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Original Scientific Paper

Nitroso Compounds by Reaction of Organomercurials with Nitrosyl Chloride*

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By the reaction of RHgX (X = Cl, Br, OAc) with NOCl, mercury is eliminated as ClHgX and, if R is aromatic, nitroso compounds are obtained, *i.e.*, nitrosobenzene, 1-nitrosonaphthalene, 4-nitroso-*N*,*N*-dimethylaniline, 2-nitrosophenol, 4-nitrosophenol and methyl 3-nitrososalicylate. If R is aliphatic or alicyclic, with RHgX to NOCl 1 : 3, *gem*-chloronitroso compounds are obtained that have not been described previously, *i.e.*, 2-chloro-2-nitrosocyclohexanol, 1-acetoxy-2-chloro-2-nitrosocyclohexane, 1-chloro-2-methoxy-1-nitrosocyclopentane, methyl 2-chloro-2-nitroso-3-methoxypropionate, 1-chloro-1-nitrosoethane and 2-chloro-2-nitrosoethanol. All products have been characterized by chemical and IR spectral analysis.

INTRODUCTION

The reaction of organomercury compounds with nitrosyl halides was reported as early as in 1874.[1] Only lately has the reaction been used for the preparation of nitrosopolymethylbenzenes,[2] then for nitrosoperfluoroalkanes[3] and finally for 1-nitrosoacetylenes.[4] Our aim was to establish the applicability of this reaction to the preparation of organic nitroso compounds *via* organomercurials which are generally easily accessible. Organomercurials of the RHgX type were used, with R being aromatic, alicyclic and aliphatic, and X equal to Cl, Br and OAc, as exemplified by: chloromercuriobenzene[5] (**1**), 1-chloromercurionaphthalene[6] (**2**), 4-acetoxymercurio-*N*,*N*-dimethylaniline[7,8] (**3**), 2-chloromercuriophenol[9,10] (**4**), 4-chloromercuriophenol[9,10] (**5**), methyl 3-acetoxymercuriosalicylate[11](**6**), 2-bromomercuriocyclohexanol[12] (**7**),

* Dedicated to the memory of Professor Stanko Borčić.

1-acetoxy-2-chloromercuriocyclohexane[13] (**8**), 1-chloromercurio-2-methoxycyclopentane[14] (**9**), methyl 2-bromomercurio-3-methoxypropionate[15] (**10**), 2-chloromercuriopropionic acid[16] (**11**) and 2-chloromercurioethanol[17] (**12**), prepared by published methods. In all cases, demercuration took place with the final product dependent on R as reported below.

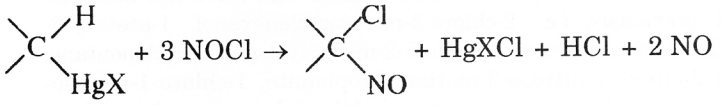
RESULTS AND DISCUSSION

In the case of aromatic organomercurials, *i.e.*, if R in RHgX is phenyl, substituted phenyl or naphthyl, the reaction product with nitrosyl chloride is defined by equation (1):

$$\mathrm{RHgX + NOCl \rightarrow R\text{-}NO + HgXCl} \qquad (1)$$

The only difference is the form in which R-NO appears. Among the examined aromatic organomercurials, (**1**), (**2**) and (**3**) gave simple nitroso compounds, while (**4**), (**5**) and (**6**) gave the corresponding ketoximes as proved by comparison of the observed properties with literature data, as well as by infrared spectroscopy.

In the case of all examined alicyclic and aliphatic organomercurials from (**7**) to (**12**), the final products are *gem*-chloronitroso compounds (equation 2):



(2)

in agreement with previously reported observations.[18–20] Consequently, by the reaction of nitrosyl chloride with alicyclic organomercurials (**7**), (**8**) and (**9**), 2-chloro-2-nitrosocyclohexanol, 1-acetoxy-2-chloro-2-nitrosocyclohexane and 1-chloro-2-methoxy-1-nitrosocyclopentane, respectively, were obtained. The reaction with aliphatic organomercurials (**10**), (**11**) and (**12**) also gave *gem*-chloronitroso compounds; however, in the case of (**11**), decarboxylation took place. Thus, the products were methyl 2-chloro-2-nitroso-3-methoxypropionate, 1-chloro-1-nitrosoethane and 2-chloro-2-nitrosoethanol, respectively. Methyl 3-nitrososalicylate and all of the *gem*-chloronitroso compounds, except for 1-chloro-1-nitrosoethane, were prepared for the first time.

EXPERIMENTAL

Nitrosyl chloride, prepared by standard methodology,[21] was collected under cooling with dry ice in acetone, weighed and dissolved in a known volume of chloroform or carbon tetrachloride, to produce 4 g of NOCl to 100 mL of solvent.

Infrared spectra were obtained with a Perkin-Elmer FT-IR Spectrometer 1600. IR spectra of solid samples were recorded using KBr disks. The products, when ne-

cessary, were identified by elemental analysis by standard microanalytical methods. Melting points and decomposition data are uncorrected.

General Procedure

A defined volume of nitrosyl chloride solution was added dropwise, by means of a dropping funnel with a pressure equalization arm, to a solution or suspension of the organomercurial in chloroform or carbon tetrachloride under cooling (salt/ice) and magnetic stirring during 1 to 3 hours. Unreacted nitrosyl chloride was pumped out, the mercury salt filtered off and further treated depending on the reaction product.

In the case of aromatic nitroso compounds, the filtrate was washed with aqueous KI (1 g in 100 mL), then with water in order to remove the dissolved mercury salt, dried over anhydrous sodium sulfate and evaporated under vacuo. In all cases, except for 4-nitrosophenol, methyl 3-nitroso-salicylate and 1-chloro-1-nitrosoethane, steam distillation was used as the first purification. The distillate was extracted with an organic solvent, the solution was separated from the aqueous layer, dried over anhydrous sodium sulfate and evaporated under vacuo. Solutions of *gem*-chloronitroso compounds were evaporated by means of a Vigreoux column.

Nitrosobenzene

A suspension of chloromercuriobenzene (**1**) (5 g, 0.016 mol) in chloroform (25 mL) and a solution of nitrosyl chloride (1.05 g, 0.016 mol) in chloroform (20 mL) were kept in an ice bath and stirred for 2 hours, concentrated on a steam bath to half volume and filtered. Colourless needles 0.39 g (24%); m.p. 67 °C (reported[22,23] 68°C); IR ν_{max}/cm^{-1}: 1378 s (N=O).

1-Nitrosonaphthalene

A suspension of 1-chloromercurionaphthalene (**2**) (10 g, 0.0275 mol) in carbon tetrachloride (25 mL) and a solution of nitrosyl chloride (2 g, 0.03 mol) in carbon tetrachloride (40 mL) were stirred for 1 hour. The crude product was recrystallized from a benzene/petroleum ether mixture. Yellow needle-shaped crystals 1.2 g (31%); m.p. 134 °C decomp. (reported[1] 134 °C decomp.); IR ν_{max}/cm^{-1}: 1388 s (N=O).

4-Nitroso-N,N-*dimethylaniline*

A solution of 4-acetoxymercurio-*N,N*-dimethylaniline (**3**) (3 g, 7.5 mmol) in chloroform (25 mL) was treated with a solution of nitrosyl chloride (0.5 g, 7.6 mmol) in chloroform (10 mL) for 1 hour. Evaporation of the dried chloroform extract gave green lustrous leaflets from light petroleum (b.p. 40–70 °C), 0.7 g (59 %); m.p. 85 °C (reported[24] 85 °C); IR ν_{max}/cm^{-1}: 1530 s (N=O).

2-Nitrosophenol

A suspension of 2-chloromercuriophenol (**4**) (5 g, 0.015 mol) in carbon tetrachloride (25 mL) and a solution of nitrosyl chloride (1 g, 0.015 mol) in carbon tetrachloride (20 mL) were stirred for 1 hour. Yellowish green needles by sublimation (1.2 g, 64%), identified as sodium salt.[25] IR ν_{max}/cm^{-1}: 3242 m (NO-H), 1084 s (C=O), 1029 s (C=N).

Anal. Calcd. for $C_6H_4O_2NNa$: Na 15.85%; found: Na 15.61%.

4-Nitrosophenol

A suspension of 4-chloromercuriophenol (**5**) (4.5 g, 0.014 mol) in carbon tetrachloride (25 mL) and a solution of nitrosyl chloride (0.9 g, 0.014 mol) in carbon tetrachloride (20 mL) were stirred for 3 hours. The product was crystallized from a hot aqueous solution and cooled in ice-water. Yellow needles, 0.5 g (31 %); m.p. 124 °C (decomp.) (reported[26] 124–126 °C (decomp.), 133 °C); IR ν_{max}/cm^{-1}: 3271 m (NO-H), 1627 m (C=O), 1538 m (C=N).

Methyl 3-Nitrososalicylate

A suspension of methyl 3-acetoxymercuriosalicylate (**6**) (4.5 g, 0.01 mol) in chloroform (25 mL) and a solution of nitrosyl chloride (0.8 g, 0.012 mol) in chloroform (20 mL) were stirred for 3 hours. The mixture was concentrated until a solid appeared from the hot solution. The crude product was collected by filtration and purified by dissolving in a warm (2 : 5) mixture of ethyl acetate/petroleum (b.p. 140–170 °C). After cooling to room temperature, some dark red tar was separated and the solution was concentrated by evaporation. Methyl 3-nitrososalicylate was obtained as a white crystalline solid, 0.97 g (48%); m.p. 102 °C; IR ν_{max}/cm^{-1}: 3240 m NO-H), 1682 s (C=O), 1589 s (C=N).

Anal. Calcd. for $C_8H_7O_4N$: C 53.31, H 3.89, N 7.74 %; found: C 53.25, H 3.87, N 7.45%.

2-Chloro-2-nitrosocyclohexanol

A suspension of 2-bromomercuriocyclohexanol (**7**) (2.5 g, 6.7 mmol) in chloroform (20 mL) and a solution of nitrosyl chloride (1.3 g, 0.02 mol) in chloroform (30 mL) were stirred for 2 hours in the absence of light. A blue oily liquid 0.77 g (71%); IR ν_{max}/cm^{-1}: 1652 s, 1555 s (N=O).

Anal. Calcd. for $C_6H_{10}O_2NCl$: C 44.05, H 6.16, N 8.56, Cl 21.67%; found: C 44.09, H 6.22, N 8.81, Cl 21.81%.

1-Acetoxy-2-chloro-2-nitrosocyclohexane

A solution of 1-acetoxy-2-chloromercuriocyclohexane (**8**) (1.75 g, 4.6 mmol) in chloroform (20 mL) and a solution of nitrosyl chloride (0.9 g, 0.013 mol) in chloroform (30 mL) were stirred for 2 hours. A bluish green liquid, yield 0.75 g (79%); IR ν_{max}/cm^{-1}: 1641 s, 1568 s (N=O).

Anal. Calcd. for $C_8H_{12}O_3NCl$: C 46.72, H 5.88, N 6.81, Cl 17.24%; found: C 46.68, H 6.02, N 6.69, Cl 17.04%.

1-Chloro-2-methoxy-1-nitrosocyclopentane

Gaseous nitrosyl chloride (1 g, 0.015 mol) was introduced into a solution of 1-chloromercurio-2-methoxycyclopentane (**9**) (1.7 g, 5 mmol) in chloroform (10 mL) for 2 hours in the absence of light. A bluish green liquid, 0.46 g (55%); IR $_{max}/cm^{-1}$: 1637 s, 1546 s (N=O).

Anal. Calcd. for $C_6H_{10}O_2NCl$: C 44.05, H 6.16, N 8.56, Cl 21.67%; found: C 44.08, H 6.18, N 8.81, Cl 21.59%.

Methyl 2-Chloro-2-nitroso-3-methoxypropionate

A solution of methyl 2-bromomercurio-3-methoxypropionate (**10**) (3.5 g, 8.8 mmol) in chloroform (20 mL) and a solution of nitrosyl chloride (1.75 g, 0.027 mol)

in chloroform (50 mL) were stirred for 2 hours in the absence of light. A green volatile liquid, 1 g (62%); IR ν_{max}/cm^{-1}: 1666 s, 1567 s (N=O).

Anal. Calcd. for $C_5H_8O_4NCl$: C 33.07, H 4.47, N 7.72, Cl 19.52%; found: C 32.95, H 4.43, N 7.68, Cl 19.47%.

1-Chloro-1-nitrosoethane

A suspension of 2-chloromercuriopropionic acid (11) (3 g, 9.7 mmol) in chloroform (20 mL) and a solution of nitrosyl chloride (2 g, 0.03 mol) in chloroform (50 mL) were stirred for 2 hours in the absence of light. During this period, the evolution of CO_2 was proved by means of barium hydroxide solution. After the solution volume had been reduced to 1 or 2 mL, petroleum (b.p. 140–170 °C, 10 mL) was added, the solution filtered and evaporated, and the volatile product was condensed in a receiver cooled by a dry ice/acetone mixture. White crystalline solid, 0.16 g (18%); m.p. 63 °C (reported[27] 65 °C); IR ν_{max}/cm^{-1}: 1450 s (N=O).

2-Chloro-2-nitrosoethanol

A suspension of 2-chloromercurioethanol (**12**) (2 g, 7.91 mmol) in chloroform (20 mL) and a solution of nitrosyl chloride (1.5 g, 0.023 mol) in chloroform (40 mL) were stirred for 2 hours. By removal of the solvent by distillation in vacuo, a yellowish green liquid was obtained, 0.46 g (54%); IR ν_{max}/cm^{-1}: 3668-3580 s, br (O-H), 1564 s (C=N).

Anal. Calcd. for $C_2H_4O_2NCl$: C 21.93, H 3.68, N 12.79, Cl 32.37%; found: C 22.04, H 3.62, N 12.54, Cl 32.18%.

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SAŽETAK

Priprava nitrozo-spojeva reakcijom organomerkuriala s nitrozil-kloridom

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Reakcijom RHgX (X = Cl, Br, OAc) s NOCl, živa je odvojena kao ClHgX. Kada je R bio aromatski ostatak, dobiveni su odgovarajući nitrozo-spojevi: nitrozobenzen, 1-nitrozonaftalen, 4-nitrozo-*N*,*N*-dimetilanilin, 2-nitrozofenol, 4-nitrozofenol i metil-3-nitrozosalicilat. Ako je R bio alifatski ili aliciklički, s omjerom RHgX i NOCl 1 : 3, kao produkti nastaju odgovarajući *gem*-kloronitrozo-spojevi, što prethodno nije bilo opisano: 2-klor-2-nitrozo-cikloheksanol, 1-acetoksi-2-klor-2-nitrozocikloheksan, 1-klor-2-metoksi-1-nitrozociklopentan, metil-(2-klor-3-metoksi-2-nitrozo)-propionat, 1-klor-1-nitrozoetan i 2-klor-2-nitrozoetanol. Svi produkti identificirani su kemijski i IR spektrima.