

New systems for classical nitrosohalogenation of alkenes

1. Reactions of alkenes with ethyl nitrite in the presence of phosphorus halides and thionyl chloride*

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Studies of nitrosation of norbornene and norbornadiene derivatives and dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-*cis-endo*-dicarboxylate demonstrated that nitrosation of alkenes with EtONO–PHal₃, EtONO–POHal₃ (Hal = Cl or Br), and EtONO–SOCl₂ systems can afford nitroso halides in high yields without the formation of by-products (ketones and oximes). The reactions with 5-substituted norbornenes are nonregioselective. The *trans* dimer of *endo*-5-trifluoromethyl-*cis-exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane was studied by X-ray diffraction.

Key words: ethyl nitrite, thionyl chloride, phosphorus(III) halides, phosphorus(V) oxohalides, alkenes, dimers of nitroso halides, X-ray diffraction study.

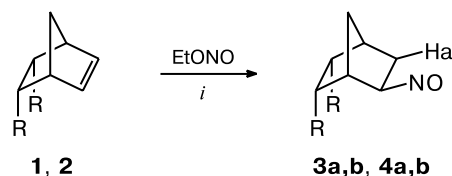
Alkene nitrosochlorination products are successfully used in organic synthesis, for example, for the construction of various heterocycles (pyrazines,¹ thiazoles,² and thiadiazines³) and in the original synthesis of cyclohept-4-ene-1-carboxylic acid.⁴ A search for new nitrosohalogenating systems is a topical problem. Nitrosohalogenation of unsaturated substrates can be performed according to the following two main procedures: the direct reaction with nitrosyl halides^{5–8} or the reaction with nitrosyl halides generated *in situ* by activation of alkyl nitrites with protic acids.^{6–12} However, both reactions afford halo ketones or halo oximes as by-products or even the major products.

Results and Discussion

Earlier,¹³ we have developed a new procedure for nitrosobromination of olefins by their reactions with ethyl nitrite in the presence of phosphorus tribromide. In the present study, we examined the possibility of activation of ethyl nitrite with PHal₃, POHal₃ (Hal = Cl or Br), and SOCl₂. Compounds **1** and **2** of the norbornene series afford *cis-exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane (**3a**), *cis-exo*-2-bromo-3-nitrosobicyclo[2.2.1]heptane (**3b**), *cis-endo*-5,6-di(methoxycarbonyl)-*cis-exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane (**4a**), and *cis-endo*-5,6-di(methoxycarbonyl)-*cis-exo*-2-bromo-3-nitrosobicyclo[2.2.1]heptane (**4b**) in preparative yields as

white crystals, which is characteristic of dimers of nitroso compounds (Scheme 1, Table 1).

Scheme 1



R = H (**1**, **3a,b**), COOMe (**2**, **4a,b**); Hal = Cl (**3a**, **4a**), Br (**3b**, **4b**)

Reagents i. PCl₃, PBr₃, SOCl₂, POCl₃, or POBr₃.

The highest yields were achieved at the PHal₃ : olefin molar ratio of 1 : 2. The reaction was completed in 30 min. The reaction with POHal₃ requires a longer time for completion (48 h; POHal₃ : olefin = 1 : 1; see Table 1).

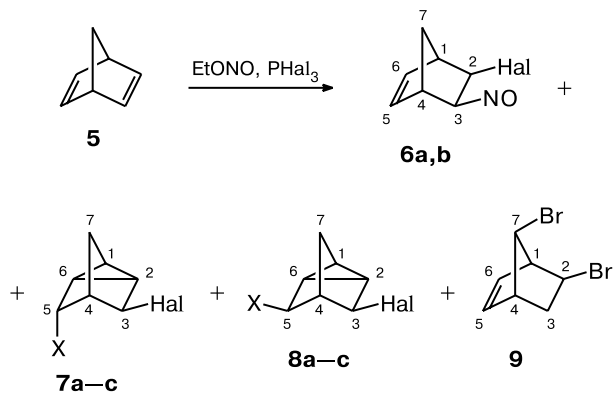
The compositions and structures of the reaction products were established by ¹H and ¹³C NMR spectroscopy (Tables 2 and 3, respectively), IR spectroscopy, and elemental analysis (Table 4). The coupling constants in the ¹H NMR spectra of compounds **3** and **4** (*J*_{3,2} = 6.5–7.1 Hz) correspond to the *cis*-di-*exo* arrangement of the substituents.¹⁴

In reactions with "effectively strong" electrophiles,¹⁵ alkenes of the norbornadiene series are prone to skeletal rearrangements and are characterized by homoallylic assistance of the second double bond involved in stabilization of the intermediate carbocation. To obtain additional

* Dedicated to Academician N. S. Zefirov on the occasion of his 70th birthday.

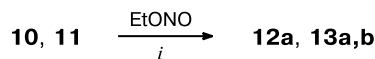
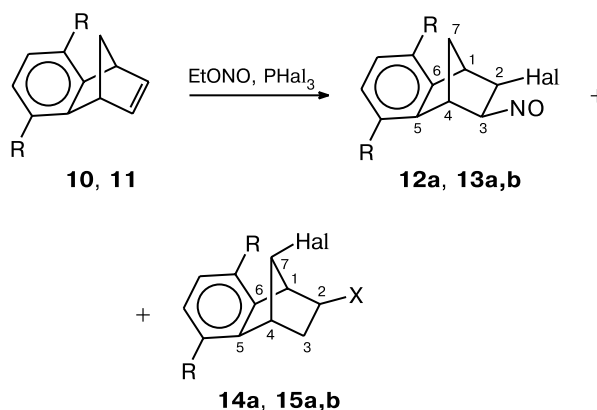
Table 1. Yields of nitrosohalogenation products

Olefin	Lewis acid	Product	Yield (%)
1	PCl ₃	3a	70
	POCl ₃		10
	SOCl ₂		65
	PBr ₃	3b	77
	POBr ₃		60
2	PCl ₃	4a	76
	SOCl ₂		70
	PBr ₃	4b	72
	POBr ₃		43
5	PCl ₃	6a	68
	SOCl ₂		79
	PBr ₃		60
	POBr ₃	6b	54
			43
10	PCl ₃	12a	68
	POCl ₃		30
	SOCl ₂		86
11	PCl ₃	13a	70
	PBr ₃		61
	POBr ₃	13b	41
16	PCl ₃	18 + 20	53 ^a
17	SOCl ₂	19 + 21	23 ^b
22	PCl ₃	23a	76
	SOCl ₂		59
	PBr ₃		56

^a **18** : **20** ≈ 1 : 1.^b **19** : **21** ≈ 1 : 1.**Scheme 2**

Compound	EtONO, SOCl_2		Compound	EtONO, POBr_3	
	Hal	X		Hal	X
6a	Cl	—	7c	Cl	ONO ₂
6b	Br	—	8a	Cl	Cl
7a	Cl	Cl	8b	Br	Br
7b	Br	Br	8c	Cl	ONO ₂

data on the reaction mechanism and the nature of the reagents under study, we thoroughly analyzed the compositions of the products prepared by the reaction of norbornadiene **5** with EtONO — PHal_3 systems. In addition to nitroso halides **6**, we isolated small amounts and identified dihalides **7a,b**, **8a,b**, and **9** and chloro nitrates **7c** and **8c** (Scheme 2). Under the same conditions, the reactions of benzonorbornadienes **10** and **11** afforded nitroso halides **12a** and **13a,b**, chloro nitrates **14a** and **15a**, and dibromide **15b** (Scheme 3).

Scheme 3

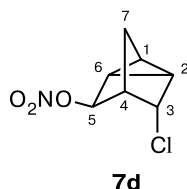
Compound	R	Hal	X	Compound	R	Hal	X
10	OMe	—	—	13b	H	Br	—
11	H	—	—	14a	OMe	Cl	ONO ₂
12a	OMe	Cl	—	15a	H	Cl	ONO ₂
13a	H	Cl	—	15b	H	Br	Br

Reagents: *i.* POCl_3 (SOCl_2 or POBr_3).

The physicochemical characteristics of compounds **7a**, **8a**, and **15a** are consistent with the published data.^{16–18} The presence of a double bond in product **9** is evidenced by a signal for the olefinic protons at δ 6.20 in the ^1H NMR spectrum. The conclusion about the rearranged character of compound **9** was made based on the multiplicity of the signal for the proton $\text{H}(2)\text{Br}$ (δ 3.76). This signal appears as a doublet of doublets of doublets with two vicinal coupling constants ($J_{2,3\text{endo}} = 8.0$ Hz and $J_{2,3\text{exo}} = 4.0$ Hz) and a W coupling constant with the proton *anti*- $\text{H}(7)\text{Br}$ ($J_{2,7} = 1.3$ Hz).

Dibromides **7b** and **8b** with nortricyclane structures were isolated and characterized as a mixture. The assignment of the chemical shifts of the protons at the substituents was made based on the criteria proposed in the study.¹⁹ The ^{13}C NMR spectra of compounds **7b** and **8b** correspond to those recorded earlier.²⁰

The functional compositions of nitrates **7c**, **8c**, **14a**, and **15a** were determined by IR spectroscopy²¹ and were confirmed by elemental analysis (see Table 4). Chloro nitrates **7c** and **8c** were isolated and characterized as a mixture. To establish the structures of these compounds, we examined the possibility of the formation of the following three isomers: **7c**, **8c**, and hypothetical structure **7d**.



The chemical shifts of the protons at the substituents were calculated by the equation $\delta_3 = \delta_0 + \Delta_s + \Delta_{de}$, where δ_3 is the chemical shift of the proton of the HCCl or HCONO₂ group in a 3,5-disubstituted nortricyclane, δ_0 is the chemical shift of the proton at the C(3) atom in the 3-nortricyclane system ($\delta_0(\text{HCCl}) = 3.85 \pm 0.03$ and $\delta_0(\text{HCONO}_2) = 4.77$), Δ_s is the change in the chemical shift of the proton due to the presence of a substituent at position 5 (*endo* or *exo*) (for HCCl and HCONO₂, $\Delta_s = 0.0$), and Δ_{de} is the deshielding effect of an *endo* substituent at position 5 ($\Delta_{de}(\text{HCCl}) = 0.76 \pm 0.07$ and $\Delta_{de}(\text{HCONO}_2) \approx 0.6$).¹⁹ A comparison of the calculated data with the experimental results (Table 5) led us to conclude that the reaction affords *exo*-3-chloro-*endo*-5-nitroxytricyclo[2.2.1.0^{2,6}]heptane (**7c**) and *exo*-3-chloro-*exo*-5-nitroxytricyclo[2.2.1.0^{2,6}]heptane (**8c**).

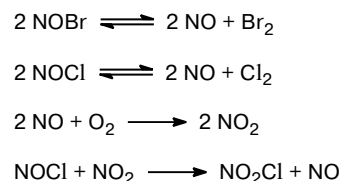
The fact that the formation of nitrates **14a** and **15a** is accompanied by a rearrangement is evidenced by the presence of two vicinal coupling constants of the proton HC(2)O with the protons of the adjacent methylene group, *viz.*, 2 H(3), ($J_{2,3endo} = 7.5$ Hz and $J_{2,3exo} = 3.5$ and 3.7 Hz for **14a** and **15a**, respectively) in the ¹H NMR spectra of these compounds. The *endo* arrangement of the proton HC(2)O is confirmed by the presence of a long-range W coupling constant $J_{2,7anti} = 1.0$ Hz (Table 6, see Ref. 14).

Consequently, neither the Wagner–Meerwein rearrangement nor homoallylic assistance products of the second double bond, nor the conjugated addition product involving an ester group as the nucleophile, were present among the resulting nitroso halides. These results are consistent with the published data^{5–12} on the addition of nitrosyl chloride to such alkenes and suggest that the reaction is accompanied by the *in situ* generation of nitrosyl halides, which react with olefins.

The formation of by-products under the conditions of nitrosohalogenation of olefins used in the present study is apparently attributed to the reaction of alkenes with traces of halides and nitril chloride generated as a result of partial decomposition of nitrosyl halides (Scheme 4).^{24,25}

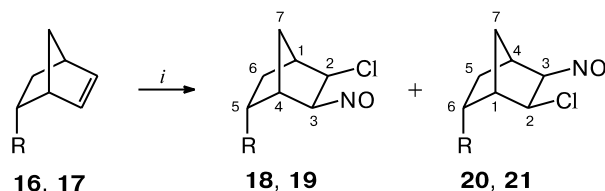
However, the yields of compounds **7–9**, **14**, and **15** are so low (see Experimental) that their formation does not impair the synthetic importance of this method. Besides, the use of Lewis acids (aprotic acids) for the activation of ethyl nitrite prevents the formation of ketones and oximes.

Scheme 4



In spite of the fact that nitrosochlorination has long been in use, there is no general agreement as to its mechanism. Hence, it was of interest to study the influence of electron-withdrawing groups at position 5 of norbornene on the regio- and stereoselectivity of the reaction. We examined 5-trifluoromethylbicyclo[2.2.1]hept-2-ene* (**16**) and *endo*-5-nitrobicyclo[2.2.1]hept-2-ene (**17**) as model substrates. In both cases, two regioisomers in a ratio of approximately 1 : 1 were isolated (Scheme 5, see Table 1).

Scheme 5



R = CF₃ (**16**, **18**, **19**), NO₂ (**17**, **19**, **21**)

i. EtONO, PCl₃ (or SOCl₂).

The dimer of *endo*-5-trifluoromethyl-*cis*-*exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane (**18**) was isolated in individual form by recrystallization from CHCl₃. However, we failed to purify the dimer of *endo*-6-trifluoromethyl-*cis*-*exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane (**20**), which remained in the mother liquor, from an impurity of compound **18** by recrystallization. The structures of these compounds were established based on the analysis of the chemical shifts in the ¹H NMR spectrum. In particular, the signal for the proton HC(3)N in product **18** is shifted downfield by δ 0.47 compared to the signal for the proton HC(3)N in compound **20** due to the deshielding effect of the trifluoromethyl group.

X-ray diffraction study of compound **18** confirmed the assignment of the signals. The overall view of the molecule and the atomic numbering scheme** are shown in Fig. 1. The bond lengths and bond angles calculated

* The reaction was carried out with a mixture of isomers in an *exo* : *endo* ratio of 1 : 3. We failed to isolate and characterize isomers obtained from 5-*exo*-trifluoromethylnorbornene.

** The atomic numbering scheme does not correspond to the IUPAC nomenclature.

Table 2. ^1H NMR spectra of the compounds synthesized (in CDCl_3)

Compound	δ ($J_{\text{H,H}}/\text{Hz}$)					
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)
3a	2.47 (br.d, $J_{1,6\text{exo}} = 4.5$)	4.36 (dd, $J_{2,3} = 6.7$, $J_{2,7\text{anti}} = 1.4$)	4.87 (dd, $J_{3,7\text{anti}} = 1.2$)	2.80 (dd, $J_{4,5\text{exo}} = 4.3$)	endo: 1.27 (m) exo: 1.71 (m)	endo: 1.27 (m) exo: 1.62 (m)
3b	2.57 (dd, $J_{1,6\text{exo}} = 4.1$, $J_{7,1\text{syn}} = 1.7$)	4.41 (dd, $J_{2,3} = 6.7$, $J_{2\text{anti},7} = 1.8$)	4.87 (dd, $J_{3,7} = 0.9$)	2.80 (dd, $J_{4,5\text{exo}} = 2.7$, $J_{4,7} = 1.1$)	endo: 1.30 (m) exo: 1.72 (m)	endo: 1.30 (m) exo: 1.62 (m)
4a^a	2.79 (br.d)	4.80 (dd, $J_{2,3} = 6.7$, $J_{2,7\text{anti}} = 1.5$)	5.65 (dd, $J_{3,7\text{anti}} = 0.9$)	3.18 (dd)	3.04 (dd, $J_{5,6} = 12.2$, $J_{5,4} = 4.0$)	3.30 (dd, $J_{6,1} = 4.3$)
4b^b	2.86 (dd)	4.86 (dd, $J_{2,3} = 7.0$, $J_{2,7\text{anti}} = 2.0$)	5.68 (dd, $J_{3,7\text{anti}} = 1.4$)	3.14 (dd)	3.03 (dd, $J_{5,6} = 12.0$, $J_{5,4} = 4.0$)	3.27 (dd, $J_{6,1} = 4.9$)
6a	3.07 (br.s)	4.33 (dd, $J_{2,3} = 6.5$, $J_{2,7\text{anti}} = 1.8$)	4.89 (dd, $J_{3,7\text{anti}} = 1.8$)	3.29 (dd, $J_{4,6} = 3.5$, $J_{4,7} = 1.7$)	6.28 (t, 2 H, $J = 1.9$)	2.36 (d, $J_{7,7} = 9.6$)
6b	3.15 (d, $J_{1,7} = 1.5$)	4.32 (dd, $J_{2,3} = 6.7$, $J_{2,7\text{anti}} = 2.1$)	4.87 (dd, $J_{3,7\text{anti}} = 1.5$)	3.28 (dd, $J_{4,6} = 3.4$, $J_{4,7} = 1.8$)	6.26 (t, 2 H, $J = 1.9$)	2.41 (d, $J_{7,7} = 9.5$)
7a^c	1.57 (td, $J_{1,2} = J_{1,6} = 5.1$, $J_{1,4} = 1.3$)	1.62 (tt, $J_{2,6} = 5.1$, $J_{2,3} = J_{2,4} = 1.2$)	4.60 (s)	2.21 (br.s)	4.00 (t, $J_{5,4} = J_{5,6} = 1.5$)	1.69 (tt, $J_{6,4} = 1.1$)
7b^d	1.54 (t, $J_{1,2} = J_{1,6} = 5.1$)	1.66 (tdd, $J_{2,6} = 5.2$, $J_{2,3} = 1.5$, $J_{2,4} = 0.9$)	4.60 (t, $J_{3,4} = 1.6$)	2.30 (m)	3.97 (t, $J_{5,4} = J_{5,6} = 1.6$)	1.66 (tdd, $J_{6,4} = 0.9$)
7c^e	1.61 (tt, $J_{1,2} = J_{1,6} = 5.1$)	1.70 (tt, $J_{2,6} = 5.5$, $J_{2,3} = J_{2,4} = 1.1$)	4.40 (br.s)	2.35 (br.s)	5.00 (t, $J_{5,4} \approx J_{5,6} = 1.6$)	1.77 (t)
8a^e	1.63—1.66 ^f (m)	1.63—1.66 ^f (m)	3.90 (d, $J = 1.5$)	2.28 (br.s)	3.90 (d, $J = 1.5$)	1.63—1.66 ^f (m)

(to be continued)

Table 2 (continued)

Com- pound	δ ($J_{\text{H,H}}/\text{Hz}$)							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	syn-H(7)	anti-H(7)
8b^d	1.68 ^g (br.s)	1.68 ^g (br.s)	3.95 (d, $J = 1.3$)	2.36 (br.s)	3.95 (d, $J = 1.3$)	1.68 ^g (br.s)	2.16 (m)	2.16 (m)
8c^e	1.64 ^h	1.70 ^h	4.05 (br.s)	2.45 (br.s)	4.80 (t, $J_{5,4} \approx J_{5,6} = 1.6$)	1.78 ^h	2.08 (d, $J_{7,7} = 11.5$)	1.91 (d)
9	3.21 (m)	3.76 (ddd, $J_{2,3\text{endo}} = 8.0$, $J_{2,3\text{exo}} = 4.0$, $J_{2,7} = 1.3$)	exo: 2.60 (dt, $J_{3,3} = 13.0$, $J_{3,4} = 4.0$) endo: 2.06 (dd)	3.00 (m)	6.20 (m)	6.20 (m)	4.10 (t, $J_{7,4} = 1.3$)	
18	2.58 (d, $J_{1,6\text{exo}} = 5.1$)	4.40 (dd, $J_{2,3} = 7.1$, $J_{2,7\text{anti}} = 1.9$)	5.42 (d)	3.06 (dd, $J_{4,5} = 4.0$, $J_{4,7} = 1.5$)	2.65 (dqdd, $J_{5,6\text{exo}} = 12.0$, $^2J_{5,\text{F}} = 10.1$, $J_{5,6\text{endo}} = 6.3$)	exo: 2.04 (ddd, $J_{6,6} = 14.2$, $J_{6,1} = 5.1$) endo: 1.45 (ddd, $J_{6,7\text{syn}} = 2.2$)	2.38 (br.d, $J_{7,7} = 11.6$)	1.55 (br.d)
19ⁱ	2.62 (d)	4.54 (dd, $J_{2,3} = 7.0$, $J_{2,7\text{anti}} = 2.0$)	5.08 (dd, $J_{3,7\text{anti}} = 1.1$)	3.48 (m)	4.86 (dt, $J_{5,6\text{exo}} = 11.0$, $J_{5,6\text{endo}} \approx J_{5,4} = 5.0$)	exo: 2.30 (ddd, $J_{6,6} = 15.0$, $J_{6,1} = 5.0$) endo: 2.11 (ddd, $J_{6,7\text{syn}} = 3.0$)	2.43 (br.d, $J_{7,7} = 11.4$)	1.63 (br.d)
20	2.74 (br.s)	4.85 (dd, $J_{2,3} = 6.9$, $J_{2,7\text{anti}} = 1.5$)	4.95 (dd, $J_{3,7\text{anti}} = 1.5$)	2.94 (d, $J_{4,5\text{exo}} = 4.8$)	exo: 2.00 (ddd, $J_{5,5} = 13.7$, $J_{5,6} = 12.0$) endo: 1.43 (ddd, $J_{5,6} = 5.1$, $J_{5,7\text{syn}} = 2.8$)	2.70 (m)	2.38 (dt, $J_{7,7} = 11.5$)	1.55 (d)
21ⁱ	2.98 (m)	4.48 (dd, $J_{2,3} = 7.0$, $J_{2,7\text{anti}} = 2.0$)	5.12 (dd, $J_{3,7\text{anti}} = 1.1$)	3.12 (d, $J_{4,5\text{exo}} = 5.0$)	endo, exo: 2.19–2.13 (m, 2 H)	4.94 (dt, $J_{6,5\text{exo}} = 9.5$, $J_{6,5\text{endo}} \approx J_{6,1} = 5.0$)	2.45 (br.d, $J_{7,7} = 11.4$)	1.67 (br.d)

^a Other signals: 3.62 and 3.71 (both s, 3 H each, CH₃O).^b Other signals: 3.61 and 3.70 (both s, 3 H each, CH₃O).^c In a mixture of isomers **7a** and **8a**.^d In a mixture of isomers **7b** and **8b**.^e In a mixture of isomers **7c** and **8c**.^f The signals overlap with the signals of compound **7a**.^g The signals overlap with the signals of compound **7b**.^h The signals overlap with the signals of compound **7c**.ⁱ In a mixture of isomers **19** and **21**.

Table 3. ^{13}C NMR spectra of the compounds synthesized (in CDCl_3)

Compound	δ ($J_{\text{C,F}}$ /Hz)						
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
3a	45.4	62.5	73.9	39.1	26.3	26.0	35.3
3b	46.1	54.0	73.6	39.7	27.1	26.4	35.8
4a^a	49.1	58.4	69.4	42.0	45.4	45.1	36.7
4b^b	49.5	49.7	68.9	42.5	46.0	45.2	37.3
6a	50.5	57.9	69.8	46.1	138.1	137.9	44.3
6b	51.1	49.0	69.5	46.4	138.4	137.5	44.8
7a^c	15.1	18.8	62.7	43.9	63.6	21.6	29.3
7b^d	15.6	19.4	53.7	44.0	54.3	22.2	29.2
7c^e	14.9	19.5	61.0	40.2	87.5	16.5	28.2
8a^c	15.1	22.0	60.7	43.9	60.7	22.0	27.6
8b^d	13.6	22.4	51.1	44.2	51.1	22.4	30.2
8c^e	14.9	21.8	59.5	40.5	83.7	17.4	27.7
12a^{f,g}	49.2	58.9	73.4	46.2	148.8	148.3	43.1
13a^{f,h}	52.5	59.7	71.7	46.7	144.6	144.4	46.2
13b^{f,i}	53.0	50.6	71.4	46.7	145.0	144.2	47.1
14a^{f,j}	49.8	83.6	31.4	45.7	—	—	65.67
15a^{f,k}	53.4	83.9	31.6	49.2	139.5	144.5	65.5
15b^{f,l}	51.0	55.5	36.5	45.1	142.9	143.5	56.4
18^m	45.9	61.5	68.2	40.6	42.1	27.1	36.8
			($J = 3.2$)	($J = 2.4$)	($J = 27$)	($J = 2.4$)	
19ⁿ	44.7	60.9	68.1	45.6	84.4	30.8	35.7 ^o
20^m	46.5	61.4	73.3	39.5	27.4	42.7	37.2
	($J = 3.1$)					($J = 29$)	
21ⁿ	50.6	56.6	72.5	39.6	31.2	83.1	36.4 ^o

^a 51.9, 52.2 (OCH_3); 170.9, 171.3 ($\text{C}=\text{O}$).^b 51.86, 52.2 (OCH_3); 170.9, 171.4 ($\text{C}=\text{O}$).^c In a mixture of isomers **7a** and **8a**.^d In a mixture of isomers **7b** and **8b**; the spectrum is consistent with the published data.²⁰^e In a mixture of isomers **7c** and **8c**.^f The atomic numbering scheme does not correspond to the IUPAC nomenclature and is presented in Scheme 3.^g 57.2, 57.6 (OCH_3); 113.8, 114.4, 133.7, 134.7 (C_{arom}) (in $\text{CDCl}_3 + \text{CF}_3\text{COOH}$).^h 122.2, 122.5, 127.4, 127.6 (C_{arom}).ⁱ 122.2, 122.5, 127.5, 127.7 (C_{arom}).^j 55.9, 56.0 (OCH_3), 110.55, 111.35 (C_{arom}).^k 121.9, 122.6, 127.5, 128.1 (C_{arom}).^l 121.3, 121.7, 127.2, 127.8 (C_{arom}).^m 127.2 (CF_3 , $J_{\text{C,F}} = 276$ Hz).ⁿ In a mixture of isomers **19** and **21**; the assignment of the chemical shifts was made using an additive scheme accounting for the α , β , and γ effects of the substituents.^{22,23}^o A precise assignment is absent.

from the X-ray diffraction data (Table 7) demonstrate that the $\text{CN}(\text{O})\text{—N}(\text{O})\text{C}$ fragment is planar. The C—N bond length in the dimer (1.480(3) Å) is similar to the C—N bond length in amines (1.47 Å), whereas the N—N bond (1.313(3) Å) is intermediate between single and double bonds. The N—O bond length is 1.263(2) Å. Therefore, the bond lengths and bond angles in the $\text{CN}(\text{O})\text{—N}(\text{O})\text{C}$ fragment are typical of diazene dioxides and agree well with the data for the *trans*-dimer of 2-chloro-2-methyl-3-nitrosobutane.²⁶ The C—Cl bond length (1.795(3) Å) is only slightly larger than the stan-

dard value (1.78 Å). A decrease in the $\text{C}(5)\text{—C}(8)$ bond length to 1.485(4) Å due to the influence of the electronegative substituents (F(1), F(2), and F(3)) has been observed earlier in 5-trifluoromethylnorbornane derivatives.²⁷

Compounds **19** and **21** were isolated and characterized as a mixture. Due to the difference in solubility of the isomers in CHCl_3 , the ^1H NMR spectrum of compound **19** as the main component of the mixture could be recorded. The signal for the proton H(1) of this isomer is observed at higher field (δ 2.62) than the signal for the

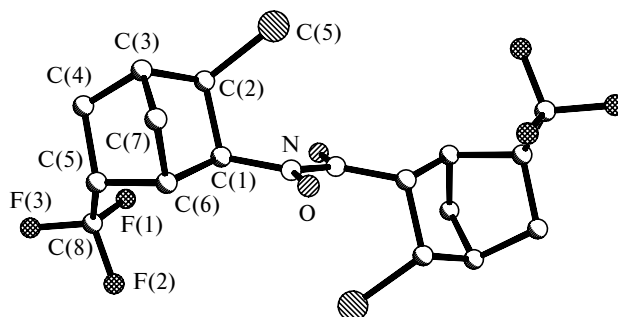
Table 4. Melting points, elemental analysis data, and IR spectra of the compounds synthesized

Compound	M.p./°C (solvent)	Found Calculated (%)			Molecular formula	IR, ν/cm ⁻¹
		C	H	N		
3a^a	156–158 (MeOH)	<u>52.61</u> 52.66	<u>6.46</u> 6.27	<u>8.78</u> 8.78	C ₇ H ₁₀ ClNO	1230
3b	122–123 (MeOH)	<u>41.11</u> 41.18	<u>4.93</u> 4.90	<u>6.80</u> 6.86	C ₇ H ₁₀ BrNO	1230
4a^b	167–168 (Et ₂ O)	<u>47.52</u> 47.91	<u>5.31</u> 5.08	—	C ₁₁ H ₁₄ ClNO ₅	1740 (C=O), 1280, 1250, 1200
4b	160 (MeOH)	<u>40.46</u> 41.25	<u>4.27</u> 4.38	<u>4.09</u> 4.38	C ₁₁ H ₁₄ BrNO ₅	1730 (C=O); 1290, 1280, 1210
6a	164–165 (MeOH)	<u>53.37</u> 53.33	<u>5.17</u> 5.08	<u>8.87</u> 8.89	C ₇ H ₈ ClNO	1250, 1220
6b	164 (MeOH)	<u>41.86</u> 41.58	<u>3.84</u> 3.96	<u>7.14</u> 6.93	C ₇ H ₈ BrNO	1250, 1220
7c + 8c	—	<u>44.70</u> 44.33	<u>4.42</u> 4.22	—	C ₇ H ₈ ClNO ₃	1640, 1285, 870 (ONO ₂)
12a^c	165–166 (Et ₂ O)	<u>57.88</u> 58.32	<u>5.23</u> 5.23	<u>5.13</u> 5.23	C ₁₃ H ₁₄ ClNO ₃	1250, 1220
13a	148–150 (MeOH)	<u>63.60</u> 63.61	<u>4.67</u> 4.85	<u>6.57</u> 6.74	C ₁₁ H ₁₀ ClNO	1280, 1270, 1255, 1215
13b	140–141 (MeOH)	<u>51.91</u> 52.38	<u>3.87</u> 3.97	<u>5.32</u> 5.56	C ₁₁ H ₁₀ BrNO	1280, 1265, 1260, 1225, 1210
14a	—	<u>52.49</u> 52.09	<u>4.35</u> 4.67	<u>4.69</u> 4.67	C ₁₃ H ₁₄ ClNO ₅	1640, 1270, 855 (ONO ₂), 1510
18 + 20	208–210 ^d (CHCl ₃)	<u>42.21</u> 42.20	<u>4.03</u> 3.96	<u>6.23</u> 6.15	C ₈ H ₉ ClF ₃ NO	1280, 1250, 1165 ^e
19 + 21	150 (CHCl ₃)	<u>40.97</u> 41.08	<u>4.36</u> 4.40	<u>13.50</u> 13.69	C ₇ H ₉ ClN ₂ O ₃	1550, 1380(NO ₂); 1235
23a	172–175 (MeOH)	<u>53.64</u> 53.59	<u>4.91</u> 5.10	<u>4.21</u> 4.47	C ₁₄ H ₁₆ ClNO ₅	1750 (C=O); 1220, 1180
23b	165 (MeOH)	<u>46.39</u> 46.93	<u>4.25</u> 4.47	<u>3.75</u> 3.91	C ₁₄ H ₁₆ BrNO ₅	1750 (C=O); 1220, 1180

^a Found (%): Cl, 21.75. C₇H₁₀ClNO. Calculated (%): Cl, 22.26.^b Found (%): Cl, 12.57. C₁₁H₁₄ClNO₅. Calculated (%): Cl, 12.89.^c Found (%): Cl, 13.18. C₁₃H₁₄ClNO₃. Calculated (%): Cl, 13.27.^d For isomer **18**.^e The IR spectrum of a mixture of isomers **18** and **20** is identical with that of individual compound **18**.**Table 5.** Calculated and experimental chemical shifts for the protons at the carbon atoms bearing substituents in nortricyclane chloro nitrates

Compound	δ			
	Calculated		Found	
	H(3)	H(5)	H(3)	H(5)
7c	4.45±0.03	4.77	4.40	5.00
7d	3.85	5.53±0.07	—	—
8c	3.85	4.77	4.05	4.80

proton H(4) of isomer **21** (δ 3.12) due to the weaker deshielding effect of the chlorine atom compared to the NO group. This also accounts for the smaller chemical

**Fig. 1.** Molecular structure of the dimer of *endo*-5-trifluoromethyl-*cis*-*exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane **18**.

shift of the proton H(1) of compound **21** (δ 2.98) compared to that of the proton H(4) of isomer **19** (δ 3.48).

Table 6. ^1H NMR spectra of compounds **12a**, **13a,b**, **14a**, and **15a,b** (in CDCl_3)

Com- pound	δ ($J_{\text{H,H}}/\text{Hz}$)					
	H(1)	H(2)	H(3)	H(4)	<i>syn</i> -H(7)	<i>anti</i> -H(7)
12a^{a,b}	3.74 ^c	4.42 (dd, $J_{2,3} = 6.7$, $J_{2,7\text{anti}} = 1.7$)	4.96 (dd, $J_{3,7\text{anti}} = 1.4$)	3.99 (d)	2.05 (dt, $J_{7,7} = 10.0$, $J_{7,1} = J_{7,4} = 1.6$)	2.58 (dt)
13a^{a,d}	3.52 (br.s)	4.43 (dd, $J_{2,3} = 6.4$, $J_{2,7\text{anti}} = 1.6$)	4.96 (br.d)	3.77 (br.s)	2.10 (dt, $J_{7,7} = 9.9$, $J_{7,1} \approx J_{7,4} = 1.5$)	2.62 (dt, $J_{7,3} = 1.0$)
13b^{a,e}	3.62 (s)	4.44 (dd, $J_{2,3} = 6.7$, $J_{2,7\text{anti}} = 1.7$)	4.96 (dd, $J_{3,2} = 6.7$)	3.76 (s)	2.15 (d, $J_{7,7} = 9.9$)	2.67 (dt, $J_{7,3} = 1.4$)
14a^{a,f}	3.96 (br.s)	4.92 (ddd, $J_{2,3\text{endo}} = 7.5$, $J_{2,3\text{exo}} = 3.5$, $J_{2,7\text{anti}} = 1.0$)	<i>exo</i> : 2.49 (dt, $J_{3,3} = 13.0$, $J_{3,4} = 3.5$) <i>endo</i> : 2.17 (dd, $J_{3,3} = 13.0$, $J_{3,2} = 7.5$)	3.71 (m)	4.09 (t, $J_{7,4} = 1.5$)	
15a^{a,g}	3.72 (br.s)	4.89 (ddd, $J_{2,3\text{endo}} = 7.5$, $J_{2,3\text{exo}} = 3.7$, $J_{2,7\text{anti}} = 1.0$)	<i>exo</i> : 2.50 (dt, $J_{3,3} = 13.5$, $J_{3,4} = 3.7$) <i>endo</i> : 2.12 (dd, $J_{3,3} = 13.5$, $J_{3,2} = 7.5$)	3.48 (m)	4.09 (t, $J_{7,4} = 1.5$)	
15b^{a,h}	3.72 (br.s)	3.77 (ddd, $J_{2,3\text{endo}} = 8.0$, $J_{2,3\text{exo}} = 4.0$, $J_{2,7} = 1.2$)	<i>exo</i> : 2.84 (dt, $J_{3,3} = 13.0$, $J_{3,4} = 4.0$) <i>endo</i> : 2.18 (dd)	3.48 (m)	4.11 (t, $J_{7,4} = 1.2$)	

^a The atomic numbering scheme does not correspond to the IUPAC nomenclature and is presented in Scheme 3.

^b Other signals: 3.74^c and 3.80 (both s, 3 H each, CH_3O); 6.65 (br.s, 2 H, H_{arom}).

^c The signals in the spectrum overlap.

^d Other signals: 7.15 and 7.24 (both m, 2 H each, H_{arom}).

^e Other signals: 7.15 and 7.23 (both m, 2 H each, H_{arom}).

^f Other signals: 3.79 and 3.82 (both s, 3 H each, CH_3O); 6.70 (d, 2 H, H_{arom} , $J = 2.0$ Hz).

^g Other signals: 7.15 and 7.20 (both m, 2 H each, H_{arom}).

^h Other signals: 7.20 and 7.28 (both m, 2 H each, H_{arom}).

Table 7. Selected interatomic distances (d) and bond angles (ω) in compound **18**

Bond	$d/\text{\AA}$	Angle	ω/deg
Cl—C(2)	1.795(3)	O—N—N	120.8(2)
F(1)—C(8)	1.338(3)	O—N—C(1)	122.95(17)
F(2)—C(8)	1.321(4)	N—N—C(1)	116.2(2)
F(3)—C(8)	1.340(3)	N—C(1)—C(6)	111.14(17)
O—N	1.263(2)	N—C(1)—C(2)	113.28(18)
N—N	1.313(3)	F(2)—C(8)—F(1)	106.1(3)
N—C(1)	1.480(3)	F(2)—C(8)—F(3)	106.6(3)
C(5)—C(8)	1.485(4)	F(1)—C(8)—F(3)	105.8(3)
		F(2)—C(8)—C(5)	112.6(3)
		F(1)—C(8)—C(5)	114.2(3)
		F(3)—C(8)—C(5)	111.0(3)

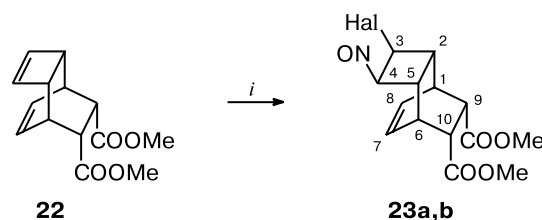
The above assignments suggest that product **19** has the structure of the dimer of *endo*-5-nitro-*cis*-*exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane, and compound **21** has the structure of the dimer of *endo*-6-nitro-*cis*-*exo*-2-chloro-3-nitrosobicyclo[2.2.1]heptane.

The fact that the reaction with 5-nitrobicyclo[2.2.1]hept-2-ene **17** is nonregioselective can be accounted for by the dual influence of the nitro group. On the one hand, due to high electronegativity of the substituent, the electrophilic addition gives rise to a cation in which the positive charge on the carbon atom is at the maximum distance from this electron-withdrawing substituent.²⁸ On the other hand, the nitro group can be

involved in stabilization of the resulting carbocation.²⁹ However, the fact that the reaction with 5-trifluoromethyl-substituted compound **16** produced two isomeric nitroso chlorides in a ratio of 1 : 1 was unexpected.

We believe that high stereospecificity and the absence of regioselectivity of the reactions with 5-substituted norbornenes either confirm the assumption that NOCl adds to alkenes of the bicyclo[2.2.1]heptene series by cyclic electron transfer in a four-center transition state⁷ or are a consequence of the fact that nitrosation, contrary to typical electrophilic addition reactions, proceeds *via* a π complex rather than *via* a σ intermediate.³⁰

Nitrosahalogenation of diester **22**, which is highly prone to transannular cross-cyclizations,³¹ also afforded exclusively *cis*-*exo*-addition products to the double bond of the cyclobutane ring (Scheme 6).

Scheme 6

Hal = Cl (**a**), Br (**b**)

i. EtONO, PCl_3 (SOCl_2 or PBr_3).

The structures of the reaction products were established by ^1H and ^{13}C NMR spectroscopy (Tables 8 and 9). Analysis of the spectra and subsequent structural assignments were made taking into account the data on the influence of substituents on the chemical shifts, the ^1H – ^1H coupling constants, and the results of homo-nuclear selective double resonance and NOE experiments.

The presence of signals for olefinic protons in the ^1H NMR spectra of nitroso halides **23a,b** indicates that the reaction is not accompanied by a rearrangement. The signals for the protons in nitroso chloride **23a** were assigned with the use of NOE experiments. For example, irradiation at the frequency of the signal for the proton HC(4)N led to a change in the integral intensity of the signals for the protons of the double bond (2.6%) and the proton HC(3)Cl (9.1%). At the same time, irradiation of the proton HC(3)Cl gave NOE on the protons of the double bond (2.2%) and the proton HC(4)N (8.0%). This is evidence for the *cis*-di-*exo* arrangement of the substituents. In addition, irradiation at a frequency of the signal of HC(4)N gave a signal at δ 3.12 (0.9%). Hence, this signal was assigned to the proton H(6).

To determine coupling constants in the spectrum of product **23a**, we carried out additional NMR experiments using the H–{ ^1H } double resonance method. Spin-spin decoupling from the proton H(5) revealed the coupling constants of this proton with the proton HC(4)N ($J = 5.1$ Hz), the proton H(2) ($J = 10.0$ Hz), and the proton H(6) ($J \approx 3.0$ Hz). Spin-spin decoupling from the

proton H(2) revealed the coupling constants of the proton H(2) with the proton HC(3)Cl ($J = 3.9$ Hz), the proton H(5) ($J = 10.0$ Hz), and the proton H(1) ($J = 3.9$ Hz).

The assignment of the signals for the protons of nitroso bromide **23b** was made taking into account the results obtained for product **23a**. The following constants were revealed for structure **23b** using the double resonance method: $^3J_{4,5} = 5.4$ Hz, $^3J_{5,2} = 10.0$ Hz, $^3J_{5,6} = 3.0$ Hz, and $^3J_{3,2} = 3.8$ Hz. The constant $J_{2,1}$ was also detected, but its precise value could not be determined.

Spin-spin decoupling from the proton H(2) in nitroso halides **23** simplifies the triplet-like signal for HC(4)N to a doublet of doublets, which is indicative of the presence of a W coupling constant ($^4J_{2,4} \leq 1$ Hz).

The set of the coupling constants $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ for compounds **23a** and **23b** is characteristic of *cis*-*exo* derivatives of tricyclo[4.2.2.0^{2,5}]dec-7-ene.^{32,33} Hence, we assigned the structures *cis*-endo-9,10-di(methoxycarbonyl)-*cis*-exo-3-chloro-4-nitrosotricyclo[4.2.2.0^{2,5}]dec-7-ene and *cis*-endo-9,10-di(methoxycarbonyl)-*cis*-exo-3-bromo-4-nitrosotricyclo[4.2.2.0^{2,5}]dec-7-ene to compounds **23a** and **23b**, respectively.

To summarize, nitrosohalogenation of olefins of the norbornene and norbornadiene series and dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-*cis*-endo-dicarboxylate was studied using EtONO–Phal₃, EtONO–POHal₃ (Hal = Cl or Br), and EtONO–SOCl₂ systems. Nitroso halides NOHal that were generated in these systems were demonstrated to serve as nitrosating agents. Nitrosation

Table 8. ^1H NMR spectra of compounds **23a,b** in CDCl_3 containing 10% of trifluoroacetic acid

Compound	δ ($J_{\text{H,H}}/\text{Hz}$)					
	H(1), m	H(2)	H(3), dd	H(4), ddd	H(5), ddd	H(6), m
23a ^a	3.26	2.75 (dt, $J_{2,5} = 10.0$, $J_{2,1} = 3.9$)	4.22 ($J_{3,4} = 7.4$, $J_{3,2} = 3.9$)	5.10 ^b ($J_{4,5} = 5.1$, $J_{4,2} \approx 1.0$)	3.57 ($J_{5,2} = 10.0$, $J_{5,6} \approx 3.0$)	3.12
23b ^c	3.28	2.90 (dm, $J_{2,5} = 10.0$)	4.30 ($J_{3,4} = 7.8$, $J_{3,2} = 3.8$)	5.15 ^d ($J_{4,5} = 5.4$, $J_{4,2} \approx 1.0$)	3.56 ($J_{5,2} = 10.0$, $J_{5,6} \approx 3.0$)	3.12

^a Other signals: 3.00 (dd, H(10), $J_{10,9} = 11.0$ Hz, $J_{10,6} = 1.6$ Hz); 3.05 (d, H(9), $J_{9,10} = 11.0$ Hz); 3.66 and 3.67 (both s, 3 H each, OCH_3); 6.55 (t, 2 H, H(7), H(8), $J = 3.4$ Hz).

^b As follows from the experiments with the use of the double resonance method. The signal in the ^1H NMR spectrum appears as a triplet with the coupling constant $J = 6.1$ Hz.

^c Other signals: 3.00 (dd, H(10), $J_{10,9} = 10.5$ Hz, $J_{10,6} = 1.7$ Hz); 3.04 (dd, H(9), $J_{9,10} = 10.5$ Hz, $J_{9,1} = 1.4$ Hz); 3.66 and 3.67 (both s, 3 H each, OCH_3); 6.55 (t, 2 H, H(7), H(8), $J = 4.0$ Hz).

^d As follows from experiments with the use of the double resonance method. The signal in the ^1H NMR spectrum appears as a triplet with the coupling constant $J = 6.4$ Hz.

Table 9. ^{13}C NMR spectra of compounds **23a,b** (in CDCl_3 with an admixture of CF_3COOH)

Compound	δ									
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7), C(8)	C(9), C(10)	C=O	OCH_3
23a	34.4	47.4	53.2	69.0	37.1	35.2	133.6, 133.0	46.3, 46.1	176.4	53.6
23b	34.5	47.6	41.9	68.9	37.7	35.5	133.5, 132.9	46.2, 46.0	176.3	53.5

of alkenes with ethyl nitrite in the presence of phosphorus(III) halides, phosphorus(V) oxohalides, or thionyl chloride is a convenient procedure for the synthesis of 1,2-nitrosyl halides, because the reactions proceed rather selectively without the formation of ketones and oximes as by-products.

Experimental

The ^1H and ^{13}C 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 Me_4Si as the internal standard. The IR spectra were measured on UR-20 (in thin films or Nujol mulls) and Specord 75 IR (in Nujol mulls) instruments. The melting points were determined in open capillary tubes on a heating block and are uncorrected.

The solvents were purified according to standard procedures.¹⁴ Ethyl nitrite was synthesized according to a known procedure.³⁴

Nitrosation of olefins with ethyl nitrite in the presence of phosphorus(III) halides, phosphorus(V) oxohalides, and thionyl chloride (general procedure). A solution of phosphorus(III) halide, thionyl chloride, or phosphorus(V) oxochloride in anhydrous CH_2Cl_2 (or CHCl_3) (olefin : $\text{P}(\text{OR})_3$ (or SOCl_2) = 2 : 1, and olefin : $\text{PO}(\text{OR})_3$ = 1 : 1) was slowly added dropwise with stirring to a solution of an olefin and ethyl nitrite (the olefin : ethyl nitrite molar ratio \approx 1 : 3) in the same solvent at -30 °C under dry argon. The reaction mixture was stirred at this temperature for 0.5 h, after which the mixture was slowly warmed to room temperature (in the reactions with the use of $\text{PO}(\text{OR})_3$, the temperature was raised to 0 °C, and the mixture was stirred at this temperature for 48 h). The solvent was distilled off, and the product was purified by recrystallization from ethanol. The crystals were filtered off. The mother liquor was concentrated, and the residue was separated by preparative TLC on Silufol plates.

The yields of the reaction products are given in Table 1. The physicochemical characteristics of the products are listed in Tables 2–4 and 6–9.

The reactions of norbornene **1** with $\text{EtONO}-\text{PCl}_3$ (SOCl_2 or POCl_3) and $\text{EtONO}-\text{PBr}_3$ (or POBr_3) (see Table 1) gave *cis-exo-2-chloro-3-nitrosobicyclo[2.2.1]heptane* (**3a**) and *cis-exo-2-bromo-3-nitrosobicyclo[2.2.1]heptane* (**3b**), respectively.

The reactions of norbornene **2** with $\text{EtONO}-\text{PCl}_3$ (or SOCl_2) and $\text{EtONO}-\text{PBr}_3$ (or POBr_3) produced *cis-endo-5,6-di(methoxycarbonyl)-cis-exo-2-chloro-3-nitrosobicyclo[2.2.1]heptane* (**4a**) and *cis-endo-5,6-di(methoxycarbonyl)-cis-exo-2-bromo-3-nitrosobicyclo[2.2.1]heptane* (**4b**), respectively.

Reaction of norbornadiene (5) with ethyl nitrite in the presence of PCl_3 . The product prepared by the reaction of norbornadiene (0.70 g, 7.6 mmol) with ethyl nitrite (1.85 g, 24.7 mmol) in CHCl_3 (30 mL) and PCl_3 (0.525 g, 3.8 mmol) in CHCl_3 (15 mL) was recrystallized from MeOH and *cis-exo-2-chloro-3-nitrosobicyclo[2.2.1]hept-5-ene* (**6a**) was obtained in a yield of 0.81 g as white crystals. Preparative TLC (light petroleum—EtOAc, 10 : 1) of the mother liquor afforded a mixture of *exo-3-endo-5-dichlorotricyclo[2.2.1.0^{2,6}]heptane* (**7a**) and *exo-3-exo-5-dichlorotricyclo[2.2.1.0^{2,6}]heptane* (**8a**) (R_f 0.90) in a yield of 0.05 g (4%) as a transparent oil, **7a** : **8a** = 2.7 : 1

(determined from the intensity ratio of the signals in the ^1H NMR spectrum of the mixture; these data are consistent with the published data^{16,17}); b) a mixture of *exo-3-chloro-endo-5-nitrosotricyclo[2.2.1.0^{2,6}]heptane* (**7c**) and *exo-3-chloro-exo-5-nitrosotricyclo[2.2.1.0^{2,6}]heptane* (**8c**) (R_f 0.85) in a yield of 0.05 g (3.5%) as a transparent oil, **7c** : **8c** = 4 : 1 (^1H NMR).

Reaction of norbornadiene (5) with ethyl nitrite in the presence of PBr_3 . The product prepared by the reaction of norbornadiene (0.60 g, 6.5 mmol) with ethyl nitrite (1.5 g, 20 mmol) in CHCl_3 (30 mL) and PBr_3 (0.88 g, 3.25 mmol) in CHCl_3 (15 mL) was recrystallized from MeOH and *cis-exo-2-bromo-3-nitrosobicyclo[2.2.1]hept-5-ene* (**6b**) was obtained in a yield of 0.79 g as white crystals. Preparative TLC (light petroleum—EtOAc, 3 : 1) of the mother liquor afforded a) a mixture of *endo-5-exo-3-dibromotricyclo[2.2.1.0^{2,6}]heptane* (**7b**) and *exo-5-exo-3-dibromotricyclo[2.2.1.0^{2,6}]heptane* (**8b**) in a yield of 0.12 g (7.3%) (R_f 0.72) as a pale-yellow oil, **7b** : **8b** = 3 : 1 (^1H NMR, these data are consistent with the published data²⁰); b) *exo-5-bromo-syn-7-bromobicyclo[2.2.1]hept-2-ene* (**9**) (R_f 0.67) in a yield of 0.025 g (1.5%) as a pale-yellow oil.

Reaction of 3,6-dimethoxybenzonorbornadiene (10) with ethyl nitrite in the presence of PCl_3 . The product prepared by the reaction of 3,6-dimethoxybenzonorbornadiene (0.31 g, 1.5 mmol) with ethyl nitrite (0.40 g, 5.3 mmol) in CHCl_3 (25 mL) and PCl_3 (0.105 g, 0.76 mmol) in CHCl_3 (15 mL) was recrystallized from MeOH and *3,6-dimethoxy-cis-exo-10-chloro-9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene* (**12a**) was obtained in a yield of 0.28 g as white crystals. Preparative TLC (light petroleum—EtOAc, 3 : 1) of the mother liquor afforded *3,6-dimethoxy-exo-syn-11-chloro-9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene* (**14a**) (R_f 0.65) in a yield of 0.02 g (4.3%) as a transparent crystallizable oil.

Reaction of benzonorbornadiene (11) with ethyl nitrite in the presence of PCl_3 . The product prepared by the reaction of benzonorbornadiene **11** (0.66 g, 4.6 mmol) with ethyl nitrite (1.20 g, 16.0 mmol) in CHCl_3 (25 mL) and PCl_3 (0.32 g, 2.3 mmol) in CHCl_3 (20 mL) was recrystallized from MeOH and *cis-exo-10-chloro-9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene* (**13a**) was obtained in a yield of 0.67 g as white crystals. Preparative TLC (light petroleum—EtOAc, 3 : 1) of the mother liquor afforded *exo-syn-11-chloro-9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene* (**15a**) (R_f 0.57) in a yield of 0.06 g (5.4%) as a pale-yellow oil.

Reaction of benzonorbornadiene (11) with ethyl nitrite in the presence of PBr_3 . The product prepared by the reaction of benzonorbornadiene **11** (0.525 g, 3.7 mmol) with ethyl nitrite (1.20 g, 16 mmol) in CHCl_3 (25 mL) and PBr_3 (0.5 g, 1.85 mmol) in CHCl_3 (20 mL) was recrystallized from MeOH and *cis-exo-10-bromo-9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene* (**13b**) was obtained in a yield of 0.57 g as white crystals. Preparative TLC (light petroleum—EtOAc, 3 : 1) of the mother liquor afforded *exo-9-bromo-syn-11-bromotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene* (**15b**) (R_f 0.71) in a yield of 0.142 g (13%) as a pale-yellow oil (the results are consistent with the published data¹⁸).

Using the above-described general procedure, *endo-5-trifluoromethyl-cis-exo-2-chloro-3-nitrosobicyclo[2.2.1]heptane* (**18**) and *endo-6-trifluoromethyl-cis-exo-2-chloro-3-nitrosobicyclo[2.2.1]heptane* (**20**) were prepared from compound **16**, *endo-5-nitro-cis-exo-2-chloro-3-nitrosobicyclo[2.2.1]heptane* (**19**) and *endo-6-nitro-cis-exo-2-chloro-3-nitrosobicy-*

clo[2.2.1]heptane (**21**) were prepared from compound **17**, and *cis-endo-9,10-di(methoxycarbonyl)-cis-exo-3-chloro-4-nitrosotricyclo[4.2.2.0^{2,5}]dec-7-ene* (**23a**) and *cis-endo-9,10-di(methoxycarbonyl)-cis-exo-3-bromo-4-nitrosotricyclo[4.2.2.0^{2,5}]dec-7-ene* (**23b**) were prepared from compound **22**.

X-ray diffraction study of compound 18. Crystals suitable for X-ray diffraction study were grown as colorless prisms of dimensions 0.50×0.35×0.25 mm by slow evaporation of a solution in chloroform. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer (Mo-K α 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.³⁵ The atomic coordinates for the structure of **18** 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 7. Principal crystallographic data, details of X-ray data collection, and characteristics of structure refinement are listed in Table 10.

Table 10. Crystallographic data, details of X-ray data collection, and characteristics of structure refinement of compound **18**

Parameter	Characteristic
Molecular formula	C ₈ H ₉ ClF ₃ NO
Molecular weight	227.61
Crystal system	Monoclinic
Space group	$P2_1/c$
T/K	293(2)
$\lambda/\text{\AA}$	0.71073
$a/\text{\AA}$	6.572(10)
$b/\text{\AA}$	11.574(2)
$c/\text{\AA}$	12.726(3)
α/deg	90
β/deg	98.47(3)
γ/deg	90
$V/\text{\AA}^3$	957.4(3)
Z	4
$d_{\text{calc}}/\text{g cm}^{-3}$	1.579
μ/mm^{-1}	0.410
$F(000)$	464
Scan range, θ/deg	3.13–24.95
Scanning mode	$\theta/2\theta$
Ranges of indices	$-7 \leq h \leq 0$, $-13 \leq k \leq 0$, $-14 \leq l \leq 14$
Number of measured reflections	1138
Number of reflections with $I > 2\sigma(I)$	1040
R_{int}	0.0142
Number of parameters in refinement	164
GOOF on F^2	1.058
R_1/wR_2 ($I > 2\sigma(I)$)	0.0276/0.0689
R_1/wR_2 (based on all reflections)	0.0276/0.0689
Extinction coefficient	0.0045(15)
Residual electron density, max/min, e \AA^{-3}	0.150/–0.150

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