Dinitramide and its salts

9.* Mercury(II) dinitramidate, a new reagent in chemistry of organomercury compounds

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The potentialities of synthesis on the basis of mercury(II) dinitramidate $Hg(N_3O_4)_2$ in mercuration, addition to the double carbon—carbon bond, alkylation, and complexation are shown.

Key words: mercury(II) dinitramidate, *N*-alkyl-*N,N*-dinitramines, olefins, mercuration, alkylation, complexation.

The nature of the anion is of importance in reactions of mercury(II) salts with organic compounds of different classes. For example, addition of $Hg[C(NO_2)_3]$ to ethylene in an aqueous solution gives $(NO_2)_3CHgCH_2CH_2C(NO_2)_3$, whereas the use of $Hg(MeCOO)_2$ under analogous conditions affords the ethanol derivative $MeCOOHgCH_2CH_2OH$ (see Ref. 1).

As part of continuing studies of dinitramide,[2] we obtained mercury(II) dinitramidate ($Hg(N_3O_4)_2$) upon treatment of freshly precipitated HgO with an ether solution of dinitramide.[3] Unusual properties of mercury dinitramidate (the mercury—dinitramide bond is covalent,[3] and the compound is readily soluble in ether) drew our attention to studies of its behavior in reactions common to mercury(II) salts, particularly, in aprotic organic solvents. Note that $Hg(N_3O_4)_2$ obtained by the above-mentioned method appeared to be sufficiently suitable without further purification (though the sample contains 1—2 % H_2O) for the synthetic purposes in hand. Water can be removed by recrystallization from anhydrous benzene or nitromethane although with a substantial loss of the compound.

We have studied several types of reactions with the participation of $Hg(N_3O_4)_2$.

Complexation of $Hg(N_3O_4)_2$. The complexes of $Hg(N_3O_4)_2$ with compounds of different classes that we obtained are listed in Table 1.

Synthetic possibilities of complexation reactions are substantially enhanced when low-polarity solvents like ether are used. When $Hg(N_3O_4)_2$ reacts with aniline in an ether solution, adduct **1** precipitates, whereas in an alcohol solution, the products of mercuration of aniline into the nucleus are formed. The reaction of $Hg(N_3O_4)_2$ with pyridine is terminated at the stage of formation of complex **2** because mercuration of pyridine into the nucleus usually proceeds under rather severe conditions.[1]

According to the data of IR spectroscopy, formation of compounds **1—4** is attended with a change in the character of the mercury—dinitramide bond from covalent to ionic (absorption bands 1520—1540, 1180—1210, and 1010—1035 cm^{-1} typical of the $N_3O_4^-$ anion). A different situation is observed in the case of adduct **5**; this adduct precipitates from a ~10 % solution of $Hg(N_3O_4)_2$ in ether upon addition of diethyl malonate and rapid cooling to −78 °C. The IR spectra of this adduct (1605, 1525, 1200, and 1015 cm^{-1}) indicate that the mercury—dinitramide bond is unchanged and remains covalent in the process of complex formation.

Alkylation of $Hg(N_3O_4)_2$ with alkyl iodides. Previously, it was found[4] that AgN_3O_4 reacts with primary or secondary alkyl iodides in ether or acetonitrile for 2—3 days to give a mixture of products of *N*- and *O*-alkylation in ratios that depend on the character of alkyl halide.

Under these conditions, KN_3O_4 is not virtually alkylated, apparently, because of a very low nucleophilicity of the $N_3O_4^-$ anion.

Therefore, it is of interest to elucidate the possibility of alkylation of $Hg(N_3O_4)_2$. Immediately an ether solution of mercury dinitramidate was mixed with the corresponding alkyl iodide at 0—5 °C, formation of insoluble solid and liquid colorless adducts was observed; after 10—15 min these adducts converted to the red HgI_2; a mixture of *N*-alkyl-*N,N*-dinitramines (**6a—e**) and *N*-alkoxy-*N'*-nitrodiazene *N*-oxides (**7a—e**) (Table 2) remained in the solution.

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* For Communication 8, see Ref. 3.

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Table 1. Complex compounds with $Hg(N_3O_4)_2$

Compound	Yield (%)	M.p./°C (solvent)	C	H	N
			Found/Calculated (%)		
$[Hg(PhNH_2)_2](N_3O_4)_2$ (**1**)	88	145 (decomp.)	—	—	19.51 18.73
$[HgPy_2](N_3O_4)_2$ (**2**)	80	176—178 (decomp.)	—	—	19.77 19.65
$[Hg(Ph_3P)_2](N_3O_4)_2$ (**3**)	74	165—170 (MeCN)	—	—	9.35 8.97
$[Hg(Me_2S)_2](N_3O_4)_2$ (**4**)	90	133—134 (decomp.) (MeOH)	9.47 9.95	2.58 2.24	—
$Hg(N_3O_4)_2\cdot 2CH_2(COOEt)$ (**5**)	63	63—64 (decomp.)	22.85 22.95	3.18 3.25	11.62 11.45

$$Hg(N_3O_4)_2 + RI \xrightarrow{10-15\text{ min}} [Hg(N_3O_4)_2\cdot nRI] \longrightarrow RN(NO_2)_2 + RON(O){=}NNO_2$$

6a—e **7a—e**

R = Me (**a**); Et (**b**); Pr^n (**c**); Bu^n (**d**); Pr^i (**e**)

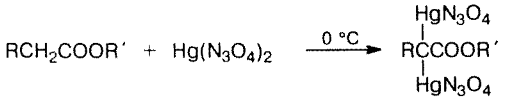
The ratio of the products of *N*- and *O*-alkylation (**6a—e** and **7a—e**) was determined from the ^1H NMR spectra by the method previously reported.[4] The inconsistency between the yield of HgI_2 and the total yield of alkylation products is, apparently, attributable to the specificity of isolation of the products as well as to their instability.[4]

Mercuration with the participation of $Hg(N_3O_4)_2$. It is known[1] that mercuration of aliphatic compounds containing activated methylene groups may afford mono- and polymercurated products. We found that $Hg(N_3O_4)_2$ readily mercurates compounds like acetone, acetylacetone, malonic, nitroacetic, and nitromalonic esters in nonpolar and polar organic solvents and in water.

Mercuration of acetone and acetylacetone with mercury dinitramidate at room temperature in ether results in the replacement of only one hydrogen atom, whereas nitroacetic and ethylmalonic esters afford dimercurated products under similar conditions:

$$MeCOCH_2R + Hg(N_3O_4)_2 \xrightarrow{20\ °C} MeCOCHRHgN_3O_4$$

8: R = H
9: R = COMe

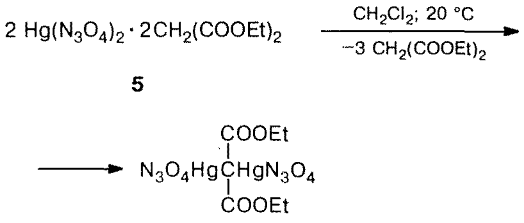


$$RCH_2COOR' + Hg(N_3O_4)_2 \xrightarrow{0\ °C} RC(HgN_3O_4)_2COOR'$$

10: R = NO_2, R′ = Me
11: R = COOEt, R′ = E

Under these conditions, compound **11** appeared to be contaminated with the products of further mercuration. When this reaction is performed in water, oligomeric products are formed instead of **11**; the UV spectra of these products in an aqueous KOH solution show absorption bands of the $N_3O_4^-$ anion, and the results of elemental analysis approximately correspond to the formula $N_3O_4HgCR_2HgCR_2HgCR_2HgN_3O_4$, where R = COOEt.

Heating of $Hg(N_3O_4)_2$ with malonic ester without the solvent at 100 °C for 30 min affords a poorly soluble product that contain no $N_3O_4^-$ at all and which is, apparently, a polymeric compound ...—CR_2HgCR_2Hg—... (R = COOEt). In the pure form, compound **11** was obtained by an alternative procedure. Unlike $Hg(N_3O_4)_2$, adduct **5** (see Table 1) is readily soluble in CH_2Cl_2 or $CHCl_3$, and in this case analytically pure compound **11** is precipitated at 25 °C for 2.5 h in 75 % yield.



$$2\,Hg(N_3O_4)_2\cdot 2CH_2(COOEt)_2 \xrightarrow[-3\ CH_2(COOEt)_2]{CH_2Cl_2;\ 20\ °C} N_3O_4HgC(COOEt)_2HgN_3O_4$$

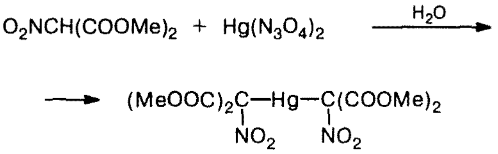
5 **11**

Table 2. Product of alkylation of $Hg(N_3O_4)_2$ with alkyl iodides in ether

R	Yield of HgI_2 (%)	Total yield of products **7**+**8** (%)	Ratio of **7** : **8** (from ^1H NMR)
Me	82	40	4.6 : 1
Et	81	22	1 : 1.2
Pr^n	85	36	1 : 1.7
Bu^n	81	30	1 : 1.5
Pr^i	92	42	only **7**

In this case, higher purity of **11** is, apparently, attributable to its insolubility in CH_2Cl_2 that prevents further mercuration of malonic ester.

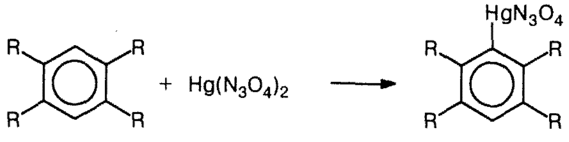
One more example of the reaction, in which the product of the first stage of mercuration acts further as a mercurating agent, should be given:



$$O_2NCH(COOMe)_2 + Hg(N_3O_4)_2 \xrightarrow{H_2O} (MeOOC)_2\underset{NO_2}{C}{-}Hg{-}\underset{NO_2}{C}(COOMe)_2$$

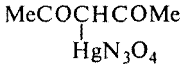
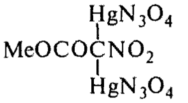
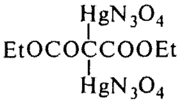
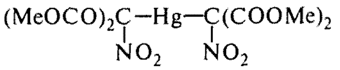
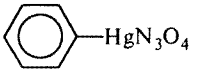
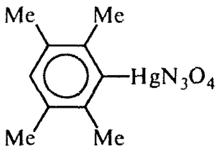
12

Mercuration of aromatic compounds is the reaction of electrophilic substitution proceeding the easier the higher is nucleophilicity of the aromatic nucleus. Benzene is not mercurated with $Hg(N_3O_4)_2$ in ether, whereas upon prolonged boiling of $Hg(N_3O_4)_2$ with benzene without a solvent, the process of decomposition of the mercury salt advances mercuration. However, boiling of an aqueous $Hg(N_3O_4)_2$ solution with benzene for 2 h affords the expected product **13** in 55 % yield. More nucleophilic 1,2,4,5-tetramethylbenzene is readily mercurated upon boiling in a methanol solution of $Hg(N_3O_4)_2$; this reaction proceeds at room temperature with the appreciable rate even in ether.



13: R = H
14: R = Me

Table 3. Products of mercuration with $Hg(N_3O_4)_2$

Compound	Yield (%)	Reaction time/h	M.p./°C (solvent)	Found / Calculated (%)		
				C	H	N
$MeCOCH_2HgN_3O_4$ (**8**)	77	24	124 (decomp.) (ether—acetone, 2 : 1)	10.12 9.92	1.50 1.38	—
 $MeCO\underset{HgN_3O_4}{C}HCOMe$ (**9**)	81	0.3	103—105 (decomp.)	14.85 14.81	1.69 1.72	10.68 10.37
 $MeOCO\overset{HgN_3O_4}{\underset{HgN_3O_4}{C}}NO_2$ (**10**)	25	48	129—130 (decomp.)	—	—	13.48 13.44
 $EtOCO\overset{HgN_3O_4}{\underset{HgN_3O_4}{C}}COOEt$ (**11**)	75	2.5	210—213	11.30 10.91	1.65 1.30	11.34 10.91
 $(MeOCO)_2\underset{NO_2}{C}{-}Hg{-}\underset{NO_2}{C}(COOMe)_2$ (**12**)	24	2	152 (decomp.)	—	—	5.59 5.15
 (**13**)	55	2	152—154	—	—	—
 (**14**)	33	0.75	209 (decomp.) (MeCOOEt) 27.33	27.48 2.96	3.30 9.79	9.78

We have mentioned that aniline reacts with $Hg(N_3O_4)_2$ in ether to give complex compound **1**. In an alcohol solution, the reaction proceeds as the mercuration of aniline into the nucleus and is completed in few minutes; the reaction with *N,N*-dimethylaniline proceeds in a similar way (the ratio of isomers was not studied).

Reactions of $Hg(N_3O_4)_2$ *with olefins.* It is known that the addition reaction of mercury salts with olefins is determined to a large extent by the nature of the solvent and the anion of the salt.[5] When studying this reaction for $Hg(N_3O_4)_2$, we used ethylene, propylene, *cis*- and *trans*-2-butenes, and norbornene. In most cases, we used water, methanol, or diethyl ether as solvents (Table 3).

When ethylene was passed through an aqueous solution of $Hg(N_3O_4)_2$ for 5 h, the derivative of diethyl ether **15** was precipitated in 51 % yield:

$$2\,CH_2{=}CH_2 + Hg(N_3O_4)_2 + H_2O \xrightarrow[-2\,HN_3O_4]{} O(CH_2CH_2HgN_3O_4)_2$$

15

In the IR spectrum of compound **15**, bands that could be assigned to the OH group are absent but the band at 1105 cm^{-1} is present, which corresponds, apparently, to the CH_2OCH_2 fragment. In the ^1H NMR spectrum, the OH proton signal is also absent. Note also that the IR spectrum of ether **15** shows bands corresponding to dinitramide covalently bonded to the mercury atom[3] (1605, 1525, 1200, and 1015 cm^{-1}). Formation of mercurated ethers in reactions of conjugated oxymercuration along with primary addition products ($HOCH_2CH_2HgX$) was described in the literature.[5–8] We proposed that the corresponding derivative of ethanol can be detected if the effect of the strong acid dinitramide, which is obtained as a result of this reaction, is eliminated. Actually, it appeared that if the reaction was performed in the presence of excess HgO that binds dinitramide, dinitramidatemercuryethanol **16** soluble in water was formed in 96 % yield; the IR spectrum of this compound showed the band corresponding to the hydroxyl group (3200—3500 cm^{-1}), whereas the band of the CH_2OCH_2 fragment (1100 cm^{-1}) was absent. Alcohol **16** readily converts to ether **15** not only under the action of HN_3O_4 but upon heating in different solvents and even on storage.

A product with an unknown structure, which is insoluble in water and organic solvents, is precipitated from an aqueous solution of $Hg(N_3O_4)_2$ with propylene. As in the case of ethylene, addition of $Hg(N_3O_4)_2$ to *cis*- and *trans*-butenes in water affords the corresponding dimercurated ethers **17** and **18**, different addition products (apparently, *threo* and *erythro* isomers) being formed depending on the structure of the olefin. Their melting points are nearly the same; however, their ^1H NMR spectra are different (see Table 2). In the case of *cis*-2-butene, the yield of the product is slightly higher than that in the case of the *trans* isomer, which is in agreement with data in the literature indicating that oxymercuration proceeds at a higher rate.[9] Note also that, for example, oxymercuration of *cis* and *trans*-2-butenes with mercuric chloride in an aqueous solution affords *threo* and *erythro*-3-chloromercuro-2-butanols rather than the corresponding ethers.[10] According to the results of IR spectroscopy, the product of addition of $Hg(N_3O_4)_2$ to cyclohexene in water (**19**) is also the mercury derivative of the corresponding ether rather than of alcohol.

Therefore, in all examples mentioned above, addition of $Hg(N_3O_4)_2$ to olefin in water proceeds as a usual conjugated oxymercuration, although with the difference that the final products of the reaction are mercury derivatives of ethers rather than of alcohols. However, when MeOH was used as the solvent in these reactions, the $N_3O_4^-$ anion gains the competition for the mercuric cation. Thus, when ethylene reacts with $Hg(N_3O_4)_2$ in methanol, the *N,N*-dinitro-β-dinitramidemercuroethylamine (**20**) is formed in 95 % yield, and the product of conjugated mercuration of conjugated methoxymercuration **21** is formed only in 5 % yield.

$$CH_2{=}CH_2 + Hg(N_3O_4)_2 \xrightarrow{MeOH} \begin{cases} N_3O_4HgCH_2CH_2N(NO_2)_2 \\ \quad \textbf{20}\ (\sim95\ \%) \\ N_3O_4HgCH_2CH_2OMe \\ \quad \textbf{21}\ (\sim5\ \%) \end{cases}$$

Dinitramine **20** is rather stable at room temperature and even can be purified by recrystallization. The IR spectrum of **20** contains the bands of the *N,N*-dinitramine moiety (1650, 1605, and 1250 cm^{-1}) and of dinitramide covalently bonded to the mercury atom (1605, 1525, 1200, and 1015 cm^{-1}). Therefore, this reaction is a new method of preparation of *N,N*-dinitramines.

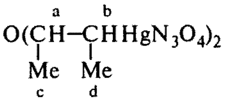
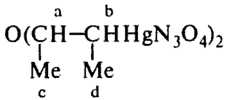
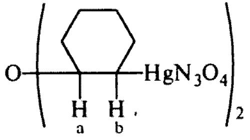
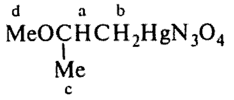
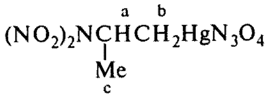
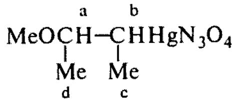
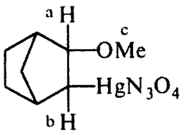
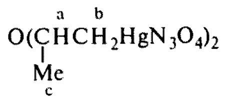
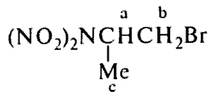
When an alcohol solution of compound **20** is treated with HCl, elimination of olefin occurs with the formation of $HgCl_2$ and HN_3O_4. For the products of addition of mercury salts to unsaturated systems, these reactions have the general character. When these products are treated with halides, halidemercuration is usually observed, the analogous process occurs also in the case under consideration.

$$\textbf{20} + Hal_2 \xrightarrow[0\ ^\circ C]{CH_2Cl_2} HalCH_2CH_2N(NO_2)_2$$

22: Hal = Br

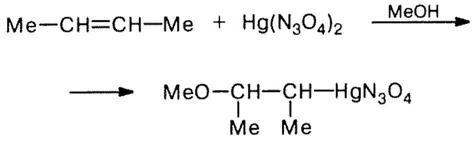
23: Hal = Cl

Table 4. Chemical shifts of protons (δ) in the ^{1}H NMR spectra (acetone-d$_6$) and elemental analysis of the products of reactions of $Hg(N_3O_4)_2$ with olefins

Compound	^{1}H MNR, δ				Found / Calculated (%)		
	a	b	c	d	C	H	N
$O(\overset{a}{C}H_2\overset{b}{C}H_2HgN_3O_4)_2$ (**15**)*	3.78 t	2.40 t		— 7.02	7.25 1.17	1.32 12.28	12.30
$HO\overset{a}{C}H_2\overset{b}{C}H_2HgN_3O_4$ (**16**)*	3.80 t	2.35 t	—	—	—	—	—
 $O(\underset{\underset{c}{Me}}{\overset{a}{C}H}-\underset{\underset{d}{Me}}{\overset{b}{C}H}HgN_3O_4)_2$ (**17**, α-isomer)*	3.90 m	3.0 m	1.51 d	1.26 d	13.18 12.96	2.19 2.16	11.17 11.32
 $O(\underset{\underset{c}{Me}}{\overset{a}{C}H}-\underset{\underset{d}{Me}}{\overset{b}{C}H}HgN_3O_4)_2$ (**18**, β-isomer)*	3.95 m	3.4 m	1.40 d	1.26 d	13.11 12.96	2.17 2.16	—
 (**19**)	3.65 m	2.9 m	—	—	—	—	—
$(NO_2)_2N\overset{a}{C}H_2\overset{b}{C}H_2HgN_3O_4$ (**20**)*	4.70 m	2.30 m	—	—	5.87 5.45	1.34 0.91	19.58 19.09
$\overset{c}{Me}O\overset{a}{C}H_2\overset{b}{C}H_2HgN_3O_4$ (**21**)*	3.62 m	2.33 t	2.97 s	—	—	—	—
$(NO_2)_2N\overset{a}{C}H_2\overset{b}{C}H_2Br$ (**22**)*	4.52 t	3.55 t	—	—	11.13 11.21	2.12 1.87	37.44 (Br) 37.38
$(NO_2)_2N\overset{a}{C}H_2\overset{b}{C}H_2Cl$ (**23**)*	4.50 t	3.78 t	—	—	—	—	—
 $\overset{d}{Me}O\underset{\underset{c}{Me}}{\overset{a}{C}H}\overset{b}{C}H_2HgN_3O_4$ (**24**)	3.80 m	2.40 d	1.55 d	3.25 s	—	—	—
 $(NO_2)_2N\underset{\underset{c}{Me}}{\overset{a}{C}H}\overset{b}{C}H_2HgN_3O_4$ (**25**)	4.90 m	2.55 d	1.58 d	—	—	—	—
 $MeO\underset{\underset{d}{Me}}{\overset{a}{C}H}-\underset{\underset{c}{Me}}{\overset{b}{C}H}HgN_3O_4$ (**26**)	3.75 m	3.00 m	1.50 d	1.20 d	—	—	—
 (**27**, *cis-exo*)	2.81 d	2.27 m	2.97 s	—	—	—	—
 $O(\underset{\underset{c}{Me}}{\overset{a}{C}H}\overset{b}{C}H_2HgN_3O_4)_2$ (**28**)	4.05 m	2.40 d	1.55 d	—	—	—	—
 $(NO_2)_2N\underset{\underset{c}{Me}}{\overset{a}{C}H}\overset{b}{C}H_2Br$ (**29**)**	4.8 m	3.7 d	1.55 d	—	—	—	—

* Compound was isolated in the pure form. ** The ^{1}H NMR spectrum in CCl_4.

The direction of the reaction of conjugated mercuration with the use of $Hg(N_3O_4)_2$ appeared to be very sensitive not only to the nature of the solvent but to the structure of olefin as well. The ratio of the addition products of $Hg(N_3O_4)_2$ in methanol substantially changes in going from ethylene to its alkyl-substituted derivatives. According to the ^1H NMR spectra, in the case of propylene, the product of methoxymercuration **24** prevails over *N,N*-dinitramine **25** (Table 4), whereas, in the case of 2-butenes we were able to detect only compounds of the following type:



$$\mathrm{Me{-}CH{=}CH{-}Me} + \mathrm{Hg(N_3O_4)_2} \xrightarrow{\mathrm{MeOH}} \mathrm{MeO{-}\underset{Me}{CH}{-}\underset{Me}{CH}{-}HgN_3O_4}$$

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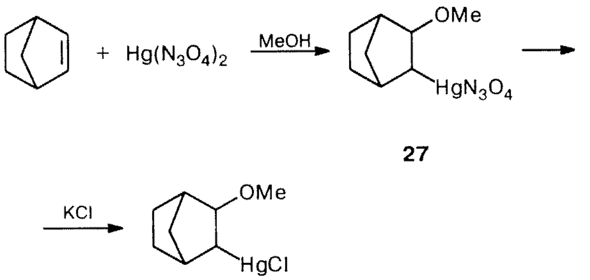
It is known that oxy- and methoxymercuration of strained bicyclo(2.2.1)heptene (norbornene) proceeds as *cis*-exo-addition.[11] Addition of $Hg(N_3O_4)_2$ to norbornene in MeOH proceeds with the formation of only the product of methoxymercuration **27** (see Table 2). A comparison of the ^1H NMR spectrum of compound **27** with the ^1H NMR spectrum of the product of addition of $HgCl_2$ to norbornene[12,13] as well as the formation of the latter from **27** upon its treatment with KCl in alcohol makes it possible to assign the *cis-exo* structure also to compound **27**:



27

Reactions of $Hg(N_3O_4)_2$ with ethylene and propylene were also studied in aprotic solvents. Addition of $Hg(N_3O_4)_2$ to ethylene in acetonitrile or dioxane affords, as was expected, only one product, compound **20**. This reaction in ether gives a more unexpected result. It was mentioned above that a small amount of H_2O (~1—2 %) is present in mercury dinitramidate, which we used; this H_2O did not manifest itself at all when methanol, acetonitrile, or dioxane was used. However, when wet $Hg(N_3O_4)_2$ is used in the reaction with ethylene in ether, in addition to the expected compound **20**, ether **15** is formed in amounts directly proportional to the concentration of H_2O. Compound **15** is not formed when $Hg(N_3O_4)_2$ is predried by recrystallization from benzene and anhydrous ether is used.

When wet $Hg(N_3O_4)_2$ is used in ether, the major product of the reaction is compound **28**, which is the product of oxymercuration of propylene (see Table 2); as was mentioned above, in an aqueous solution we failed to obtain this compound. Anhydrous $Hg(N_3O_4)_2$ in anhydrous ether reacts with propylene to give dinitramine **25**; the structure of this compound was confirmed by bromodemercuration with the formation of **29** as well as by spectral characteristics.

According to Scheme 1, mercury derivatives of alcohols **A** initially formed convert to ethers **B** in an aqueous medium as a result of acid catalysis; these ethers exhibit, among other things, the lowest solubility. The presence of even small amounts of moisture in an ether solution favors predominantly the formation of products **B** because of their low solubility and, therefore, a lower rate of deoxymercuration. In MeOH, in which all reaction products are soluble, almost a sole exclusively product **D** is formed, which is, apparently, thermodynamically more stable and has the smallest rate constant of the reverse reaction. In going to alkylated ethylenes, thermodynamical stabilities of products **D** decrease faster than those of products **C**, apparently, because of the mutual repulsion between bulky electron-withdrawing groups, and products **C** predominate in this case. In none of the cases we found products **E**, which is, apparently, a result of a substantially higher rate of their deoxymercuration and a lower thermodynamic stability.

Experimental

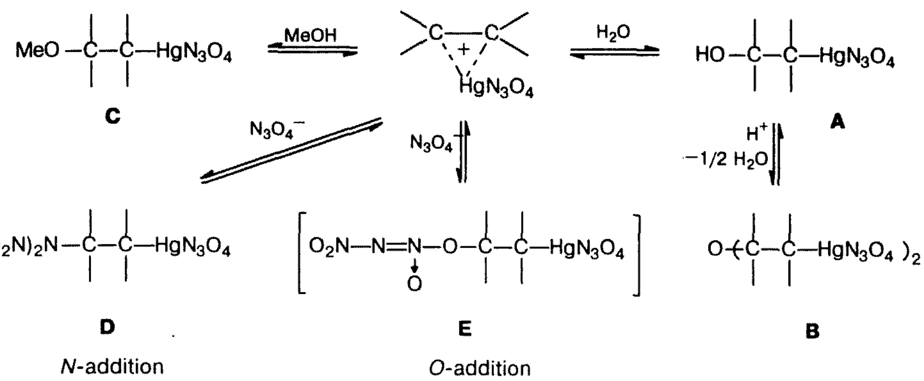
Melting points were determined in a glass capillary in a metal block. The ^1H NMR spectra were recorded on a Perkin-Elmer R-12 instrument (60 MHz); the IR spectra were obtained on a UR-10 instrument (solid samples were run either as KBr pellets or on a germanium plate; liquid samples were run as cast films between KBr or NaCl glasses); the UV spectra were recorded on an SP-800A instrument.

Mercury(II) dinitramidate $Hg(N_3O_4)_2$ was obtained by treatment of an ether solution of dinitramide with freshly precipitated HgO (see Ref. 3).

Bis(aniline)mercury(II) dinitramidate (1), bis(pyridine)-mercury(II) dinitramidate (2), bis(triphenylphosphine)-mercury(II) dinitramidate (3), and bis(dimethylsulfide)-mercury(II) dinitramidate (4). General procedure. A solution of the corresponding ligand (6 mmol) in 10 mL of ether was added with stirring at 20 °C to a solution of $Hg(N_3O_4)_2$ (1.03 g, 2.5 mmol) in 10 mL of ether; the precipitate formed was filtered off (see Table 1). Ethanol was used as the solvent for preparation of compound **2**.

Adduct of mercury(II) dinitramidate—diethyl malonate (1/2) (5). Malonic ester (0.8 g, 5 mmol) was added to a solution of $Hg(N_3O_4)_2$ (1.03 g, 2.5 mmol) in 10 mL of ether at 20 °C, the reaction mixture was rapidly cooled to −78 °C, and crystals of compound **5** precipitated were filtered off.

Reaction of $Hg(N_3O_4)_2$ with alkyl iodides. General procedure. Equimolar amount of the corresponding alkyl iodide was added with stirring to a solution of $Hg(N_3O_4)_2$ (2.06 g, Scheme 1



5 mmol) in 8 mL of ether at 0—5 °C, and then the reaction mixture was kept for 20 min without cooling. The white precipitate initially formed (sometimes oily liquid) converted to the red HgI_2 in this time. The mixture was filtered off, the filtrate was diluted with 40 mL of ether, washed with water and a 35 % $NaHCO_3$ solution, and dried over Na_2SO_4, and then the solvent was removed at 0—5 °C on a rotary evaporator. The nature and the ratio of products **6a—e** and **7a—e** were established from the ^1H NMR and IR spectra[4] (see Table 2).

Dinitramidemercuroacetone (8), dinitramidemercuroacetylacetone (9), and dimethyl bis(dinitramidemercury)nitroacetate (10). General procedure. A mixture of $Hg(N_3O_4)_2$ (1.03 g, 2.5 mmol) and acetone, acetylacetone, or methyl nitroacetate (3 mmol), respectively, was kept at 20 °C (see Table 3), and the products precipitated were filtered off.

Diethyl bis(dinitramidemercury)malonate (11). A solution of adduct **5** (0.72 g) in 4 mL of CH_2Cl_2 was kept at 25 °C for 2.5 h, and compound **11** was filtered off (see Table 3).

Bis(dicarbonylmethoxynitromethyl)mercury (12). A solution of $Hg(N_3O_4)_2$ (1.03 g, 2.5 mmol) in 15 mL of H_2O was shaken with methyl nitromalonate (0.42 g, 2.5 mmol). The mixture was kept at 20 °C for 2 h, and product **12** was filtered off (see Table 3).

Phenylmercury dinitramidate (13). A mixture of $Hg(N_3O_4)_2$ (2.06 g) and benzene (10 mL) in 10 mL of H_2O was refluxed for 2 h, the benzene was distilled off on a rotary evaporator, and product **13** was filtered off (see Table 3). To identify compound **13**, it was treated with KI in acetone, and phenylmercury iodide was obtained, m.p. 265—266 °C (see Ref. 14: m.p. 266 °C).

1,2,4,5-Tetramethylphenylmercury dinitramidate (14). A solution of $Hg(N_3O_4)_2$ (1.03 g) and 1,2,4,5-tetramethylbenzol (0.5 g) in 16 mL of methanol was refluxed for 45 min, and product **14** was filtered off (see Table 3).

Bis(2,2′-dinitramidemercury)diethyl ether (15). Ethylene was passed through a solution of $Hg(N_3O_4)_2$ (4.12 g, 10 mmol) in 20 mL of H_2O at 20 °C for 5 h, and product **15** was filtered off. The yield of compound **15** was 1.78 g (51 %) m.p. 131—132 °C (from methanol).

Ethanolmercurodinitramidate (16). Ethylene was passed through a mixture of $Hg(N_3O_4)_2$ (2.06 g, 5 mmol) with an excess of HgO (from 4 g of $(MeCOO)_2Hg$) in 30 mL of H_2O at 20 °C for 4 h. The mixture was filtered off, the filtrate was evaporated at 20 °C (1 Torr). The yield of compound **16** was 3.42 g (96 %), m.p. 69—72 °C. In the process of recrystallization or upon storage, alcohol **16** converted to ether **15**.

2-Dinitraminoethylmercury dinitramidate (20). A. Ethylene was passed through a solution of $Hg(N_3O_4)_2$ (4.12 g, 10 mmol) in 20 mL of methanol at 20 °C for 2 h. The solvent was removed on a rotary evaporator. The yield of compound **20** was 4.30 g (97 %), m.p. 72—74 °C (decomp.) (from $CHCl_3$).

B. Ethylene was passed through a solution of $Hg(N_3O_4)_2$ (1.50 g) in 10 mL of anhydrous MeCN at 20 °C for 1 h; the solvent was removed on a rotary evaporator; the residue was washed with water and dried *in vacuo*. The yield of compound **20** was 1.03 g (64 %).

Addition of $Hg(N_3O_4)_2$ to ethylene in ether. Ethylene was passed through a solution of $Hg(N_3O_4)_2$ (3.09 g, 7.5 mmol) in 25 mL of ether at 20 °C for 15 min, and compound **15** was filtered off. The yield was 1.23 g (47 %). The filtrate was evaporated on a rotary evaporator. The yield of compound **20** was 1.56 g (47 %).

Addition of $Hg(N_3O_4)_2$ to 2-butenes. A. A sealed ampule containing a mixture of $Hg(N_3O_4)_2$ (2.06 g) in 10 mL of H_2O and *cis*-2-butene (4 mL) was shaked 5 h on a mechanical shaker. The precipitate was filtered off, and bis(2-dinitramidemercury)diisobutyl ether **17** (α-isomer) was obtained, m.p. 171—176 °C (decomp.).

B. Under analogous conditions, compound **18** (β-isomer) was obtained from *trans*-2-butene in a yield of 0.86 g (47 %), m.p. 174—178 °C (decomp.).

Addition of $Hg(N_3O_4)_2$ to cyclohexene. Cyclohexene (1 mL) was added to a solution of $Hg(N_3O_4)_2$ (2.06 g) in 10 mL of H_2O at 20 °C; the mixture was stirred for 3 h and was kept for 15 h, then the precipitate was filtered off, dissolved in MeOH, and reprecipitated with water. The yield of bis(2-dinitramidemercury)dicyclohexyl ether **19** was 0.75 g (30 %), m.p. 91—101 °C (decomp.). IR, ν/cm^{-1}: 1000—1015, 1220, 1525, 1595—1605, 2860, 2940.

Addition of $Hg(N_3O_4)_2$ to norbornene. A mixture of $Hg(N_3O_4)_2$ (4.12 g, 10 mmol) and norbornene (0.96 g, 10 mmol) in 20 mL of MeOH was kept at 20 °C for 1.5 h, the solvent was removed on a rotary evaporator, and the residue was recrystallized from the 1 : 1 ether—hexane mixture. The yield of 3-methoxynorcamphanyl-2-mercury **21** was 1.8 g (43 %), m.p. 57—59 °C.

***N,N*-Dinitramino-2-bromoethane (22).** A solution of compound **20** (4.4 g, 10 mmol) in CH_2Cl_2 (25 mL) at 20 °C was treated with bromine until a steady color appeared, the residue of $HgBr_2$ was filtered off, the filtrate was evaporated at 0 °C (10 Pa), and the residue was distilled twice. The yield of compound **22** was 0.4 g (18.7 %), b.p. 45—45 °C (0.9 Pa), n_D^{24} 1.5090.

***N,N*-Dinitramino-2-chloroethane (23).** Cl_2 was passed through a solution of compound **20** (8.0 g) in 20 mL of CH_2Cl_2 at 20 °C for 30 min; the solvent was removed at 0 °C on a rotary evaporator, and the residue was distilled off. The yield of compound **23** was 0.55 g (18 %), b.p. 25—27 °C (0.4 Torr) (with decomp.). IR (cast film on Ge), $N(NO_2)_2$, ν/cm^{-1}: 1655, 1615, 1250.

2-(*N,N*-Dinitramino)-1-bromopropane (29). Propylene was passed through a solution of $Hg(N_3O_4)_2$ (10 g) in 100 mL of anhydrous ether for 15 min, the precipitated oil was separated, ether was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and was treated with bromine at 20 °C until a steady color appeared. After distillation, compound **29** was obtained in a yield of 1.0 g, b.p. 50—51 °C (0.8 Torr). IR (cast film on Ge) $(N(NO_2)_2$, ν/cm^{-1}: 1655, 1615, 1255.

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