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THE EFFECT OF INTRAMOLECULAR COORDINATION ON REACTIONS OF ORGANOMETALLIC COMPOUNDS

I. ORGANOMERCURIC FULMINATES

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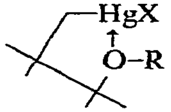
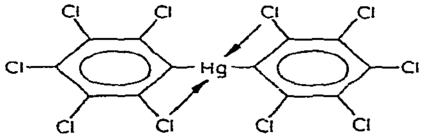
Several instances are known in which intramolecular coordination in β- and γ-substituted organometallic compounds has been postulated.

Pakhomov[1] in the course of an X-ray examination of organomercuric compounds declared that there is an intramolecular coordination in a number of these compounds, *e.g.*, in a system such as

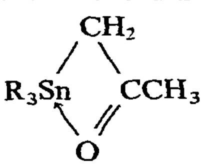


where X = SCN, R = Et; X = I, R = Me.

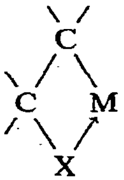
Bregadze *et al.*[2] have shown that there is some coordination in crystals of bis(pentachlorophenyl)mercury between the mercury atom and the two chlorine atoms of different rings (NQR-spectroscopy):



The presence of marked quadrupole splitting of the Mössbauer spectral lines in tributylstannylacetone confirms the suggestion of Khrapov and co-workers[3] that there is a coordination interaction between tin and oxygen atoms:

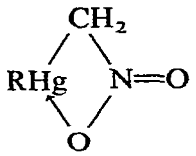


If coordination interaction of this type is a sufficiently common phenomenon, it should become apparent in the chemical behaviour of β- and γ-functional derivatives of organometallic compounds such as



where X is the electronegative atom (β-chlorovinyl compounds, chloromercuracetaldehyde, etc.). It may well be that both σ,π- or σ,σ-conjugation[4] and intramolecular coordination must be taken into account when explaining some features of the chemical properties of such compounds (*e.g.* β-elimination).

This kind of coordination must be present in the α-nitroalkyl derivatives of mercury especially in its nitromethyl derivatives:



These compounds are so far unknown but their trinitromethyl analogs have been investigated in detail[5,6]. Petukhov[7] described the preparation of phenyl(nitromethyl) mercury from nitromethane and phenylmercuric hydroxide:

$$C_6H_5HgOH+CH_3NO_2 \rightarrow C_6H_5HgCH_2NO_2+H_2O$$

but we found that phenylmercuric fulminate is the actual product of this reaction. Phenyl(nitromethyl)mercury is unstable and immediately changes into the fulminate by means of dehydration and rearrangement:

$$C_6H_5HgOH+CH_3NO_2 \rightarrow 2\,H_2O+C_6H_5HgONC^{*}$$

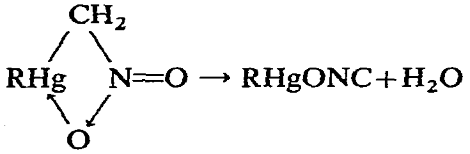
There are no absorption peaks of the NO_2-group in the IR-spectra of organomercuric fulminates but the very strong peaks at 1200 and 2200 cm^{-1} may be the fundamental frequencies of the symmetric and antisymmetric vibrations of the ONC-group[8,9].

Phenylmercuric fulminate obtained *via* nitromethane is identical with the product recently described[8].

Bis(methylmercuric)oxide reacts with nitromethane in the same manner giving methylmercuric fulminate:

$$(CH_3Hg)_2O+2\,CH_3NO_2 \rightarrow 3\,H_2O+2\,CH_3HgONC$$

The factor which makes the rearrangement of nitromethyl derivatives possible is intramolecular coordination:



Freshly-precipitated mercury oxide reacts with nitromethane giving a mixture of substances which contain nitro-groups and ONC-groups as is evident from the IR-spectra. The content of fulminate groups gradually increases. As the recent article on the preparation of some organomercuric fulminates from mercury dialkyls and mercury fulminate[9] was not available, methyl-, butyl- and phenylmercuric

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[*] The structure of fulminates (–ON=C or –C≡NO) is not clearly known[9]. The formula, RHgONC, is intended as an empirical expression of composition, only.

fulminates were prepared by reacting the corresponding mercury dialkyls with the product of interaction between mercury oxide and nitromethane (this product apparently stored unchanged)

$$R_2Hg + Hg(ONC)CH_2NO_2 \rightarrow 2\,RHgONC + H_2O \qquad (R = CH_3, C_4H_9, C_6H_5)$$

In view of the tendency of the nitromethyl derivatives of mercury to change into fulminates, the relative stability of the trinitromethyl derivatives of the $ArHgC(NO_2)_3$ type as described by Novikov, *et al.*[5,6] is surprising. The mercuration reaction that was used by these authors could not lead to alkyl(trinitromethyl)mercury. We obtained butyl(trinitromethyl)mercury by means of the disproportionation reaction or by the dealkylation of dibutylmercury by trinitromethane:

$$(C_4H_9)_2Hg \xrightarrow{HC(NO_2)_3} C_4H_9HgC(NO_2)_3 \xrightarrow{Bu_2Hg} Hg[C(NO_2)_3]_2$$

Diphenylmercury reacts in the same manner.

Butyl(trinitromethyl)mercury and its aromatic analogs proved to be reasonably stable. It may be that the possibility of dehydration is an indispensable condition of the rearrangement.

In common with Dr. Pakhomov we undertook an X-ray investigation of phenylmercuric fulminate so far as the structure is in question[8,9]. The preliminary data are as follows:

Crystals belong to rhombic singony with lattice parameters, a 20.49; b 6.61; c 5.75 Å. There are four molecules in the elementary cell. The most likely space group is $Pn2_1a$.

EXPERIMENTAL

Phenylmercuric fulminate

(a). Phenylmercuric hydroxide[10] (4.0 g, 0.013 mole) and nitromethane (8.0 g, 0.13 mole) were stirred at 20° until the mixture solidified. The solid was recrystallized from benzene to give 2.4 g (60%) of phenylmercuric fulminate, m.p. 178° (with a flare); Petukhov[7] reports 174°. (Found: C, 26.8; H, 1.6; Hg, 62.7. C_7H_5ONHg calcd.: C, 26.3; H, 1.6; Hg, 62.8%.)

(b). Freshly-precipitated mercuric oxide (0.32 g, 0.0015 mole) was suspended in a large excess of nitromethane and the mixture was left overnight. The resulting solid was washed with ethanol. Diphenylmercury (0.53 g, 0.0015 mole) in ethanol (50 ml) was added. The mixture was refluxed for 5 h, filtered, and the solvent removed. Phenylmercuric fulminate was obtained in 62% yield after recrystallization, first from ethanol and finally, benzene; m.p. and mixed (a+b) m.p. 178°. The IR-spectra of both (a) and (b) products are identical and contain very strong bands at 1220 and 2200 cm^{-1}. There are no bands corresponding to the absorption of the NO_2-group*.

Methylmercuric fulminate

(a). Bis(methylmercuric)oxide[11] (m.p. 139°, 4.58 g, 0.01 mole) and nitromethane (2.0 g, 0.03 mole) were dissolved in ethanol (75 ml). The mixture was refluxed

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* IR-spectra were examined in KBr discs with a UR-10 double-beam spectrograph.

for 2 h. Methylmercuric fulminate was obtained in quantitative yield, m.p. 146° dec. (from cyclohexane). (Found: C, 9.53; H, 1.22; Hg, 77.45; N, 5.42. C_2H_3HgNO calcd.: C, 9.32; H, 1.16; Hg, 77.80; N, 5.43%.)

(b). This compound was prepared by a procedure similar to that used for phenylmercuric fulminate (b). The substance was obtained in 88% yield from mercury oxide (0.64 g, 0.003 mole), excess of nitromethane and dimethylmercury (0.70 g, 0.003 mole) in ethanol (30 ml); m.p. and mixed m.p. 146° (from cyclohexane). The IR-spectrum contains strong absorption bands in the regions 1220 and 2220 cm^{-1}.

Butylmercuric fulminate

This was prepared by essentially the same procedure from mercuric oxide (0.18 g, 0.00083 mole), nitromethane and dibutylmercury (0.90 g, 0.003 mole). Recrystallization from cyclohexane gave 0.28 g (53%) of butylmercuric fulminate, m.p. 82–83° dec. (Found: C, 19.95; H, 3.06; Hg, 65.64; N, 4.53. C_5H_9HgNO calcd.: C, 20.02; H, 3.00; Hg, 66.95; N, 4.67%.) The IR-spectrum contains strong bands at 1220 and 2220 cm^{-1}.

Butyl(trinitromethyl)mercury

Bis(trinitromethyl)mercury[5] (1.20 g, 0.002 mole) and dibutylmercury (0.63 g, 0.002 mole) in ethanol (30 ml) were refluxed for 6 h. The solvent was removed *in vacuo* and the residual solid recrystallized from heptane to give 0.60 g (50%) butyl(trinitromethyl)mercury, m.p. 87° dec. (Found: C, 14.87; H, 2.34; Hg, 49.85; N, 10.16. $C_5H_{10}HgN_3O_6$ calcd.: C, 14.73; H, 2.23; Hg, 49.20; N, 10.30%.) The IR-spectrum contains strong bands near 800, 1300 and 1600 cm^{-1} which represent the absorption of the NO_2-group[12].

The same compound was obtained by treating dibutylmercury with trinitromethane in ethanol.

Phenyl(trinitromethyl)mercury

This was prepared by the same procedure from bis(trinitromethyl)mercury (0.60 g, 0.001 mole) and diphenylmercury (0.35 g, 0.001 mole) in ethanol (30 ml). Recrystallization from carbon tetrachloride gave 0.73 g (86%) phenyl(trinitromethyl)-mercury, m.p. 146° dec. Novikov and co-workers report m.p. 146°. (Found: C, 19.26; H, 1.28; Hg, 46.65; N, 9.04. $C_7H_7HgN_3O_6$ calcd.: C, 19.70; H, 1.18; Hg, 46.90; N, 9.85%.) The IR-spectrum contains strong bands near 800, 1300 and 1600 cm^{-1}.

SUMMARY

1. The preparation of organomercuric fulminates from the corresponding hydroxides and nitromethane is described.

2. Literary data for obtaining phenyl(nitromethyl)mercury are in error.

3. Bis(trinitromethyl)mercury reacts with mercury dialkyls to give mixed compounds, $RHgC(NO_2)_3$.

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