyde. The infrared spectrum of lithium vinylate also confirmed the data on the structure of this compound. In the infrared spectrum there is no band characterizing the carbonyl group, and there is a band at 1600 cm^{-1} characterizing the double bond.

As a result of our development of simple methods for the synthesis of mercuribisacetaldehyde (^{5}) and of the easy cleavage of this compound by alkali metals in liquid ammonia, the simplest metallic enolates, not previously described, became accessible.

Already in one of the first articles on the reactions of monomercurated carbonyl compounds (^{2}) we indicated the probability of formation of the alcoholate of vinyl alcohol in the reaction of phenylmagnesium bromide with bromomercuriacetaldehyde according to the equation

$$\mathrm{BrHgCH_2CHO + C_6H_5MgBr \rightarrow C_6H_5HgBr + CH_2 = CHOMgBr.}$$

Our unsuccessful attempts to carry out the symmetrization reaction of α-halomercuriketones by such symmetrizing agents as potassium iodide, sodium iodide, potassium rhodanide, sodium thiosulfate, etc. (^{6}) are also connected with enolate formation; in all these cases, instead of symmetrization, we observed extremely easy hydrolysis of the Hg–C bond.

At present we believe that cleavage of the Hg–C bond in attempts to symmetrize mercury salts of aldehydes and ketones by the action of various complexing agents proceeds through the intermediate formation of an enolate:

$$\mathrm{ClHgCH_2CHO + 4NaJ \rightarrow Na_2HgJ_4 + NaCl + [CH_2 = CHONa].}$$

The latter is readily hydrolyzed in aqueous medium, liberating the aldehyde (or, correspondingly, the ketone). Under analogous conditions, rupture of the Hg–C bond occurs in esters of mercurated carboxylic acids. The strongly expressed σ–π conjugation in the case of mercury derivatives of carbonyl compounds makes it possible to carry out cleavage of the Hg–C bond in these substances even with such weak complexing agents as potassium chloride. Aqueous solutions of mercuribisacetaldehyde slowly at room temperature, and rapidly on heating, decompose completely with a 10% solution of potassium chloride,

$$\mathrm{Hg(CH_2CHO)_2 + KCl \rightarrow ClHgCH_2CHO + [CH_2 = CHOK] \xrightarrow{H_2O} CH_3CHO + KOH.}$$

The organomercury salt and the carbonyl compound formed in such decomposition, under the alkaline conditions of the medium, give amorphous precipitates insoluble in anything, as was previously found by Reynolds (^{7}), Nef (^{8}), and others.

To isolate metallic derivatives of vinyl alcohol by the exchange reaction of a metal halide with halomercuriacetaldehyde, we excluded the aqueous medium and carried out the reaction between anhydrous ferric chloride and chloromercuriacetaldehyde in dry acetone.

The composition and structure of the iron vinylate oxychloride thus obtained by us, $CH_2-CHOFe(OH)Cl$, were proved by analyses and ozonization*.

Attempts at alkylation and acylation of lithium and sodium vinylates under various conditions with butyl bromide, allyl halides, dimethyl sulfate, benzoyl chloride, and others were unsuccessful because of the readily occurring strong resinification of the reaction mixture. These failures are evidently connected with the action of alkali-metal vinylates on the expected reaction products—the aldehydes:

$$CH_2 = CHONa + RX \rightarrow RCH_2CHO + NaX.$$

The halide salt can be isolated in yields close to quantitative.

It may be assumed that a detailed investigation of metallic derivatives of the simplest enolic system, which we shall continue, will provide important material for further study of the problem of bond conjugation and transfer of the reaction center of the molecule.

Experimental Part

Reaction of chloromercuriacetaldehyde with ferric chloride. To 14 g (0.05 mole) of chloromercuriacetaldehyde, dried over P_2O_5 and thoroughly ground, 20 ml of dry acetone was added, and, with stirring, a solution of 2.8 g (0.017 mole) of anhydrous ferric chloride in 40 ml of acetone was added. To the filtered solution 200 ml of absolute ether was added. The orange precipitate that separated was isolated, washed three times with ether, and reprecipitated twice with absolute ether from an acetone solution. According to analysis, the substance obtained corresponds to iron vinylate oxychloride of composition $CH_2 = CHOFe(OH)Cl$. Yield 2.5 g (83% of theory). On heating the substance decomposes; it is readily hydrolyzed by water with formation of acetaldehyde, and is soluble in acetone and pyridine.

* One chlorine atom is apparently hydrolyzed at the expense of water liberated during partial condensation of acetone under the influence of anhydrous ferric chloride.

$CH_2{=}CHOFe(OH)Cl$. Found, %: C 15.60; 15.46; H 2.74; 2.65; Fe 35.7; 36.6
Calculated, %: C 15.80; H 2.64; Fe 36.6

Ozonation of iron vinylate oxychloride. A suspension of $CH_2{=}CHOFe(OH)Cl$ (from 14 g of chloromercuriacetaldehyde and 2.8 g of anhydrous $FeCl_3$) in 40 ml of dry chloroform was subjected to ozonation. After 2% ozone had been passed for 14 h at a rate of 4 l/h, the entire precipitate of iron vinylate dissolved, and the solution acquired an orange color. The chloroform solution was poured into 50 ml of water acidified with H_2SO_4 and containing 0.5 g of $FeSO_4$. After complete decolorization of the chloroform solution, the aqueous extract was divided into two parts. To one part a saturated aqueous solution of 1.5 g of dimedone was added. After 2 h, 0.4 g of the dimedone derivative of formaldehyde was separated, mp 189° (twice from alcohol). Literature data ([9]) mp 189°. The second part of the aqueous solution was neutralized with soda and evaporated to dryness; by heating the dry residue with an aqueous-alcoholic solution of *p*-chlorophenacyl bromide, the *p*-chlorophenacyl ester of formic acid was obtained, mp 127-127.5°. Literature data ([10]) mp 128°.

Preparation of sodium vinylate. To a solution of 3 g of sodium in 120 ml of liquid ammonia, with vigorous stirring, chloromercuriacetaldehyde was added in small portions exactly until the blue color of the solution disappeared; this required about 13.7 g of the mercury compound (even a small excess of chloromercuriacetaldehyde causes resinification of the reaction mixture). In all operations, careful protection of the reaction mixture from moisture and carbon dioxide in the air is necessary. The reaction mixture is centrifuged, the solution is decanted from the amalgam, and filtered through a fine-porosity glass filter. After evaporation of the ammonia, the white crystalline residue is dried for several hours in vacuo. Yield of sodium vinylate: 5 g (80% of theory).

$CH_2{=}CHONa$. Found, %: C 35.69; 35.20; H 4.76; 4.71; Na 35.6
Calculated, %: C 35.35; H 4.58; Na 34.8

Preparation of lithium vinylate. Under conditions analogous to those described above, from 14.3 g of chloromercuriacetaldehyde and 1 g of lithium in 120 ml of liquid ammonia, 3.8 g (78% of theory) of lithium vinylate was obtained as a white crystalline substance. Lithium vinylate is soluble in benzene and ether.

$CH_2{=}CHOLi$. Found, %: C 47.68; 47.70; H 6.67; 6.67
Calculated, %: C 48.03; H 6.05

Hydrolysis of lithium vinylate. To 300 ml of a saturated aqueous solution of dimedone, 10 ml of a 1 N sulfuric acid solution was added, and then 0.3 g of lithium vinylate. After several days, 1 g (60% of theory) of crystals of the dimedone derivative was separated, mp 136°. A mixed melting-point test with the dimedone derivative of acetaldehyde gave no depression of the melting temperature. Literature data ([9]) mp 138°.

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CITED LITERATURE

1. A. N. Nesmeyanov, I. F. Lutsenko, N. N. Vereshchagina, *Izv. AN SSSR, OKhN*, 1947, 63.
2. A. N. Nesmeyanov, I. F. Lutsenko, *DAN*, **59**, 707 (1948).
3. A. N. Nesmeyanov, I. F. Lutsenko, Z. M. Tumanova, *Izv. AN SSSR, OKhN*, 1949, 601.
4. A. N. Nesmeyanov, E. T. Perevalova, *Izv. AN SSSR*, 1954, 1002.
5. I. F. Lutsenko, R. M. Khomutov, *DAN*, **102**, 97 (1955).
6. A. N. Nesmeyanov, I. F. Lutsenko, R. M. Khomutov, *DAN*, **88**, 837 (1953).
7. J. Reynolds, *Ber.*, **4**, 483 (1871).
8. J. Nef, *Lieb. Ann.*, **298**, 316 (1898).
9. D. Vorländer, *Zs. anal. Chem.*, **77**, 31 (1929).
10. C. Moses, *J. Am. Chem. Soc.*, **54**, 2101 (1932).

Note: Figure translations are in progress. See original paper for figures.