Organic Chemistry

Dinitramide and its salts
6.* Dinitramide salts derived from ammonium bases

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The methods for preparation and the properties of dinitramide salts with ammonia, hydrazine, hydroxylamine, formamidine, their alkylated and aminated derivatives, *etc.* are described.

Key words: dinitramide, ammonium salts.

Representatives of a novel class of organic compounds, *viz.*, salts of dinitramide, HN_3O_4 (DNA),[1] are of interest not only from the theoretical but also from the practical standpoint as highly power-consuming and ecologically pure compounds.

In previous communications,[1–3] the preparation of a number of DNA salts of metals and ammonia has been described. In the present work we report methods for the synthesis of DNA salts with nitrogen-containing bases: ammonia, hydrazine, hydroxylamine, formamidine, various products of their alkylation or amination, and some of their functional derivatives.

One of these methods involves treatment of β-functionally substituted *N,N*-dinitramines[1,2] with bases (reaction (1)) and is used almost exclusively for preparing $NH_4N(NO_2)_2$.

$$XCH_2CH_2N(NO_2)_2 + NH_3 \longrightarrow NH_4N(NO_2)_2 \quad (1)$$

X = CN, COMe, COPh, CO_2Me

The second method is based on ion exchange between salts (reaction (2)).

$$MN(NO_2)_2 + M'X \rightleftharpoons M'N(NO_2)_2 + MX \quad (2)$$

In laboratory practice, it is convenient to use AgN_3O_4 as the starting DNA salt and a halide (M'Hal). The use of KN_3O_4 also often leads to good results.

The most convenient method for preparing salts of DNA with bases (B) stable in the individual state is neutralization of DNA with these bases (reaction (3)).

$$HN(NO_2)_2 + B \longrightarrow HBN(NO_2)_2 \quad (3)$$

Ammonium salts of DNA can also be prepared by heating a free non-volatile base with a DNA salt derived from a volatile base (reaction (4)).

$$NH_4N(NO_2)_2 + RNH_2 \longrightarrow RNH_3N(NO_2)_2 + NH_3 \quad (4)$$

The DNA salts synthesized according to methods (2)—(4) and their properties are listed in Table 1.

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It was found that DNA readily forms stable salts with almost all of the bases studied, including primary, secondary, and tertiary amines, quaternary aliphatic bases, aromatic and heterocyclic amines, hydrazines, hydroxylamines, amidines, guanidine and its amino derivatives, aromatic diazo compounds, *N*-nitropyridinium or methyleniminium cations, *etc.* Even strong electron-withdrawing substituents located in the β-position with respect to the quaternary N atom do not hamper the formation of stable salts; this makes it possible, in particular, to prepare double DNA salts, for example, those derived from ethylenediamine and ethylenedihydrazine.

On the other hand, it should be noted that attempts to prepare the corresponding double salts from methylenediamine dihydrochloride or methylenedihydrazine dihydrochloride and AgN_3O_4 were unsuccessful: in the former case, only $NH_4N_3O_4$ could be isolated as an individual product, and in the latter case, the $NH_2NH_2 \cdot HN_3O_4$ salt was obtained. We also did not manage to isolate individual double salts of DNA with hydrazine, methylhydrazine, and dimethylhydrazine, since these were formed as liquids or crystalline solids (with broad ranges of melting points) with varying compositions, which transformed into mono salts of DNA and the corresponding bases in the course of purification. The reaction of urea nitrate with KN_3O_4 in ethanol afforded a product with m.p. 98—100 °C, which was the urea salt of DNA according to UV and IR spectra. However, all of the attempts to purify this compound resulted in its decomposition. It is likely that in a solution of a DNA salt derived from a weak base, the equilibrium is substantially shifted to the free base and DNA, which is unstable in the individual state.

The DNA salts prepared are, as a rule, colorless crystalline solids with rather low melting points (15—150 °C) and decomposition points. The latter depend essentially on the nature and the strength of the base. The salts derived from simple aliphatic amines decompose at ~120—140 °C. Only quaternary ammonium and hydrazonium salts have higher melting and decomposition points (175—228 °C). It is noteworthy that the latter are readily converted into a waxy mass at an elevated pressure.

Ammonium salts of DNA are usually readily soluble in nitromethane, methyl acetate, or acetonitrile, but insoluble in ether, benzene, or hexane. The fact that the DNA salts derived from hydroxylamine or methoxyamine are readily soluble in some nonpolar solvents, for example, in ether, also deserves attention.

The hygroscopic properties of the DNA salts prepared vary widely. Some of them were non-hygroscopic (quaternary salts, aminoguanidine salts, acetamidine salts, *etc.*), and some other were rather hygroscopic (the salts with methylamine and dimethylamine, the dimethylmethyleniminium salt, *etc.*).

The sensitivity of these salts to mechanical action also varies over a wide interval. Salts with hydrazine and triaminoguanidine are the most dangerous to handle.

Experimental

The starting salts and bases were prepared according to the published procedures. The melting points were determined in a metallic unit.

Attention! Dinitramide salts are dangerous explosive compounds and require the appropriate handling.

The preparation of dinitramidates by ion exchange in salts (general procedure). Saturated (sometimes heated) solutions of two salts were poured together, the precipitate was filtered off, the filtrate was concentrated on a rotary evaporator in the vacuum of a water-jet pump, and the residue was recrystallized (in some cases, several times).

The preparation of dinitramidates by the reaction of bases with dinitramide (general procedure). A solution of DNA was added to a solution of a base, and the precipitate (formed immediately or after evaporation of the solvent) was separated, washed with ether or benzene, and recrystallized. In those cases when the target salts were formed as oils, they were triturated under an ether or benzene layer until they became solid and then recrystallized. In some cases reprecipitation was used instead of recrystallization.

Below we present examples of the syntheses that differ somewhat from the general procedures.

Ammonium dinitramidate (1). A solution of NH_4Cl (1.85 g) in MeOH (80 mL) was added to a solution of KN_3O_4 (1 g) in MeOH (45 mL), the precipitate was separated, and the filtrate was evaporated to dryness. 0.7 g (82 %) of salt **1** was extracted from the residue by hot EtOAc and recrystallized.

Bis(β,β-cyanoethyl)ammonium dinitramidate (7). A solution of DNA (from 2.5 g of KN_3O_4) in Et_2O (50 mL) was added to an emulsion of bis(β,β-cyanoethyl)amine (2.2 g) in anhydrous Et_2O (20 mL). The precipitate of salt **7** was filtered off, washed on the filter with small amounts of EtOH and Et_2O, and recrystallized.

Hydroxylammonium dinitramidate (19). A solution of KN_3O_4 (2 g) in warm MeOH (50 mL) was added to a solution of $NH_2OH \cdot HCl$ (5.47 g) in warm MeOH (60 mL). The reaction mixture was stirred for 3 h. The precipitate was separated, the filtrate was evaporated to dryness, and salt **19** was extracted from the precipitate with ether.

Dinitramidate of β-(dimethylamino)ethyl methacrylate (8). A mixture of salt **1** (1.24 g) and β-(dimethylamino)ethyl methacrylate (1.57 g) was heated (40—50 °C) *in vacuo* (10 Torr) for 4 h. The residue was washed with ether and recrystallized from isopropanol to give 1.88 g (71 %) of salt **8**, which was recrystallized two more times.

***N*-Nitropyridinium dinitramidate (29).** *N*-Nitropyridinium tetrafluoroborate (2.31 g) in MeCN (75 mL) was added to a solution of KN_3O_4 (1.45 g) in anhydrous MeCN (100 mL). The precipitate of KBF_4 was filtered off, and the filtrate was concentrated on a rotary evaporator at 30 °C to ~20 mL. The salt was precipitated by 20 mL of anhydrous CH_2Cl_2 and once again reprecipitated. The resulting dinitramidate is readily decomposed by water to yield nitrogen oxides and reacts with MeOH much more slowly, namely, over a period of 2 days, according to NMR spectroscopy.

Table 1. Salts of DNA (HN_3O_4) and their characteristics

Salt	Reagents	The solvent: for the reaction (for recrystallization)	The yield of the salt (%): prior to recrystallization/after recrystallization	M.p./°C: prior to recrystallization/after recrystallization	Found / Calculated (%) C	H	N
$NH_4N_3O_4$ (**1**)	AgN_3O_4, NH_4Cl	MeOH ($MeNO_2$)	—/41	—/83—89			
1	KN_3O_4, NH_4ClO_4	MeOH (dioxane—EtOAc, 5 : 1)	—/82	—/89—94			
1	KN_3O_4, NH_4Cl	The same	82/59	—/85—89			
1	NH_3, HN_3O_4	Benzene (dioxane—EtOAc)	80/71	87—93/88—94			
$MeNH_2 \cdot HN_3O_4$ (**2**)	$MeNH_2$, HN_3O_4	Et_2O—benzene (anhydr. EtOAc)	~100/—	39—43/43—47	9.00 8.70	4.45 4.35	40.29 40.58
$Me_2NH \cdot HN_3O_4$ (**3**)	Me_2NH, HN_3O_4	The same	~100/—	30—33/31—33	15.69 15.79	5.29 5.26	36.96 36.84
$Me_3N \cdot HN_3O_4$ (**4**)	Me_3N, HN_3O_4	MeOH—Et_2O (Pr^iOH)	90/—	100(decomp.)/128(decomp.)	21.61 21.68	6.02 6.02	33.90 33.72
$(Me_4N)N_3O_4$ (**5**)	Me_4NBr, AgN_3O_4	EtOH—H_2O (EtOH)	~100/—	—/228	— —	— —	31.00 31.11
$NCCH_2CH_2NH_2 \cdot HN_3O_4$ (**6**)	$NCCH_2CH_2NH_2$, HN_3O_4	Et_2O—EtOAc (anhydr. MeOH)	96/—	65—67/67—69	20.25 20.34	3.93 3.96	39.51 39.55
$(NCCH_2CH_2)_2NH \cdot HN_3O_4$ (**7**)	$(NCCH_2CH_2)_2NH$, HN_3O_4	Et_2O (MeOH)	95/—	115/115—117	31.32 31.30	4.36 4.35	36.99 36.52
$CH_2{=}CMeCO_2CH_2CH_2NMe_2 \cdot HN_3O_4$ (**8**)	$CH_2CMeCO_2CH_2CH_2NMe_2$, $NH_4N_3O_4$	— (Pr^iOH)	71/—	46—48/49—51	36.42 36.37	5.96 6.11	21.44 21.21
$PhNH_2 \cdot HN_3O_4$ (**9**)	$PhNH_2$, HN_3O_4	Et_2O (—)	80/—	99—100/—	36.02 36.00	3.97 4.00	27.97 28.00
$H_2NCH_2CH_2NH_2 \cdot 2HN_3O_4$ (**10**)	$H_2NCH_2CH_2NH_2 \cdot 2HCl$, AgN_3O_4	MeOH—H_2O, 2 : 1 (EtOH)	—/51	—/123—126	— —	— —	40.81 40.80
$H_2NNH_2 \cdot HN_3O_4$ (**11**)	$H_2NNH_2 \cdot HCl$, AgN_3O_4	MeOH ($MeNO_2$)	65.6/—	—/77—80	—	—	50.69 50.75
11	$H_2NNH_2 \cdot HCl$, KN_3O_4	The same	82/40.6	—/76—81			
11	H_2NNH_2, HN_3O_4	Benzene ($MeNO_2$)	76—80/—	—/77—82			
$MeNHNHMe \cdot HN_3O_4$ (**12**)	$MeNHNHMe \cdot 2HCl$, AgN_3O_4	EtOH (EtOH)	—/19	—/112—118	— —	— —	42.00 41.92
$(H_2NNHCH_2)_2 \cdot 2HN_3O_4$ (**13**)	$(H_2NNHCH_2)_2 \cdot 2HCl$, AgN_3O_4	MeOH—H_2O (MeOH—MeOAc)	90/75	—/79—80	7.90 7.89	4.00 3.94	46.44 46.05
13	$(H_2NNHCH_2)_2$, HN_3O_4	EtOH (MeOH—MeOAc)	—/72	—/78—81			

Table 1 (*continued*)

Salt	Reagents	The solvent: for the reaction (for recrystallization)	The yield of the salt (%): prior to recrystallization/after recrystallization	M.p./°C: prior to recrystallization/after recrystallization	Found / Calculated (%)		
					C	H	N
$(H_2NNHCH_2)_2 \cdot HN_3O_4$ (**14**)	$(H_2NNHCH_2)_2$, HN_3O_4	EtOH—Et_2O (MeOH)	—/70	—/110—115	12.35 12.57	5.58 5.58	49.92 49.75
$(H_2NNMeCH_2)_2 \cdot 2HN_3O_4$ (**15**)	$(H_2NNMeCH_2)_2 \cdot 2HCl$, AgN_3O_4	EtOH—H_2O (AcOH—EtOH, 10:1)	92/55	—/53—54	14.39 14.46	4.60 4.82	41.89 42.17
$[H_2NN(CH_2)_2]_2 \cdot 2HN_3O_4$ (**16**)	$[H_2NN(CH_2)_2]_2 \cdot 2HCl$, AgN_3O_4	MeOH (hexane to EtOH)[a]	90/—	—/132	14.83 14.53	— —	42.57 42.40
$(H_2NNMeCH_2C{\equiv})_2 \cdot HN_3O_4$ (**17**)	$(H_2NNMeCH_2C{\equiv})_2$, HN_3O_4	Et_2O (—)		Oil	28.15 28.90	6.11 6.02	38.97 39.41
$(Me_3NNH_2)N_3O_4$ (**18**)	$(Me_3NNH_2)I$, AgN_3O_4	MeOH (EtOH)	93/45	—/176—178	19.75 19.80	6.04 6.07	38.49 38.70
18	$(Me_3NNH_2)OH$, HN_3O_4	MeOH (Pr^iOH)		—/170—175			
$H_2NOH \cdot HN_3O_4$ (**19**)	$H_2NOH \cdot HCl$, KN_3O_4	MeOH (benzene to MeOAc)[a]	83/72	—/18—23	—	—	40.39 40.00
$MeONH_2 \cdot HN_3O_4$ (**20**)	$MeONH_2 \cdot HCl$, AgN_3O_4	MeOH (—)	70/—	Oil			
$HC(=NH)NH_2 \cdot HN_3O_4$ (**21**)	$HC(=NH)NH_2 \cdot AcOH$, AgN_3O_4	EtOH (EtOH)	66/30	—/100—103	7.53 7.95	3.76 3.60	46.65 46.42
21	$HC(=NH)NH_2 \cdot HCl$, AgN_3O_4	The same	95/46	—/104—107			
$MeC(=NH)NH_2 \cdot HN_3O_4$ (**22**)	$MeC(=NH)NH_2 \cdot HCl$, AgN_3O_4	MeOH (MeOAc)	93/67	—/118—120	14.66 14.55	4.28 4.25	42.64 42.42
$H_2NC(=NH)NH_2 \cdot HN_3O_4$ (**23**)	$H_2NC(=NH)NH_2 \cdot HCl$, AgN_3O_4	MeOH (EtOH)	99/23.5	—/135—139	—	—	50.71 50.65
$H_2NC(=NH)NHNH_2 \cdot HN_3O_4$ (**24**)	$H_2NC(=NH)NHNH_2 \cdot H_2CO_3$, HN_3O_4	Benzene (EtOH)	80/40	—/92—94	—	—	54.49 54.14
$H_2NNHC(=NH)NHNH_2 \cdot HN_3O_4$ (**25**)	$H_2NNHC(=NH)NHNH_2 \cdot HCl$, AgN_3O_4	EtOH (EtOH)	96/43	—/56—57	6.20 6.12	4.15 4.08	57.89 57.14
$H_2NNHC(=NNH_2)NHNH_2 \cdot HN_3O_4$ (**26**)	$H_2NNHC(=NNH_2)NHNH_2 \cdot HCl$, AgN_3O_4	H_2O (EtOH)	96/48	—/86—87	6.09 5.85	4.31 4.16	59.63 59.71
$(CH_2{=}NMe_2)N_3O_4$ (**27**)	$(CH_2{=}NMe_2)I$, AgN_3O_4	MeOH —	75/—	34—37/— [b]	21.90 22.00	5.67 4.88	—
$H_2NCONH_2 \cdot HN_3O_4$ (**28**)	$H_2NCONH_2 \cdot HNO_3$, KN_3O_4	EtOH (—)	72/—	98—100/—	—	—	—
$(C_5H_5NNO_2)N_3O_4$ (**29**)	$(C_5H_5NNO_2)BF_4$, KN_3O_4	MeCN (CH_2Cl_2 to MeCN)[a]	—/18	—/55—58	25.33 25.98	2.54 2.18	29.50 30.30
$(p\text{-}O_2NC_6H_4N_2)N_3O_4$ (**30**)	$p\text{-}O_2NC_6H_4N_2OK$, HN_3O_4	EtOH (Et_2O to MeOAc)[a]	—/81	—/59—63	—	—	32.66 32.81

[a] Precipitation. [b] Dried over P_2O_5.

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