Some Reactions of Mercuridiacetaldehyde*

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Mercuridiacetaldehyde $Hg(CH_2CHO)_2$ was first prepared by Nesmeyanov and his group in 1955; it has since been used for the synthesis of various kinds of vinyl ethers.[1-7] Mercuridiacetaldehyde and chloromercuriacetaldehyde show O-vinylation by means of the reaction of the Hg–O with C-halogen bonds in substrates. In some cases, however, the reaction proceeds in an alternative way, one in which the C-alkylation reaction takes place by means of the Hg–C bonds.[2,8] Thus mercuridiacetaldehyde can also be regarded as divinyloxymercury, a mercuric salt of vinyl alcohol. A number of vinyloxymetal compounds have been reported in the literature, such as aluminum,[9] titanium,[10] lithium,[5] sodium,[5] iron,[5] and silicon.[6] However, the chemical behavior of the unsaturated bonds in these compounds is scarcely known at all.

In the course of their synthetic study of vinyloxymetal compounds with mercuridiacetaldehyde, the present authors noticed that the latter compound was easily converted, in various organic solvents, into an insoluble and infusible substance. This phenomenon led the authors to suspect that the insoluble substance might be a polymeric material which was formed by the addition reaction of C=C double bonds in the form of divinyloxymercury. The object of the present work is to elucidate the chemical structure of the insoluble substance, and also to obtain further information on the chemical structure of the starting material, mercuridiacetaldehyde.

As a compound closely-related to mercuridiacetaldehyde, Nef's so-called mercuric salt of vinyl alcohol was also reinvestigated in the light of recent knowledge.

Results and Discussion

On Mercuridiacetaldehyde.—Two tautomeric structures, I and II, can be assumed for mercuridiacetaldehyde in view of its dual reactivities:[12]

$Hg(CH_2CHO)_2$ (I) $\qquad$ $Hg(OCH{=}CH_2)_2$ (II)

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1) A. N. Nesmeyanov, K. M. Khomtov and I. F. Lutsenko, *Izvest. Akad. Nauk SSSR, Otdet. Khim. Nauk*, **1957**, 942.

2) A. N. Nesmeyanov, I. F. Lutsenko and Z. M. Tumanova, ibid., **1949**, 601.

3) I. F. Lutsenko and R. M. Khomtov, *Dokl. Akad. Nauk SSSR*, **102**, 97 (1955).

4) I. F. Lutsenko, *Izvest, Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1956**, 27.

5) A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **120**, 1049 (1958).

6) A. N. Nesmeyanov and I. F. Lutsenko, ibid., **128**, 551 (1959).

7) A. N. Nesmeyanov, *Zhur. Obshchei Khim.*, **29**, 2817 (1959).

8) D. N. Kursanov, M. E. Volpin and I. S. Okhrem, *Dokl. Akad. Nauk SSSR*, **120**, 531 (1958).

9) L. I. Zakharkin, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1961**, 378.

10) J. H. Haslam, U. S. Pat. 2708205 (1955).

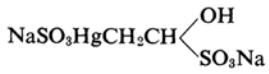
11) J. U. Nef, *Ann.*, **298**, 316 (1897).

12) A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **59**, 707 (1948).

Type I should show infrared absorptions of the carbonyl group, while type II shows those of the C=C double bond. The infrared spectrum of mercuridiacetaldehyde shows a strong band at around 1645 cm^{-1} (Table I). Nesmeyanov and Lutsenko[13] assigned the band to the stretching vibration of the carbonyl group, taking into account the fact that the ultraviolet spectrum of the compound showed the absorption maximum at 296 $m\mu$ ($\log \varepsilon = 2.90$) which is characteristic of the carbonyl absorption. In order to exlain both the large bathochromic shift of the carbonyl band and the dual reactivities of the compound, they proposed a σ-π conjugated structure.[13,14]

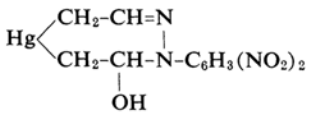
As the infared spectrum of mercuridiacetaldehyde showed an absorption band at 2720 cm^{-1} which seemed to be a normal position for the C–H stretching vibration of an aldehyde group, the reactions of the compound with typical aldehyde reagents were studied. The reactions of the compound with sodium bisulfite, 2, 4-dinitrophenylhydrazine, semicarbazide hydrochloride, and hydroxylamine hydrochloride were found to take place as follows:

$$Hg(CH_2CHO)_2 + NaHSO_3 \rightarrow$$



(III)

$$Hg(CH_2CHO)_2 + NH_2NHC_6H_3(NO_2)_2 \rightarrow$$



(IV)

$$Hg(CH_2CHO)_2 + NH_2NHCONH_2 \cdot HCl \rightarrow$$

$$ClHgCH_2CH{=}NNHCONH_2$$

(V)

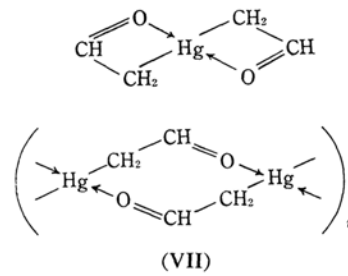
$$Hg(CH_2CHO)_2 + NH_2OH \cdot HCl \rightarrow$$

$$ClHgCH_2CH{=}NOH$$

(VI)

The structural assignment of these products was based on analysis and on a study of their infrared spectra. Structure IV is tentatively assigned as in the case of levulinaldehyde.[15] The reaction with hydrazine hydrate led to the liberation of metallic mercury. Thus, it was shown that mercuridiacetaldehyde behaved like usual aldehydes.

The infrared spectrum of mercuridiacetaldehyde (Table I) shows a band at 553 cm^{-1} which may be assigned to Hg–C. The wave number is almost the same as that reported for dimethylmercury (550 cm^{-1}),[16] suggesting a covalent nature of the Hg–C bond. As the carbonyl absorption at about 1645 cm^{-1} corresponds to an intermediate of a metal chelate (1600—1530 cm^{-1}) and normal carbonyl, the carbony oxygen group in the compound might be weakly chelated to the mercury atom in the same molecule or form a polymer through coordination to the mercury atom in the next molecule. Thus, the structure may be best represented by VII, as has been suggested by Nesmeyanov.



(VII)

The structure of the decomposition product, which will be discussed below, also seems to support these chelated structures.

The Decomposition of Mercuridiacetaldehyde in Alcohol.—Mercuridiacetaldehyde synthesized according to the method described in the literature[3] showed a melting point of 84—86°C, which was rather low compared with the reported value (91°C).

Purification by recrystallization from various solvents was unsuccessful, because of the instability of the crude compound in solution. Table II shows the solubility of the compound in ordinary organic solvents and its stability after it has stood overnight. Water was the best solvent, and in its dilute solution the compound was considerably stable, but in a concentrated solution the compound decomposed rapidly with the separation of metallic mercury. The compound, after the solvent treatment, generally showed much higher melting points, became insoluble, and showed a higher mercury-content than the original sample. Since a survey of the infrared spectra of the high-melting sapmles thus obtained usually showed new common absorption bands, the change brought about by this treatment is considered to be due to the formation of the same decomposition product. In order to elucidate the decomposition reaction, therefore, the reaction in ethanol was then studied in more detail.

13) A. N. Nesmeyanov and I. F. Lutsenko, ibid., **127**, 115 (1959).
14) A. N. Nesmeyanov, *Zhur. Obshchei Khim.*, **25**, 41 (1955).
15) C. Harries and M. Boegemann, *Chem. Ber.*, **42**, 442 (1901).
16) K. Bradersen, ibid., **90**, 2703 (1957).

TABLE I. INFRARED SPECTRA OF MERCURIDIACETALDEHYDE AND THE RELATED COMPOUNDS

$Hg(CH_2CHO)_2$	$ClHgCH_2CHO$	$Hg_2(CH_2CHO)_2$ (Decomp. product)	Nef's Compd.
2720 (w)	2720 (w)	2720 (w)	2720 (w)
1645 (vs)	1645 (vs)	1650 (m)	1650 (m)
		1580 (s)	1580 (s)
1410 (m)	1425 (w)	1420 (w)	
1390 (m)	1390 (m)	1400 (w)	1400 (w)
	1300 (w)	1300 (w)	
1148 (s)	1152 (s)	1160 (s)	1160 (m)
		1120 (w)	1140 (m)
1058 (m)	1080 (m)	1050 (m)	1030 (w)
1025 (s)	1020 (m)	1020 (w)	
930 (w)	955 (w)	940 (w)	940 (w)
553 (m)	553 (m)	545 (m)	545 (m)
		541 (m)	
456 (s)	488 (m)	448 (s)	448 (m)

TABLE II. SOLUBILITY AND STABILITY OF MERCURIDIACETALDEHYDE IN VARIOUS SOLVENTS

Treatment[a]	Solubility[b]	Hg% after treatment	Change of m. p. after the treatment, °C
Untreated		69.9	84
Ethanol	+		200—250 (d)
Ethanol, refluxed for 5—6 hr.		77.3	200—250 (d)
Benzene	−	64.7	
Benzene, refluxed for 5—6 hr.		72.6	250 (d)
Acetone	++	63.3	
Acetone, 3 days		78.4	250 (d)
Ethyl methyl ketone	+	78.4	250 (d)
Tetrahydrofuran	+	74.0	250 (d)
Methanol	++		200—250 (d)
Water	++		78—79

a) A mixture of about 1 g. of sample and 1 ml. of a solvent was allowed to stand overnight and then the solvent was evaporated in vacuo.
b) −, insoluble; +, soluble; ++, readily soluble.

When an ethanol solution of mercuridiacetaldehyde was kept under reflux, a white precipitate separated after one or two hours. After the refluxing had continued for 4 hr., the mercury content of the precipitate increased to 77.3% from the original 69.9%; it remained constant thereafter. Alternatively, when a catalytic amount of an ethanol solution of sodium ethoxide was added to the solution at room temperature, the white precipitate appeared immediately. In this case, the mercury content of the product increased to 80.7%.

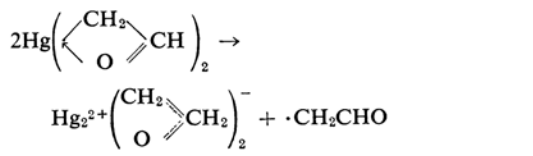
Associated with the decomposition phenomenon, the infrared spectra showed a marked change in some respects. The $\nu C{=}O$ band at 1645 cm^{-1} and the bands at 1150 and 1050 cm^{-1} diminished and new bands appeared at 1580, 1300 and 1120 cm^{-1}. The $\nu Hg{-}C$ band at 553 cm^{-1} shifted to the doublet at 545 and 541 cm^{-1}. The $\nu C{-}H$ of aldehyde at 2720 cm^{-1} showed no appreciable change.

When decomposition product was treated with bromine, bromacetaldehyde was obtained as a sole organic product. This fact suggests the existence of the $Hg{-}CH_2CHO$ group in the decomposition product.

$$-Hg{-}CH_2CHO + Br_2 \rightarrow -HgBr + BrCH_2CHO$$

The new band at 1580 cm^{-1} is considered to be due to a carbonyl bond which is weaker than that of the original mercuridiacetaldehyde (a bathochromic shift of 60 cm^{-1}). A bathochromic shift of the $\nu Hg{-}C$ bond also suggests a weaker Hg–C bond in the decomposition compound than in the original compound.

From the above-mentioned facts, the authors concluded that most of the mercuridiacetaldehyde was converted into a mercurous compound, $Hg_2(CH_2CHO)_2$ by the decomposition of the Hg–C bonds.



This conclusion is supported by the fact that the νC=O bands in mercuric and mercurous acetates are 1570 and 1540 cm^{-1} respectively, showing a bathochromic shift of 30 cm^{-1} in the change from mecuric to mercurous. The bathochloric shift of the νHg–C bond seems to be compatible with the fact that mercurous compound are generally more ionic than the corresponding mercuric compounds.

The decomposition reaction could, practically speaking, not be brought to completion, as may be seen from the analytical results and the infrared spectra, probably because of the insolubility of the product.

The decomposition of mercuridiacetaldehyde in ethanol may be interpreted in terms of a homolytic fission of the Hg–C bonds or by a nucleophilic substitution on mercury, followed by a homolytic cleavage of the Hg–OC_2H_5 bonds.

$$Hg(CH_2CHO)_2 \rightarrow HgCH_2CHO + \cdot CH_2CHO$$

or

$$Hg(CH_2CHO)_2 + C_2H_5OH \rightarrow C_2H_5OHgCH_2CHO + CH_3CHO$$

The formation of acetaldehyde was confirmed by a gas chromatographic analysis of the volatile component of the reaction mixture: about 40% of the theoretical amount of acetaldehyde was thereby detected as 2, 4-dinitrophenylhydrazone.

In the case of the base-catalyzed decomposition, it seems that the first step is a nucleophilic attack by the ethoxide anion on mercury, followed by the cleavage of the Hg–OC_2H_5 bonds. The acetaldehyde liberated during the alkaline decomposition was not detected, but it seemed to be converted into a brown polymeric material by the alkali.

As a compound closely related to mercuridiacetaldehyde, Nef's compound was reexamined. Nef[11] reported the synthesis of a mercuric salt of vinyl alcohol by the reaction of fresh mercuric oxide and aqueous acetaldehyde in the presence of sodium hydroxide. The infrared examination of Nef's compound indicated that the compound was identical with the decomposition product of the mercuridiacetaldehyde which had been obtained in the presence of sodium ethoxide.

Experimental

The Analysis of Mercury. — According to the method of Hirai and Hayatsu,[17] a sample containing mercury was digested with concentrated sulfuric acid and 30% aqueous hydrogen peroxide until a colorless solution was obtained. The mercuric ion content was determined by the usual Volhard method.

The Synthesis of Mercuridiacetaldehyde.—The method of Nesmeyanov[3] was taken, using yellow mercuric oxide, vinyl isobutyl ether, water and a catalytic amount of mercuric acetate. The crude yield was 86—89% (m. p. 82—83°C (91°C in the literature)). It was used without further purification. The presence of mercuric acetate as a catalyst was not essential for the reaction, particularly in the small-scale preparation. The yield in this case was 76—80% (m. p. 82—84°C). However, when the synthesis was carried out on a larger scale and without the addition of merric acetate, a rapid exothermic reaction after some induction period frequently resulted in the decomposition of a part of the product.

Reactions with the Aldehyde Reagents. — The sodium bisulfite adduct, 2,4-dinitrophenylhydrazone and semicarbazone were prepared in the usual manner. The sodium bisulfite adduct, which was recrystallized from water, decomposed at 133—138°C; yield, 62%. The infrared spectrum showed a νO–H band at 3450(s), bands of the sulfonate group at 1140(vs) and 650(s), a sulfite band at 980(s), and a νHg–C band at 530 cm^{-1}.

Found: Na, 10.3; Hg, 44.0. Calcd. for $C_2H_4O_7S_2Na_2Hg$: Na, 10.20; Hg, 44.50%.

The 2,4-dinitrophenylhydrazone which was recrystallized from ethanol decomposed at 138—139°C; yield, 54%. The infrared spectrum showed a νO–H band at 3300(m), a νC=N band at 1620(s), and a νHg–C band at 588(m) cm^{-1}.

Found: N, 11.4; Hg, 44.8. Calcd. for $C_{10}H_{10}O_5N_4Hg$: N, 11.99; Hg, 42.97%.

The semicarbazone recrystallized from ethanol decomposed at 159—160°C; yield, 31%. The infrared spectrum showed the νN–H bands of the amide group at 3420(m) and 3320(m), a δN–H band at 1540(s), and a νC=O band at 1660(s) cm^{-1}.

Found: N, 14.56. Calcd. for $C_3H_6ON_3HgCl$: N, 14.21%.

The reaction with hydroxylamine was carried out by mixing a freshly-prepared solution of mercuridiacetaldehyde (5 g.) in water (15 ml.) and a mixed aqueous solution of 2 g. of hydroxylamine hydrochloride and 2.8 g. of potassium acetate. A white precipitate was filtered out and recrystallized from ethanol. The yield was 11.4%. M. p. 115—116°C, with decomposition. The infrared spectrm showed a chelated νO–H band at 3170(m), ν=CH bands at 3025(m) and 3045(m), a νC=N band at 1658(s), and a δ=CH band at 840(s) cm^{-1}.

Found: N, 4.60. Calcd. for $C_2H_4ONHgCl$: N, 4.76%.

The Decomposition of Mercuridiacetaldehyde in Ethanol.—A solution of 9.87 g. of mercuridiacetaldehyde in 80 ml. of ethanol, after filtration, was refluxed for 5 to 6 hr., yielding 8.81 g. of an insoluble white precipitate (1.06 g. of weight loss).

17) M. Hirai and R. Hayatsu, *Yakugaku Zasshi*, **70**, 76 (1956).

The volatile portion of the filtrate was found by gas chromatography to contain acetaldehyde; this acetaldehyde was converted into 2,4-dinitrophenylhydrazone in the usual manner (m. p. 163°C). The mixed melting point test with an authentic sample did not show any depression. The yield was 2.43 g., which corresponded to 0.44 g. of acetaldehyde and to a 41.5% loss of the weight of the starting material. The insoluble product was found to contain 77.3% Hg, and it decomposed at 200—250°C.

The insoluble product (3.0 g.) was decomposed by an excess of a chloroform solution of bromine at room temperature. The chloroform solution, after filtration, was found by gas chromatography to contain bromacetaldehyde; it was then converted into 2,4-dinitrophenylhydrazone, the yield being 1.48 g. (m.p. 150—152°C (from ethanol)). The mixed melting point test did not show any depression.

Found: C, 31.05; H, 2.20; N, 18.38; Br, 17.01. Calcd. for $C_8H_7O_4N_4Br$: C, 31.68; H, 2.28; N, 18.48; Br, 16.40%.

Into a solution of mercuridiacetaldehyde (3.0 g.) in 30 ml. of ethanol, a few drops of a solution of sodium ethoxide in ethanol (1 N) were added; the immediate formation of a white precipitate was observed. This precipitate (2.12 g.) contained 80.7% Hg.

Nef's Compound. — Nef's procedure was used, yielding 6.6 g. of the product from 8.0 g. of mercuric chloride, 4.0 g. of acetaldehyde, and 20.0 g. of sodium hydroxide. The product decomposed at about 190—210°C, changing in color from white to orange. It was soluble in oranganic solvents and in water. The infrarred spectrum is presented in Table I. It was found to contain 77.02% Hg.

Summary

Mercuridiacetaldehyde is soluble in polar solvents and rather instable in the state of solution, yielding an insoluble and infusible substance. The decomposition reaction has been proved to include the formation of mercuri(I)-acetaldehyde $Hg_2(CH_2CHO)_2$ by the cleavage of one of the Hg–C bonds. On the other hand, mercuridiacetaldehyde reacted with aldehyde reagents as usual aldehydes. The change in the infrared spectra on these reactions has been interpreted in terms of σ-π conjugation, as has been suggested previously by Nesmeyanov.

Nef's compound, which is considered to be a mercuric salt of vinyl alcohol, has been found to be almost identical with the mercuri-(I)-acetaldehyde.

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