New systems for classical nitrosohalogenation of alkenes 2.* Generation of nitrosyl chloride in AgNO₂-SOCl₂ and AgNO₃-SOCl₂ systems**

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Study of the reactions of compounds of the norbornene series demonstrated that the $AgNO_2$ -SOCl₂ and $AgNO_3$ -SOCl₂ systems serve as nitrosochlorinating agents under the conditions of electrophilic addition. X-ray diffraction study showed that dimerization of *cis-exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane occurs heterostereospecifically. The origin of the active principle of the reagents is discussed.

Key words: silver nitrite, silver nitrate, thionyl chloride, norbornenes, dimers of nitroso chlorides, synthesis, X-ray diffraction study.

The electrophilic addition at the double carbon—carbon bond is one of the most important processes in organic chemistry and chemical technology, which is of fundamental theoretical significance and has wide practical application. The synthetic scope of the Ad_E reactions, which allow one to introduce two functional groups into a carbon skeleton, is determined, on the one hand, by the diversity of electrophilic reagents and, on the other hand, by the possible subsequent transformations of the introduced groups.

Earlier,^{2–4} we have proposed new nitrating and nitrosating reagents of the ionic nature, viz., nitronium ethyl sulfate and nitrosonium ethyl sulfate, respectively. The ethyl sulfate group was demonstrated to be a promising nucleofuge.⁴

Results and Discussion

In continuation of a search for nitrosating and nitrating electrophilic reagents, in which the nucleophilic residue can act as a potential nucleofuge in the subsequent nucleophilic substitution, we studied the reactions of alkenes with silver nitrite and nitrate in the presence of thionyl chloride in diethyl ether. These systems have been used earlier for mild and efficient nitrosation and nitration of alcohols,⁵ which confirms their nitrosating and nitrating properties. It was hypothesized⁵ that thionyl chloride nitrite CIS(O)ONO and thionyl chloride nitrate $ClS(O)ONO_2$, respectively, serve as reagents in these reactions.

We found that the $AgNO_2-SOCl_2$ (1) and $AgNO_3-SOCl_2$ (2) systems exhibit nitrosochlorinating properties with respect to alkenes of the bicycloheptene series, *viz.*, norbornene (3), dimethyl norbornene-5,6-*endo*-dicarboxylate (4), norbornadiene (5), and 3,6-di-





i. AgNO_{*n*}-SOCl₂ (n = 2, 3), Et₂O.

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Alkene	Pro- duct	Yield (%)			
		alkene : system 1		alkene : system 2	
		1:1	1:2	1:1	1:2
3	7	48	63	27	73
4	8	42	68	43	75
5	9	75	87	74	98
6	10	25	75	45	50

Table 1. Yields of the dimers of nitroso chlorides 7-10 with the use of systems 1 and 2 at different substrate : reagent ratios

methoxybenzonorbornadiene (6), to give addition products of nitrosyl chloride. For example, the reaction of 1 or 2 with norbornene (3) produces cis-exo-2-chloro-3nitrosobicyclo[2.2.1]heptane (7), which undergoes dimerization under the reaction conditions and precipitates from an ethereal solution as colorless crystals of diazene dioxide (Scheme 1).

For systems 1 and 2, the yields of dimers 7-10 prepared at different substrate : reagent ratios are given in Table 1. A twofold increase in the amount of the reagent with respect to olefin made it possible to substantially increase the yields of the target products. For example, the yields of 63 and 87% were achieved in the reactions with norbornene and norbornadiene with the use of system 1.

The structures of compounds 7-10 were established by NMR and IR spectroscopy and elemental analysis. The physicochemical characteristics of these compounds are in complete agreement with those documented in the study.¹

The *cis*-di-*exo* orientation of the substituents in compound 7 was confirmed by X-ray diffraction. The dimer of 7 was demonstrated to be the *E* isomer with respect to the N=N bond.

The carbon atoms at the substituents in the monomeric fragments of the dimer of 7 have the (R,S) and (S',R') configurations (Fig. 1). The structure as a whole is described by the space group P2(1)/c and, consequently, it is a centrosymmetric *meso* form. Therefore, dimerization of the monomer of nitroso chloride produced in the reaction occurs heterostereospecifically.⁶



Fig. 1. Molecular structure of the dimer of *cis-exo-*2-chloro-3-nitrosobicyclo[2,2,1]heptane **7**.

Table 2. Selected interatomic distances (*d*) and bond angles (ω) in compound 7

Bond	d/Å	Angle	ω/deg
Cl-C(1)	1.7946(19)	O-N-N	120.67(19)
O-N	1.262(2)	O-N-C(2)	122.75(14)
N-N	1.311(3)	N-N-C(2)	116.58(18)
N-C(2)	1.472(2)	C(6) - C(1) - C1	111.17(14)
		C(2) - C(1) - C(1)	112.63(13)
		N - C(2) - C(3)	112.73(16)
		N-C(2)-C(1)	113.24(15)

According to the results of X-ray diffraction study (Table 2), the CN(O)—N(O)C fragment is planar. The C—N bond length in the dimer (1.472(2) Å) is similar to the C—N bond length in amines (1.47 Å), whereas the N—N bond (1.311(3) Å) is intermediate between single and double bonds. The N—O bond length is 1.262(2) Å. Therefore, the bond angles and bond lengths in the CN(O)—N(O)C fragment are typical of diazene dioxides and agree well with those determined earlier for the *trans* dimer of 2-chloro-2-methyl-3-nitrosobutane.⁷

Let us note some characteristic features of the reaction, which we revealed with the use of structurally different substrates. First, the reactions with norbornene (3), norbornadiene (5), and 3,6-dimethoxybenzonorbornadiene (6) do not afford products of the Wagner-Meerwein rearrangement and homoallylic assistance of the second double bond, which is indicative of the low "effective electrophilicity" of the reagent.⁸ Second, only one double bond of norbornadiene (5) is involved in the reaction even in the presence of a twofold excess of the reagent. Third, the electrophilic addition of norbornene derivatives containing the endo-carboxy substituents can give lactonization products.^{9,10} In spite of this fact, the reactions of dimethyl norbornene-5,6-endo-dicarboxylate (4) with reagents 1 and 2 produced only the corresponding dimer of nitroso chloride 8. We did not detect products of the conjugated addition involving the ester group as a nucleophile. The IR spectrum shows absorption bands at 1200 and 1280 cm⁻¹ characteristic of the *trans* dimer of the nitroso compound and at 1740 cm⁻¹ characteristic of the ester group. The ¹H NMR spectrum has two singlets at δ 3.62 and 3.71 with an integrated intensity of 3 H for each signal. The ¹³C NMR spectrum contains signals at δ 51.86 and 52.20, which confirms the presence of two methoxy groups in compound 8.

Our experimental results agree well with the data on the addition of nitrosyl chloride to alkenes^{11–13} and are contradictory to the statement made in the study,⁵ where thionyl chloride nitrite and thionyl chloride nitrate (which are structurally similar to nitrosonium and nitronium ethyl sulfates, respectively) were considered as reagents in these systems. However, these reagents should exhibit the properties of "efficiently stronger electrophiles"⁸ and give products of skeletal rearrangements and conjugated addition reactions.

To elucidate the nature of the reagents that formed, we recorded the IR spectra of solutions, which were prepared by mixing AgNO₂ with SOCl₂ (system 1) and of AgNO₃ with SOCl₂ (system 2) in diethyl ether at 0 °C. The IR spectrum of a solution of 1 shows a band at 1840 cm⁻¹ corresponding to absorption of free NOCl.¹⁴ The IR spectrum of a solution of 2 has, in addition to the band of NOCl, an absorption band belonging to NO₂Cl (1680 cm⁻¹).^{15,16} We did not observe absorption at 2340 and 2360 cm⁻¹ characteristic of the nitrosonium cation¹⁷ and the nitronium cation,¹⁸ respectively, which is evidence that ionic thionyl chloride nitrite or nitrate are absent in the reaction mixtures.

Moreover, the reaction of norbornene with $AgNO_3$ and $SOCl_2$ in acetonitrile produced a mixture of chloroacetamides **11** and **12** and nitroso chloride **7** in a ratio of 1 : 1 (Scheme 2) rather than nitro- or nitrosoacetamides, which is consistent with the published data^{11,13,19} on the reactions of NO₂Cl and NOCl with alkenes.

Scheme 2



11 + **12** (30%); **11** : **12** = 5 : 1

Chloroacetamides **11** and **12** were isolated as a mixture and characterized by IR and NMR spectroscopy. The IR spectrum of a mixture of these compounds shows absorption bands at 3280 (NH bond), 1640 (C=O), and 1560 (NH) cm⁻¹ characteristic of amides. The conclusion that compounds **11** and **12** are rearrangement products was drawn based on the spin-spin coupling constants of the protons HCN ($J_{2,3endo} = 9.0$ and 6.8 Hz and $J_{2,3exo} =$ 4.9 and 4.0 Hz, respectively). The presence of the W coupling constant with the proton *anti*-H(7) ($J_{2,7} =$ 1.0 Hz) in isomer **11** confirms the *syn* arrangement of the chlorine atom and the acetamide group.²⁰ This is also responsible for the larger downfield chemical shift of the HN proton of compound **11** (δ 6.05) compared to the HN proton of product **12** (δ 5.60). Hence, the presence of nitrile chloride and/or nitrosyl chloride in the $AgNO_n$ -SOCl₂ systems (n = 2 or 3) is beyond doubt. However, the question arises as to the pathway of their formation.

If n = 2, decomposition of the initially formed thionyl chloride nitrite presumably affords SO₂ and NOCl. However, this scheme does not explain the appearance of the blue color of the solution as soon as the addition of SOCl₂ to AgNO₂ began. Presumably, under the reaction conditions (0 °C, diethyl ether), silver nitrite reacts with thionyl chloride to form unstable thionyl nitrite, which decomposes to give nitrous anhydride (blue in color) and sulfur dioxide. Then nitrous anhydride reacts with another molecule of thionyl chloride to form nitrosyl chloride²¹ (Scheme 3).

Scheme 3

$$SOCI_2 + 2 AgONO \xrightarrow{-AgCl} SO(ONO)_2 \longrightarrow$$

 $\longrightarrow SO_2 + N_2O_3$

$$N_2O_3 + SOCl_2 \longrightarrow 2 NOCl + SO_2$$

The reaction of silver nitrate with thionyl chloride involves, apparently, analogous transformations (Scheme 4). Two chlorine atoms in the latter compound are replaced to form unstable thionyl nitrate.

Scheme 4

$$SOCI_2 + 2 AgONO_2 \xrightarrow{-AgCI} SO(ONO_2)_2 \longrightarrow$$

 $\longrightarrow SO_3 + N_2O_4$
 $N_2O_4 + SOCI_2 \longrightarrow NOCI + SO_2 + NO_2CI$

Undoubtedly, the sequence of redox processes that occur in the reaction of silver salts with thionyl chloride requires additional study. However, it is evident that it is incorrect to consider thionyl chloride nitrate and thionyl chloride nitrite as reagents. It is more correct to speak about the nitrating and nitrosating systems, AgNO₃-SOCl₂ and AgNO₂-SOCl₂, respectively. It should be noted that the presence of nitryl chloride in the former system will cause nitration of alcohols.⁵ At the same time, nitrosyl chloride present in solution rapidly reacts with alkenes to give nitroso chlorides. The absence of nitrites as products of the reactions of alcohols with the AgNO₃-SOCl₂ system is apparently associated with the fact that nitrites, even if they are generated, are readily oxidized under the reaction conditions to form nitrates.

To summarize, we demonstrated that in the presence of thionyl chloride, silver nitrite and nitrate act as mild nitrosochlorinating reagents for compounds of the norbornene series, and the proposed scheme of the formation of the reagent is consistent with both the experimental data published earlier⁵ and the results of our study.

Experimental

The ¹H and ¹³C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) at 28 °C. The chemical shifts are given on the δ scale relative to Me₄Si as the internal standard. The IR spectra were measured on UR-20 (in Nujol mulls) and Specord 75 IR (Et₂O) instruments. The mass spectrum was obtained on a Hewlett—Packard Engine GS-MS GLC-mass spectrometer; the energy of ionizing electrons was 70 eV.

The solvents were purified according to standard procedures. $^{\mathbf{20}}$

Synthesis of reagents 1 and 2 (general procedure). Finely ground dry silver nitrite or nitrate (5 mmol) and anhydrous diethyl ether (7 mL) were placed in a two-neck flask equipped with a thermometer, a dropping funnel, and a stirrer. Then an equimolar amount of thionyl chloride (3 mL) was added dropwise with vigorous stirring to the resulting suspension cooled with ice. The blue color appeared within a few minutes, and then this color rapidly changed to yellow. The suspension was stirred for 15 min, after which the solution turned bright-orange. The solution of the reagent in diethyl ether was decanted from a precipitate of silver chloride (after drying, silver chloride was obtained in quantitative yield). The latter was twice washed with diethyl ether (2×2.5 mL). All extracts were combined, cooled to 0 °C, and used in reactions.

Reactions of olefins with systems 1 and 2 (general procedure). A solution of the reagent in diethyl ether was placed in a twoneck flask equipped with a thermometer, a dropping funnel, and a stirrer and cooled to -40--60 °C. At this temperature, a solution of alkene in diethyl ether was added dropwise with vigorous stirring. The reaction mixture was stirred for 0.5 h and then the temperature was gradually raised to -10 °C, during which the mixture turned blue or green. Then the reaction was stirred at -10 °C for 0.5 h or during a longer period (depending on the activity of the substrate used) until the color disappeared and a precipitate formed. The precipitate was filtered off and washed with diethyl ether or ethyl acetate. The mother liquor was concentrated to ~5 mL and an additional amount of the precipitate was isolated.

The yields of nitroso chlorides 7-10 are given in Table 1. The physicochemical characteristics of these compounds are consistent with those reported earlier.^{1,11-13}

Reaction of norbornene 3 with the SOCl₂-AgNO₃ system in acetonitrile. A solution of norbornene (0.19 g, 2 mmol) was added with vigorous stirring to a solution of AgNO₃ (0.34 g, 2 mmol) and SOCl₂ (0.24 g, 2 mmol) in acetonitrile (10 mL) at -40 °C. The reaction mixture was stirred at this temperature for 1 h and warmed to -20 °C. Then water was added and the solution was extracted three times with chloroform. The combined organic extracts were dried over CaCl₂. After distillation of the solvent, the crude product was purified by recrystallization from MeOH. The crystals that precipitated were filtered off. The dimer of *cis-exo*-3-nitroso-2-chlorobicyclo[2,2,1]heptane **7** was obtained in a yield of 0.95 g (30%). The mother liquor was concentrated and the residue was chromatographed on a silica gel column (ethyl acetate—petroleum ether, 1 : 1). A mixture of *N*-(*syn*-7-chloro-*exo*-bicyclo[2.2.1]hept-2-yl)acetamide (**11**) and *N*-(*anti*-7-chloro-*exo*-bicyclo[2.2.1]hept-2yl)acetamide (**12**) (R_f 0.12) was obtained in a ratio of 5 : 1 in a yield of 0.115 g (30%).

¹H NMR of compound **11**, δ : 1.10–1.40 (m, 2 H, *endo*-H(5), *endo*-H(6)); 1.52–1.58 (m, 2 H, *exo*-H(5), *exo*-H(6)); 1.78 (dtd, 1 H, *exo*-H(3), $J_{3,3} = 13.2$ Hz, $J_{3,2} = J_{3,4} = 4.9$ Hz, $J_{3,5exo} =$ 2.3 Hz); 1.89 (s, 3 H, CH₃); 1.95 (ddd, 1 H, *endo*-H(3), $J_{3,3} =$ 13.2 Hz, $J_{3,2} = 9.0$ Hz, $J_{3,7} = 1.0$ Hz); 2.20 (m, 1 H, H(4)); 2.26 (br.s, 1 H, H(1)); 3.91 (br.s, 1 H, HCCI); 4.04 (tdd, 1 H, HCN, $J_{2,3endo} = J_{2,NH} = 9.0$ Hz, $J_{2,3exo} = 4.9$ Hz, $J_{2,7} = 1.0$ Hz); 6.05 (br.s, 1 H, NH). ¹H NMR of compound **12**, δ : 3.75 (dd, 1 H, HCN, $J_{2,NH} = 10.2$ Hz, $J_{2,3endo} = 6.8$ Hz, $J_{2,3exo} = 4.0$ Hz); 3.94 (br.s, 1 H, HCCI); 5.60 (br.s, 1 H, NH), signals for the protons H(1), H(3), H(4), H(5), and H(6) overlap with the signals of compound **11**. ¹³C NMR of a mixture of **11** and **12**, δ : 23.6, 23.9, 38.2, 41.8, 48.5 (CH₃, C(3), C(7), C(4), C(1), compound **12**), 25.5, 25.7, 37.6, 42.5, 47.9 (CH₃, C(3), C(7), C(4),

 Table 3. Crystallographic data, details of X-ray data collection, and characteristics of structure refinement of compound 7

Parameter	Characteristic	
Molecular formula	C ₁₄ H ₂₀ Cl ₂ N ₂ O ₂	
Molecular weight	319.22	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
T/K	293(2)	
λ/Å	0.71073	
a/Å	9.949(2)	
b/Å	6.652(1)	
c/Å	11.178(2)	
α/deg	90	
β/deg	90.82(3)	
γ/deg	90	
$V/Å^3$	739.7(2)	
Z	2	
$d_{\rm calc}/{\rm g \ cm^{-3}}$	1.433	
μ/mm^{-1}	0.442	
<i>F</i> (000)	336	
Scan range, θ/deg	3.65-25.01	
Scanning mode	$\theta/2\theta$	
Ranges of indices	$-11 \le h \le 0,$	
	$-7 \le k \le 0,$	
	$-13 \le l \le 13$	
Number of measured reflections	1226	
Number of reflections with $I > 2\sigma(I)$	1161	
<i>R</i> _{int}	0.0474	
Number of parameters in refinement	132	
GOOF on F^2	1.101	
$R_1/wR_2 \ (I \ge 2\sigma(I))$	0.0362/0.0956	
R_1/wR_2 based on all reflections	0.0368/0.0963	
Exctinction coefficient	0.021(8)	
Residual electron density,		
max/min, e Å ⁻³	0.287/-0.292	

C(1), compound **11**), 51.7 (CN, compound **12**), 51.75 (CN, compound **11**), 64.2 (CCl, compound **12**), 66.2 (CCl, compound **11**), 169.0 (C=O). IR, v/cm⁻¹: 3280 (NH bond), 1640 (C=O), 1560 (NH). MS of **11** (EI, 70 eV), m/z (I_{rel} (%)): 190 (1.6), 189 [M + 2]⁺ (5.0), 188 (4.9), 187 [M]⁺ (16.9), 86 (45.6), 85 (100), 67 (34.7), 45 (32.6), 44 (96.7). MS of **12** (EI, 70 eV), m/z (I_{rel} (%)): 190 (0.4), 189 [M + 2]⁺ (4.9), 188 (2.6), 187 [M]⁺ (14.5), 152 (15.3), 110 (11.2), 86 (100), 85 (84.8), 67 (53.1), 45 (57.8), 44 (75.9).

X-ray diffraction study of 7. Crystals of compound 7 suitable for X-ray diffraction study were grown as colorless prisms of dimensions 0.85×0.45×0.20 mm by slow evaporation from a solution in chloroform. X-ray diffraction data were collected on a Syntex-P1 diffractometer (Mo-Ka radiation). The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were located from difference Fourier maps and refined isotropically. All calculations were carried out using the SHELXL97 program package.²² The atomic coordinates for the structure of 7 and the complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database. Selected bond lengths and bond angles are given in Table 2. Crystallographic data, details of X-ray data collection, and characteristics of structure refinement are listed in Table 3.

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