ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 4, pp. 564–570. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © O.B. Bondarenko, A.Yu. Gavrilova, M.A. Kazantseva, V.N. Tikhanushkina, E.E. Nifant'ev, L.G. Saginova, N.V. Zyk, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 4, pp. 566–572.

4,5-Dihydroisoxazoles from Arylcyclopropanes: II.* Reaction of Arylcyclopropanes with Nitrosyl Chloride Activated by Sulfur(VI) Oxide

O. B. Bondarenko[a], A. Yu. Gavrilova[a], M. A. Kazantseva[a], V. N. Tikhanushkina[b], E. E. Nifant'ev[b], L. G. Saginova[a], and N. V. Zyk[a]

[a] *Faculty of Chemistry, Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia*
e-mail: bondarenko@org.chem.msu.ru

[b] *Moscow State Pedagogical University, Moscow, Russia*

Received November 23, 2005

Abstract—Arylcyclopropanes react with nitrosyl chloride activated by sulfur(VI) oxide to give the corresponding 5-aryl-4,5-dihydro-1,2-oxazoles in quantitative yields. The complex $NOCl \cdot 2SO_3$ is a highly efficient nitrosating agent which makes it possible to involve in the process arylcyclopropanes having both donor and acceptor substituents in the aromatic ring.

DOI: 10.1134/S1070428007040136

Dihydroisoxazoles are convenient synthons for the preparation of acyclic difunctional compounds. The use in reactions with dihydroisoxazoles of new reagents, specifically complex organometallic systems, led to the discovery of novel transformation pathways and gave rise to a new turn in the development of dihydroisoxazole chemistry [2]. However, as before, classical ways of dihydroisoxazole ring opening attract researchers' interest, especially those related to the transformation of dihydroisoxazoles having no substituent on C^3 into hydroxy nitriles [3]. Search for new methods of building up C^3-unsubstituted 4,5-dihydroisoxazoles remains an important problem.

In the preceding communication we reported on the transformations of arylcyclopropanes by the action of nitrosyl chloride activated by sulfur(VI) oxide, which lead to the formation of the corresponding 5-aryl-4,5-dihydroisoxazoles [1]. The reaction is electrophilic, and the best results were obtained with substrates having electron-donor substituents in the aromatic ring. Electron-acceptor substituents deactivate the three-membered ring almost completely.

To continue studies in this line, we examined the behavior of some arylcyclopropanes in the reaction with $NOCl \cdot 2SO_3$ and found that the latter is more effective nitrosating agent [4]. The reactions were carried out with arylcyclopropanes having various substituents in the aromatic ring. Specific attention was given to the substrates possessing electron-acceptor groups.

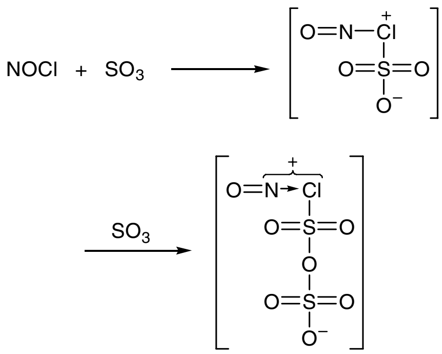
Nitrosyl chloride was shown in [5] to form 1:1 and 1:2 complexes with sulfur trioxide. The 1:2 complex $NOCl \cdot 2SO_3$ was studied by conductometry and IR spectroscopy. However, no definite IR data of $NOCl \cdot 2SO_3$ were reported. The authors only noted that the adduct may be assigned the structure of pyrochlorosulfuric acid salt $NO^+S_2O_6Cl^-$ on the basis of the spectral and conductometric data.

We performed spectral and elemental analyses of the complex. Its elemental composition corresponded to the formula $NOCl \cdot 2SO_3$ [4]. In the IR spectrum we observed several poorly resolved bands in the region 1350–1150 cm^{-1}, which are likely to belong to the pyrosulfate ion. In addition, an absorption band at 1810 cm^{-1} was present, which may be assigned to NOCl.

Taking into account the above data, we cannot assure that the reaction of NOCl with sulfur trioxide involves insertion of the latter into the N–Cl bond. On the other hand, it is possible that SO_3 coordinates the chlorine atom, thus inducing strong polarization of the N–Cl bond (Scheme 1); as a result, the chemical properties of the adduct resemble those of nitrosonium salts.

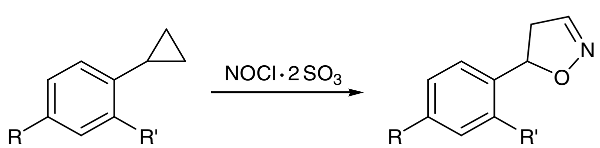
* For preceding communication, see [1].

Scheme 1.



We examined reactions of the complex $NOCl \cdot 2SO_3$ with arylcyclopropanes **Ia**–**In** at 0°C and isolated the corresponding dihydroisoxazoles **IIa**–**IIn** (Scheme 2, Table 1). The product structure was confirmed by the NMR spectra (Table 2). The elemental compositions of the newly synthesized compounds were dertemined by elemental analysis or mass spectrometry. Substrates **Ia**–**If** having electron-donor substituents in the aromatic ring gave rise to dihydrooxazoles **IIa**–**IIf** in nearly quantitative yields, the initial reactant ratio being equimolar. To ensure 100% conversion of arylcyclopropanes with electron-withdrawing groups in the aromatic ring, prolonged reaction time, increased amount of the reagent with respect to the substrate, or elevated temperature was necessary (Table 1). Although the substituent effect is compensated to a considerable extent by the high activity of the reagent, we can speak about electrophilic character of the process, as in the reaction with NOCl activated by sulfur(IV) oxide. Thus nitro- and dinitro-substituted phenylcyclopropanes turned out to be much less reactive. Among dinitro derivatives, only 2,4-dinitrophenylcyclopropane (**In**) reacted with $NOCl \cdot 2SO_3$, while its 2,6-dinitro isomer was recovered from the reaction mixture (the reaction was carried out with a mixture of 2,4- and 2,6-dinitrophenylcyclopropanes at a ratio of 3 : 1). Presumably, in this case steric factor is important in addition to the electronic effect of substituents.

Scheme 2.



Ia–In **IIa–IIn**

R' = R = H (**a**), R' = H, R = MeO (**b**), Me (**c**), Br (**d**), I (**e**), CN (**g**), MeCO (**h**), Ts (**i**), O_2N (**k**); R = H, R' = I (**f**), $PhCH_2SO_2$ (**j**), O_2N (**l**); R' = O_2N, R = Br (**m**), O_2N (**n**).

Table 1. Nitrosation of arylcyclopropanes **Ia**–**In** with the complex $NOCl \cdot 2SO_3$ in CH_2Cl_2 at 0°C

Comp. no.	Time, h	Yield, %		
		II	**III**	**IV**
Ia[a]	1	95	–	–
Ic	2	80	9	4
Id[a]	1	99	–	–
Ie[a]	1	99	–	–
If	1	96	3	–
Ig[b]	1	50	5	4
Ih[b]	5	78	–	–
Ii	1	91	–	–
Ij	1	65	–	–
Ik[c]	1	80[d]	15[e]	–
Il[f]	1	87[g]	10[h]	–
Im[i]	2	70	14	–
In[i]	4	11[j, k]	6[k]	–
In[l]	2	25[k]	50[k]	–

[a] Data of [4].
[b] 3 equiv of $NOCl \cdot 2SO_3$; 100% conversion of the substrate.
[c] A mixture of isomers **Ik** and **Il** (85 : 15).
[d] A mixture of isomers **IIk** and **IIl** (7 : 1).
[e] A mixture of isomers **IIIk** and **IIIl** (3 : 1).
[f] A mixture of isomers **Ik** and **Il** (15 : 85).
[g] A mixture of isomers **IIk** and **IIl** (1 : 5).
[h] Aldehyde **IIIl**.
[i] 2.5 equiv of $NOCl \cdot 2SO_3$.
[j] 80% of compound **In** was recovered, 2,4/2,6 ratio 2 : 1.
[k] Calculated on 2,4-dinitrophenylcyclopropane.
[l] Temperature 0–20°C.

Using the reactions of $NOCl \cdot 2SO_3$ with 4- and 2-nitrophenylcyclopropanes **Ik** and **Il** as examples we succeeded in estimating the effect of *ortho* substitution on the reactivity of the three-membered ring. When a 1 : 1 mixture of isomers **Ik** and **Il** was kept for 1 h with the complex $NOCl \cdot 2SO_3$ under standard conditions, the reaction mixture contained 35% of dihydroisoxazole **IIk**, 17% of **IIl**, 5% of cinnamaldehyde **IIIk**, 3% of **IIIl**, 15% of initial cyclopropane **Ik**, and 25% of **Il**. The product ratio was calculated from the intensities of the corresponding signals in the ^1H NMR spectrum. These data indicate that 4-nitrophenylcyclopropane (**Ik**) is twice as reactive as its 2-nitro isomer **Il**. An analogous pattern was observed in the reactions of 4- and 2-iodophenylcyclopropanes **Ie** and **If** with nitrosyl chloride in sulfur dioxide [1]. Despite formation of a considerable amount of products resulting from opening of the small ring, the lower reactivity of 2-iodophenylcyclopropane in this process is obvious.

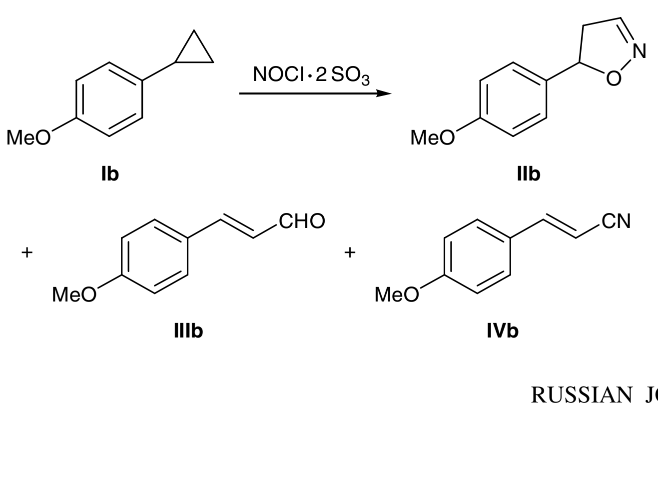
Table 2. ^{1}H NMR spectra of 5-aryl-4,5-dihydroisoxazoles **IIa–IIf** and **IIk–IIn**[a] in $CDCl_3$

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)				
	3-H	4α-H	4β-H	5-H	aromatic and other protons
IIa	7.18 t (^3J = 1.9)	3.42 d.d.d (^2J = 17.6, ^3J = 11.3, 1.9)	2.96 d.d.d (^2J = 17.6, ^3J = 7.9, 1.9)	5.51 d.d (^3J = 11.3, 7.9)	7.34 m (5H)
IIb	7.18 br.s	3.35 d.d.d (^2J = 7.6, ^3J = 11.1, 1.2)	2.93 d.d.d (^2J = 17.6, ^3J = 8.5, 1.6)	5.45 d.d (^3J = 11.1, 8.5)	6.87 d (2H, ^3J = 8.7), 7.23 d (2H, ^3J = 8.7), 3.78 s (3H, OCH_3)
IIc	7.17 t (^3J = 1.7)	3.37 d.d.d (^2J = 17.5, ^3J = 11.1, 1.7)	2.93 d.d.d (^2J = 17.5, ^3J = 8.2, 1.7)	5.46 d.d (^3J = 11.1, 8.2)	7.14 d (2H, ^3J = 8.2), 7.19 d (2H, ^3J = 8.2), 2.32 s (3H, CH_3)
IId	7.16 br.s	3.40 d.d.d (^2J = 17.5, ^3J = 11.2, 1.6)	2.90 d.d.d (^2J = 17.5, ^3J = 7.8, 1.6)	5.45 d.d (^3J = 11.2, 7.8)	7.17 d (2H, ^3J = 8.2), 7.46 d (2H, ^3J = 8.2)
IIe	7.17 t (^3J = 1.8)	3.41 d.d.d (^2J = 17.7, ^3J = 11.1, 1.8)	2.90 d.d.d (^2J = 17.7, ^3J = 7.8, 1.8)	5.45 d.d (^3J = 11.1, 7.8)	7.04 d (2H, ^3J = 8.3), 7.67 d (2H, ^3J = 8.3)
IIf	7.12 br.s	3.60 d.d.d (^2J = 17.7, ^3J = 11.4, 1.5)	2.76 d.d.d (^2J = 17.7, ^3J = 6.7, 1.6)	5.62 d.d (^3J = 11.4, 6.7)	6.97 t.d (1H, 4'-H, ^4J = 1.6, ^3J = 7.4), 7.33 t.t (1H, 5'-H, ^3J = 7.4, ^4J = 0.9), 7.38 d.d (1H, 6'-H, ^4J = 1.6, ^3J = 7.4), 7.80 d.d (1H, 3'-H, ^3J = 7.4, ^4J = 0.9)
IIk	7.24 br.s	3.56 d.d.d (^2J = 17.6, ^3J = 11.3, 1.6)	2.97 d.d.d (^2J = 17.6, ^3J = 7.3, 1.8)	5.64 d.d (^3J = 11.3, 7.3)	7.50 d (2H, ^3J = 8.8), 8.20 d (2H, ^3J = 8.8)
IIl	7.18 t (^3J = 1.7)	3.78 d.d.d (^2J = 18.2, ^3J = 11.5, 1.7)	2.88 d.d.d (^2J = 18.2, ^3J = 6.6, 1.7)	6.11 d.d (^3J = 11.5, 6.6)	7.48 t.d (1H, 4'-H, ^3J = 7.3, ^4J = 1.5), 7.68 t.d (1H, 5'-H, ^3J = 7.3, ^4J = 1.1), 7.75 d.d (1H, 6'-H, ^3J = 7.3, ^4J = 1.5), 8.11 d.d (1H, 3'-H, ^3J = 7.3, ^4J = 1.1)
IIm	7.19 t (^3J = 1.9)	3.77 d.d.d (^2J = 18.2, ^3J = 11.3, 1.9)	2.86 d.d.d (^2J = 18.2, ^3J = 6.4, 1.9)	6.04 d.d (^3J = 11.3, 6.4)	7.62 d (1H, 6'-H, ^3J = 8.5), 7.79 d.d (1H, 5'-H, ^3J = 8.5, ^4J = 1.9), 8.26 d (1H, 3'-H, ^4J = 1.9)
IIn	7.26 t (^3J = 1.7)	3.89 d.d.d (^2J = 18.3, ^3J = 11.4, 1.7)	2.95 d.d.d (^2J = 18.3, ^3J = 6.4, 1.7)	6.21 d.d (^3J = 11.4, 6.4)	8.04 d (1H, 6'-H, ^3J = 8.5), 8.54 d.d (1H, 5'-H, ^3J = 8.5, ^4J = 2.4), 9.01 d (1H, 3'-H, ^3J = 2.4)

[a] The ^{1}H NMR spectra of **IIg–IIj** were reported in [1, 4].

It should be noted that the reactions of arylcyclopropanes with $NOCl\cdot 2SO_3$ are generally characterized by high selectivity, i.e., no by-products are formed. The formation of a small amount of the corresponding substituted cinnamaldehyde **III** was observed only in reactions of a few substrates, mainly those having a substituent in the *ortho* position with respect to the small ring. Tables 3 and 4 contain spectral parameters of the isolated by-products. Anomalous results were also obtained in the reaction with 4-methoxyphenylcyclopropane (**Ib**). Its nitrosation with $NOCl\cdot 2SO_3$ led to the formation of appreciable amounts of 4-methoxycinnamaldehyde (**IIIb**) and 4-methoxycinnamonitrile (**IVb**) in addition to dihydroisoxazole **IIb** (Scheme 3), and the product ratio strongly depended on the reaction time and temperature (Table 5).** Under the standard conditions (0°C, 2 h) the yield of **IIb** was 42%, and the yields of **IIIb** and **IVb** were 11 and 41%, respectively. We succeeded in raising the

Scheme 3.



** Small amounts of aldehydes and nitriles **IIIc/IVc**, **IIIg/IVg**, and **IIId/IVd** were formed in the reactions of cyclopropanes **Ic** and **Ig** with $NOCl\cdot SO_2$ [1] and $NOCl\cdot 2SO_3$ (Tables 1, 3, 4) and during chromatographic isolation of dihydroisoxazole **Id**, respectively.

Table 3. ^{1}H NMR spectra of 3-arylprop-2-enals **III** and 3-arylprop-2-enenitriles **IV** in $CDCl_3$

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)			
	CHO	=C**H**CHO	ArC**H**=	aromatic and other protons
IIIb	9.64 d (^3J = 7.7)	6.60 d.d (^3J = 7.7, 16.0)	7.41 d (^3J = 16.0)	6.92 d (2H, ^3J = 8.9), 7.51 d (2H, ^3J = 8.9), 3.80 s (3H, CH_3O)
IIIc	9.66 d (^3J = 7.6)	6.67 d.d (^3J = 7.6, 16.0)	7.43 d (^3J = 16.0)	7.22 d (2H, ^3J = 8.0), 7.45 d (2H, ^3J = 8.0), 2.38 s (3H, CH_3)
IIId	9.70 d (^3J = 7.6)	6.68 d.d (^3J = 7.6, 16.2)	7.40 d (^3J = 16.2)	7.41 d (2H, ^3J = 8.4), 7.56 d (2H, ^3J = 8.4)
IIIf	9.75 d (^3J = 7.9)	6.59 d.d (^3J = 7.9, 15.8)	7.72 d (^3J = 15.8)	7.09 t.d (1H, 4'-H, ^3J = 7.8, ^4J = 1.6), 7.39 t.t (1H, 5'-H, ^3J = 7.8, ^4J = 1.0), 7.60 d.d (1H, 6'-H, ^3J = 7.8, ^4J = 1.6), 7.93 d.d (1H, 3'-H, ^3J = 7.8, ^4J = 1.0)
IIIg	9.75 d (^3J = 7.4)	6.76 d.d (^3J = 7.4, 16.1)	7.46 d (^3J = 16.1)	7.65 d (2H, ^3J = 8.3), 7.72 d (2H, ^3J = 8.3)
IIIk	9.75 d (^3J = 7.3)	6.82 d.d (^3J = 7.3, 16.1)	7.45 d (^3J = 16.1)	7.76 d (2H, ^3J = 8.7), 8.31 d (2H, ^3J = 8.7)
IIIl	9.78 d (^3J = 7.6)	6.66 d.d (^3J = 7.6, 15.8)	8.04 d (^3J = 15.8)	7.61 t.d (1H, 4'-H, ^3J = 7.4, ^4J = 1.7), 7.69 t.t (1H, 5'-H, ^3J = 7.4, ^4J = 1.4), 7.75 d.d (1H, 6'-H, ^3J = 7.4, ^4J = 1.7), 8.13 d.d (1H, 3'-H, ^3J = 7.4, ^4J = 1.4)
IIIm	9.76 d (^3J = 7.6)	6.63 d.d (^3J = 7.6, 15.8)	7.95 d (^3J = 15.8)	7,56 d (1H, 6'-H, ^3J = 8.5), 7.83 d.d (1H, 5'-H, ^3J = 8.5, ^4J = 2.0), 8.23 d (1H, 3'-H, ^4J = 2.0)
trans-**IIIn**[a]	9.78 d (^3J = 7.4)	6.74 d.d (^3J = 7.4, 16.0)	8.08 d (^3J = 16.0)	7.71 d (1H, 6'-H, ^3J = 8.6), 8.58 d.d (1H, 5'-H, ^3J = 8.6, ^4J = 2.2), 8.99 d (1H, 3'-H, ^4J = 2.2)
cis-**IIIn**[a]	9.63 d (^3J = 7.7)	6.48 d.d (^3J = 7.7, 11.6)	7.88 d (^3J = 11.6)	7.96 d (1H, 6'-H, ^3J = 8.7), 8.59 d.d (1H, 5'-H, ^3J = 8.7, ^4J = 2.2), 9.13 d (1H, 3'-H, ^4J = 2.2)
IVb	–	5.70 d (^3J = 16.6)	7.31 d (^3J = 16.6)	6.89 d (2H, ^3J = 8.7), 7.38 d (2H, ^3J = 8.7), 3.82 s (3H, CH_3O)
IVc	–	5.81 d (^3J = 16.6)	7.35 d (^3J = 16.6)	7.19 d (2H, ^3J = 8.0), 7.33 d (2H, ^3J = 8.0), 2.37 s (3H, CH_3)
IVd	–	5.90 d (^3J = 16.5)	7.35 d (^3J = 16.5)	7.33 d (2H, ^3J = 8.4), 7.55 d (2H, ^3J = 8.4)
trans-**IVg**[b]	–	6.00 d (^3J = 16.7)	7.43 d (^3J = 16.7)	7.58 d (2H, ^3J = 8.5), 7.73 d (2H, ^3J = 8.5)
cis-**IVg**[b]	–	5.64 d (^3J = 11.7)	7.19 d (^3J = 11.7)	7.84 d (2H, ^3J = 8.5), 7.98 d (2H, ^3J = 8.5)

[a] The spectra were recorded from a mixture of *trans* and *cis* isomers at a ratio of 4:1.
[b] The spectra were recorded from a mixture of *trans* and *cis* isomers at a ratio of 3:1.

yield of **IIb** to 75% by carrying out the reaction at reduced temperature (–30 to –40°C); simultaneously, the yields of **IIIb** and **IVb** decreased to 5 and 13%, respectively. At 20°C, the products were only compounds **IIIb** and **IVb** at a ratio of 4:5.

We also found that dihydroisoxazole **IIb** is unstable under the reaction conditions. By treatment of **IIb** with 3 equiv of $NOCl \cdot 2SO_3$ in methylene chloride at 0°C (reaction time 20 h) we obtained 68% of aldehyde **IIIb** and 10% of nitrile **IVb**, while 22% of unreacted isoxazole **IIb** was recovered from the reaction mixture (Scheme 4). Compound **IIn** was also unstable. To achieve complete conversion of 2,4-dinitrophenylcyclopropane (**In**) and raise the yield of compound **IIn**, the reaction was carried out at elevated temperature; however, the yield of the corresponding cinnamalde-

Scheme 4.

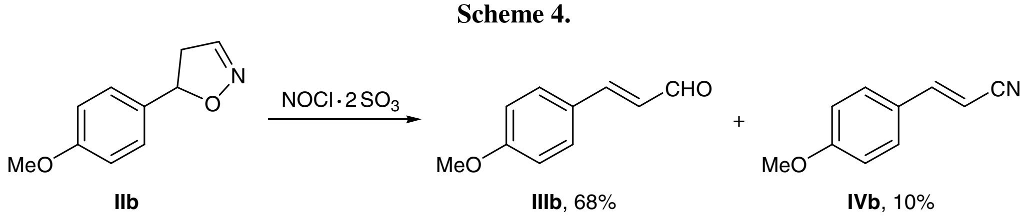


Table 4. [13]C NMR spectra (δ_C, ppm) of compounds **III** and **IV** in $CDCl_3$

Comp. no.	=CHCHO	ArCH=	Aromatic carbon atoms				CHO or CN	Other atoms
			C^1	C^2, C^6	C^3, C^5	C^4		
IIId	129.05	151.05	132.93	129.78	132.42	125.70	193.32	
IIIg	131.20	149.39	132.81	128.61	132.81	114.28	192.85	118.11
IVb	93.33	150.02	126.32	129.06	114.50	162.11	118.66	55.49
IVc	95.07	150.52	129.70	127.33	129.81	141.82	118.41	21.51
IVd	97.11	149.26	132.46	128.76	132.42	125.68	117.86	

hyde **IIIn** considerably increased instead (Table 1). Partial decomposition of **IIn** with formation of aldehyde **IIIn** was also observed during its chromatographic purification.

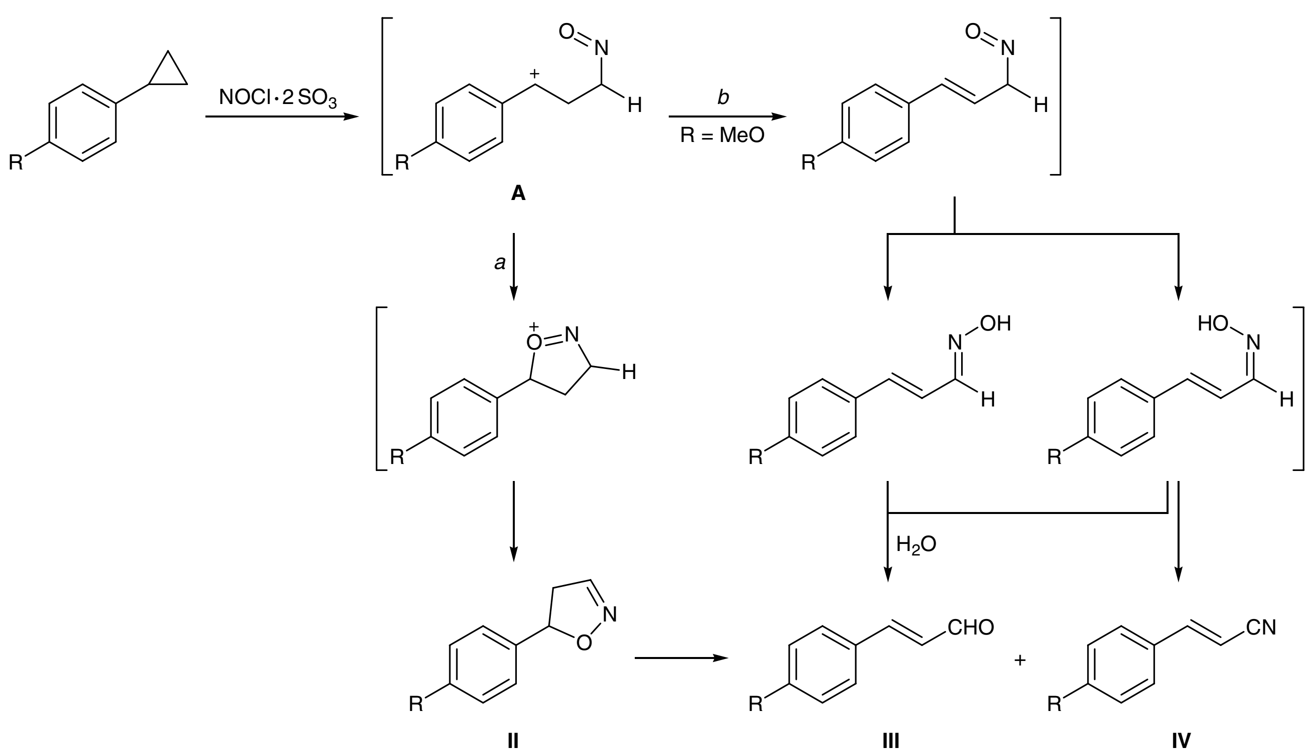
In the preceding communication [1] we proposed a scheme for the transformation of arylcyclopropanes by the action of nitrosyl chloride in liquid sulfur dioxide, which involved initial electrophilic attack by the nitrosating species with formation of benzyl carbocation and its subsequent stabilization with participation of the oxygen atom of the nitroso group or chloride anion. In the reaction with an equimolar amount of $NOCl \cdot 2SO_3$ (in the absence of free chloride ion in the system), an active nucleophile may be only the oxygen atom in the nitroso group (Scheme 5, path *a*). Stabilization of cation **A** via nucleophilic assistance by $ClS_2O_6^-$ ion is hardly probable. Therefore, side processes involving formation of oximes and their subsequent conversion into aldehydes may be excluded.

However, intermediate 4-methoxybenzylic cation formed in the reaction with cyclopropane **Ib** is rela-

Table 5. Nitrosation of 4-methoxyphenylcyclopropane (**Ib**) with the complex $NOCl \cdot 2SO_3$ in CH_2Cl_2

Temperature, °C	Time, h	Yield, %		
		IIb	**IIIb**	**IVb**
0	0.25	32	60	5
0	2	42	11	41
–30 to –40	1	75	5	13
20	20	–	42	55

Scheme 5.



tively stable; therefore, the contribution of the elimination process to stabilization of primary carbocation is likely to increase (path *b*) together with nucleophilic attack by the oxygen atom of the nitroso group. The subsequent isomerization of unsaturated nitroso compound to the corresponding oxime, followed by hydrolysis during the isolation procedure, leads to the formation of aldehyde **IIIb**.

3-(4-Methoxyphenyl)prop-2-enenitrile (**IVb**) can be formed as a result of dehydration of unsaturated oxime. This process is facilitated by *anti* arrangement of the hydrogen atom and OH group in the oxime [6]. Prolonged reaction time favors formation of nitrile **IVb**, while the fraction of aldehyde **IIIb** among the products decreases (Table 5); these data confirm the possibility for the transformation of intermediate oximes into nitrile **IVb**. In addition, 4-methoxycinnamaldehyde (**IIIb**) and 4-methoxycinnamonitrile (**IVb**) can be formed via dehydration of dihydroisoxazole **IIb** during the reaction; this pathway may also be responsible for the anomalously high yields of compounds **IIIb** and **IVb**.

Thus the results of the present study showed that arylcyclopropanes readily react with the complex $NOCl \cdot 2SO_3$ to give the corresponding 5-aryl-4,5-dihydroisoxazoles. The use of $NOCl \cdot 2SO_3$ as highly effective nitrosating agent allows considerable extension of the substrate series. In most cases, 5-aryl-4,5-dihydroisoxazoles are formed in quantitative yields, and no additional purification of the product is necessary, which makes the proposed procedure especially advantageous from the preparative viewpoint.

EXPERIMENTAL

The NMR spectra were recorded on Varian XR-400 and Bruker Avance-400 spectrometers (400 MHz for ^{1}H and 100 MHz for ^{13}C) using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The IR spectra were measured on a UR-20 spectrometer from samples prepared as thin films. The mass spectra were obtained on a Finnigan MAT SSQ-7000 GC–MS system [electron impact, 70 eV; OV-1 quartz capillary column, 25 m; oven temperature programming from 70 (2 min) to 280°C (10 min) at a rate of 20 deg/min]. The melting points were determined in open capillaries.

Reaction of arylcyclopropanes with $NOCl \cdot 2SO_3$ (*general procedure*). A solution of 1 mmol of arylcyclopropane **Ia**–**In** in 2 ml of methylene chloride was added at 0°C to a suspension of 1 mmol of $NOCl \cdot 2SO_3$ in 10 ml of methylene chloride. The solid material partially dissolved, and the solution turned colored. When the reaction was complete (TLC), the mixture was neutralized with a solution of sodium carbonate and washed with water. The aqueous phase was separated and extracted with methylene chloride (3× 10 ml), and the extracts were combined with the organic phase, dried over sodium sulfate, and evaporated. The residue was pure crystalline compound **IIa**–**IIn**. If necessary, the product can be purified by recrystallization or chromatography.

In the reaction of 0.105 g (0.7 mmol) of compound **Ib** with 0.16 g (0.7 mmol) of $NOCl \cdot 2SO_3$ at 0°C (2 h) we isolated by chromatography (silica gel, ethyl acetate–petroleum ether, 1:3) 0.05 g (41%) of *trans*-3-(4-methoxyphenyl)prop-2-enenitrile (**IVb**), 0.01 g (11%) of *trans*-3-(4-methoxyphenyl)prop-2-enal (**IIIb**), and 0.05 g (42%) of 5-(4-methoxyphenyl)-4,5-dihydroisoxazole (**IIb**).

Compound **IIb**. R_f 0.21. IR spectrum: ν 1620 cm^{-1} (C=N).

Compound **IIIb**. R_f 0.66. IR spectrum ν, cm^{-1}: 1675 (C=O), 1610, 1360, 1135, 830, 810.

Compound **IVb**. R_f 0.82. IR spectrum, ν, cm^{-1}: 2225 (CN), 1610, 1580, 1260, 1180, 1030, 810, 750. Found, %: C 75.58; H 5.80; N 8.56. $C_{10}H_9NO$. Calculated, %: C 75.47; H 5.66; N 8.81;

In the reaction of 0.35 g (1.4 mmol) of 4-bromo-2-nitrophenylcyclopropane (**Im**) with 0.25 g (1.1 mmol) of $NOCl \cdot 2SO_3$ we isolated by chromatography (silica gel, ethyl acetate–petroleum ether, 1:5) 0.05 g of an unidentified substance (R_f 0.72), 0.05 g (14%) of *trans*-3-(4-bromo-2-nitrophenyl)prop-2-enal (**IIIm**), and 0.12 g (70%) of 5-(4-bromo-2-nitrophenyl)-4,5-dihydroisoxazole (**IIm**).

Compound **IIm**. R_f 0.22, mp 85–87°C (from ethyl acetate–petroleum ether). IR spectrum, ν, cm^{-1}: 3110, 2930, 2860, 1600, 1540 (NO_2), 1470, 1430, 1350 (NO_2), 1280, 845. ^{13}C NMR spectrum, δ_C, ppm: 44.42, 75.99, 121.88 (C–Br), 127.95, 129.09, 136.76, 137.18 (C^i), 145.73 (CNO_2, HC=N). Mass spectrum, m/z (I_{rel}, %): $[M]^+$ 272/270 (1), 255/253 (8), 242/240 $[M - NO]^+$ (23), 225 (25), 212 (27), 184/182 (37), 172/170 (27), 161 (100), 131 (11), 115 (29), 90 (39), 75 (70), 63 (31).

Compound **IIIm**. R_f 0.52, mp 118–119°C (from ethyl acetate–petroleum ether). IR spectrum, ν, cm^{-1}: 2930, 2865, 1690 (C=O), 1600, 1540 (NO_2), 1460, 1350 (NO_2), 1280, 770. ^{13}C NMR spectrum, δ_C, ppm: 124.66 (C–Br), 128.21, 128.73 (C^i), 130.13, 132.83, 136.84, 145.81 (Ar**C**=, CNO_2), 192.75. Mass spectrum, m/z (I_{rel}, %): $[M]^+$ 257/255 (23), 228/226 (53), 212/210 (33), 200/198 (26), 182 (40), 172/170 (50), 157/155 (14), 145/143 (21), 118 (41), 102 (100), 90 (91), 75 (94), 63 (38), 51 (38);

In the reaction of 0.14 g (0.7 mmol) of 2,4-dinitrophenylcyclopropane (**In**, a mixture of 2,4- and 2,6-isomers at a ratio of 3:1) with 0.42 g (1.8 mmol) of $NOCl \cdot 2SO_3$ we obtained 0.09 g of a product mixture containing initial 2,6-dinitrophenylcyclopropane, aldehyde **IIIn**, and dihydroisoxazole **IIn**. By chromatography on silica gel (ethyl acetate–petroleum ether, 1:3) we isolated 0.01 g of 2,6-dinitrophenylcyclopropane, 0.05 g (50%) of 3-(2,4-dinitrophenyl)prop-2-enal (**IIIn**, a mixture of *trans* and *cis* isomers at a ratio of 4:1), and 0.03 g (25%) of 5-(2,4-dinitrophenyl)-4,5-dihydroisoxazole (**IIn**).

Compound **IIn**. R_f 0.35. IR spectrum, ν, cm^{-1}: 3110, 2930, 2860, 1600, 1540 (NO_2), 1470, 1430, 1350 (NO_2), 1280, 845. ^{13}C NMR spectrum, δ_C, ppm: 44.69, 76.05, 120.82, 128.37, 129.59, 144.00, 145.81 (CH=N, $C^2–NO_2$, $C^4–NO_2$). Mass spectrum, m/z (I_{rel}, %): $[M]^+$ 237 (3), 191 (1), 180 (9), 167 (5), 149 (25), 134 (8), 115 (3), 113 (4), 105 (9), 97 (10), 55 (19), 29 (100).

Compound **IIIn**. R_f 0.55. IR spectrum, ν, cm^{-1}: 2930, 2865, 1690 (C=O), 1600, 1540 (NO_2), 1460, 1350 (NO_2), 1280, 770. Mass spectrum, m/z (I_{rel}, %): $[M]^+$ 222 (3), 210 (14), 193 (35), 179 (4), 161 (10), 149 (3), 101 (100), 77 (41), 29 (19);

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 02-03-33347), by the Ministry of Education of the Russian Federation (program "Universities of Russia," project no. 05.03.046), and by the Presidium of the Russian Academy of Sciences (program "Theoretical and Experimental Studies on the Nature of Chemical Bond and Mechanisms of Chemical Reactions and Processes").

REFERENCES

1. Bondarenko, O.B., Gavrilova, A.Yu., Kazantseva, M.A., Tikhanushkina, V.N., Nifant'ev, E.E., Saginova, L.G., and Zyk, N.V., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 249.
2. Koroleva, E.V. and Lakhvich, F.A., *Usp. Khim.*, 1997, vol. 66, p. 31.
3. Huisgen, R. and Christl, M., *Chem. Ber.*, 1973, vol. 106, p. 3291; Trost, B.M., Li, L., and Guile, S.D., *J. Am. Chem. Soc.*, 1992, vol. 114, p. 8745; Yang, S., Hayden, W., Faber, K., and Griengl, H., *Synthesis*, 1992, p. 365.
4. Bondarenko, O.B., Gavrilova, A.Yu., Saginova, L.G., Zyk, N.V., and Zefirov, N.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, p. 741.
5. Paul, R.C., Arora, C.L., and Malhotra, K.C., *Indian J. Chem.*, 1972, vol. 10, p. 92.
6. March, J., *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, New York: Wiley, 1992, 4th ed.