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Dedicated to Academician of the Russian Academy of Sciences N.S. Zefirov on occasion of his 70th anniversary

2-Isoxazolines from Arylcyclopropanes: I. Monoarylcyclopropanes in a Reaction with Nitrosyl Chloride Activated by Sulfur(IV) Oxide

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Abstract—A reaction of monoarylcyclopropanes with nitrosyl chloride activated by sulfur (IV) oxide gave in good yields 5-arylisoxazolines. The reaction is of electrophilic character. A scheme of the reaction was suggested.

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Already for a long time quite a number of publications in the field of organic chemistry has been dealing with isoxazoles and isoxazolines. Nowadays new tendencies are observed in this line: The focus of the research tends to shift from the proper transformations of isoxalines to their practical applications in the synthesis of naturally occurring and biologically active compounds. Here a great success is achieved obviously based on the previously accumulated synthetic procedures. All these processes and their dynamics are reflected in intermittently appearing reviews that completely account for the topicality of the isoxazolines chemistry [1].

We recently reported on the new procedure for preparation of 3,5-diarylisoxazolines from 1,2-diarylcycloprpanes and nitrosyl chloride [2]. It was demonstrated that the reaction proceeded the most successfully in the liquic sulfur dioxide used as a solvent. Certain monoarylcyclopropanes brought into this reaction did not show such uniform result.

In order to determine the range of applicability of the reaction and to reveal certain specific features of arylcyclopropanes conversion effected by nitrosyl chloride we carried out a systematic investigation of the effect of substituents of various character and of different position in the aromatic ring in monoarylcyclopropanes on the reactivity of the latter. The following compounds were chosen as model substrates: phenylcyclopropane, 4-methoxy-, 4-methyl-, 4-bromo-, 4-iodo-, 2-iodo-, 4-cyano-, 4-acetyl-, 4-tosyl-, 2-benzylsulfo-, 4-nitro-, and also 2-nitrophenylcyclopropanes **Ia–Il**.

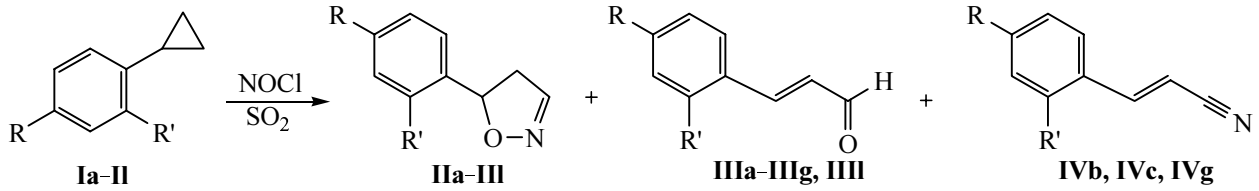
The nitrosation of monoarylcyclopropanes with nitrosyl chloride in the liquid sulfur dioxide was carried out under the conditions previously optimized for phenylcyclopropane [2] with minor variations of the temperature range and the ratio of the reagents in order to increase the yield of isoxazolines. The reaction conditions and yields of the products are given in Table 1.

We obtained from arylcyclopropanes **Ia–Il** brought into the reaction 5-arylisoxazolines **IIa–III**. As side products the corresponding cinnamic aldehydes **IIIa–IIIg** and **IIIl** were isolated, and also sometimes 3-arylacrylonitriles **IVb, IVc**, and **IVg**. The structure of compounds obtained was confirmed by NMR and IR spectra [3]. The composition of the previously unknown compounds was established by elemental analysis or mass spectrometry.

It turned out that already at the double excess of the nitrosyl chloride the conversion of 4-methoxyphenylcyclopropane (**Ib**) was quantitative; therewith 5-(4-methoxyphenyl)isoxazoline (**IIb**) formed in a 67% yield, and in small amounts the products of the three-membered ring oxidation: 4-methoxtcinnamic aldehyde (**IIIb**) and 3-(4-methoxyphenyl)acrylonitrile (**IVb**). The reduced reaction temperature made it possible to avoid the formation of the side products.

Under the same conditions 4-methylphenylcyclopropane (**Ic**) proved to be less active: 23% of the initial compound did not react. At the fivefold excess of the nitrosyl chloride within 5 h the conversion of the hydrocarbon was complete, the yield of isoxazoline (**IIc**) reached 88%, and in amount of 5% formed 4-methylcinnamic aldehyde (**IIIc**).

The introduction of a halogen into the aromatic ring (cyclopropanes **Id–If**) reduced the substrate activity



Ia–Il **IIa–III** **IIIa–IIIg, IIIl** **IVb, IVc, IVg**

R = R' = H (**Ia–IIIa**); R = MeO, R' = H (**Ib–IVb**); R = Me, R' = H (**Ic–IVc**); R = Br, R' = H (**Id–IIId**); R = I, R' = H (**Ie–IIIe**); R = H, R' = I (**If-IIIf**); R = CN, R' = H (**Ig–IVg**); R = Ac, R' = H (**Ih, IIh**); R = Ts, R' = H (**Ii, IIi**); R = H, R' = $BnSO_2$ (**Ij, IIj**); R = NO_2, R' = H (**Ik–IIIk**); R = H, R' = NO_2 (**Il–IIIl**).

(Table 1). Therewith the raising of temperature to 0°C resulted only in significant decrese in the process selectivity, and the yield of the target products **IId–IIf** did not grew notably. 5-(4-Cyanophenyl)isoxazoline (**IIg**) was isolated in a low yield although no initial cyclopropane **Ig** was recovered.

Introduction of strong electron-withdrawing substituents (nitro-, acetyl-, or sulfo groups) into the *ortho*- or *para*-position of the aromatic ring resulted in virtually total deactivation of the three-membered ring. The corresponding isoxazolines **IIh–III** were obtained in low yields notwithstanding the raised reaction and time.

Thus the research performed revealed that in reaction of arylcyclopropanes with nitrosyl chloride in the liquid sulfur dioxide the three-membered ring is activated to the attack of the nitrosating reagent by electron-donor substituents and desctivated by electron-acceptor ones. This fact evidences the electrophilic character of the reaction.

It should be noted that the yields of isoxazolines in this reaction were not quantitative apparently due to the side processes. Inasmuch as our reagents at standard conditions are gaseous we tried an alternative workup of the reaction mixtures in order to detect the probable intermediate reaction products.

A fast evaporation of the reaction mixtures on a rotary evaporator without preliminary warming and hydrolysis afforded oily compounds of blue color. The ^1H NMR

Table 1. Results of nitrosation of monoarylcyclopropanes **Ia–Il** with nitrosyl chloride in liquid sulfur dioxide

Compd. no.	Temperature, °C	Time, h	(**I**):NOCl, (mol)	Yield of reaction products, %			
				I	**II**	**III**	**IV**
Ia	–55	5	1:5	14	68	12	–
Ib	–40	2	1:2	–	67	12	12.5
	–55÷–60	5	1:2	–	80	–	–
Ic	–40	2	1:2	23	40	15	5
	–55÷–60	5	1:5	–	88	5	–
Id	0	24	1:5	38	29[a]	4	–
	–55÷–60	5	1:5	54	35	8	–
Ie	0	24	1:5	–	40[a]	15	–
	–50	8	1:5	30	50	–	–
If	0	24	1:5	30	40[a]	10	–
	–50	8	1:5	79	16	–	–
Ig	20	24	1:5	–	46	10	7
Ih	–20	18	1:4	70	14	–	–
	–50	8	1:5	92	6	–	–
Ii	–20	96	1:5	59	17	–	–
Ij	–20	96	1:5	85	12	–	–
Ik	0	3	1:5	75	5	–	–
	–50	8	1:5	80	7	–	–
Il	0	24	1:5	70	16	9	–
	20	24	1:1.5	79	7	4	–

[a] Reaction at 0°C occurred with considerable tarring.

Table 2. ^{1}H NMR spectra of the aliphatic part of compounds **V** ($CDCl_3$), δ, ppm (*J*, Hz)

Compd. no.	H (CH_2)	H (CH_2)	Ar-CH
Va	3.14 d.d (^2J 15.2, ^3J 5.8)	3.32 d.d (^2J 15.2, ^3J 8.8)	5.29 d.d (^3J 8.8, ^3J 5.8)
Vc	3.13 d.d (^2J 15.1, ^3J 5.8)	3.33 d.d (^2J 15.1, ^3J 8.8)	5.29 d.d (^3J 8.8, ^3J 5.8)
Vd	3.12 d.d (^2J 15.2, ^3J 6.3)	3.27 d.d (^2J 15.2, ^3J 8.3)	5.22 d.d (^3J 8.3, ^3J 6.3)
Ve	3.17 d.d (^2J 15.1, ^3J 6.6)	3.32 d.d (^2J 15.1, ^3J 8.3)	5.32 d.d (^3J 8.3, ^3J 6.6)
Vh	3.13 d.d (^2J 15.1, ^3J 6.6)	3.27 d.d (^2J 15.1, ^3J 8.3)	5.27 d.d (^3J 8.3, ^3J 6.6)
Vi	3.12 d.d (^2J 15.3, ^3J 6.1)	3.27 d.d (^2J 15.3, ^3J 8.6)	5.27 d.d (^3J 8.6, ^3J 6.1)
Vk	3.19 d.d (^2J 15.2, ^3J 7.5)	3.33 d.d (^2J 15.2, ^3J 7.5)	5.34 t (^3J 7.5)

spectra of reaction products thus obtained contained three sets of signals corresponding to initial arylcyclopropane I, isoxazoline **II**, and to a compound of unknown structure. The chemical shifts and the values of coupling constants of the aliphatic protons in the spectra of these compounds are given in Table 2. These compounds are lost at treating the reaction mixture with water. Regretfully, the compounds turned out to be unstable also at the chromatographic separation, and they are therefore characterized only by spectral methods in the mixtures with the other products.

The composition of the reaction mixture was studied in more detail by an example of 4-bromophenylcyclopropane (**Id**). The GC-MS analysis of the reaction mixture confirmed the presence of three components: initial substrate **Id** ([*M*]$^+$ 196), 5-(4-bromophenyl)-isoxazoline (**IId**) ([*M*]$^+$ 225), and also a compound with a molecular ion [*M*]$^+$ 259. The intensity ratio of the lines in the cluster of the molecular ion of the compound indicated the presence therein of chlorine and bromine atoms, and the mass corresponded to the empirical formula $C_9H_7BrClNO$. The appearance of a fragment ion of the mass *m/z* 203 and a characteristic distribution of lines in the cluster of the ion corresponding to the presence in the ion of chlorine and bromine made it possible to establish that the chlorine atom was linked to the benzyl carbon.

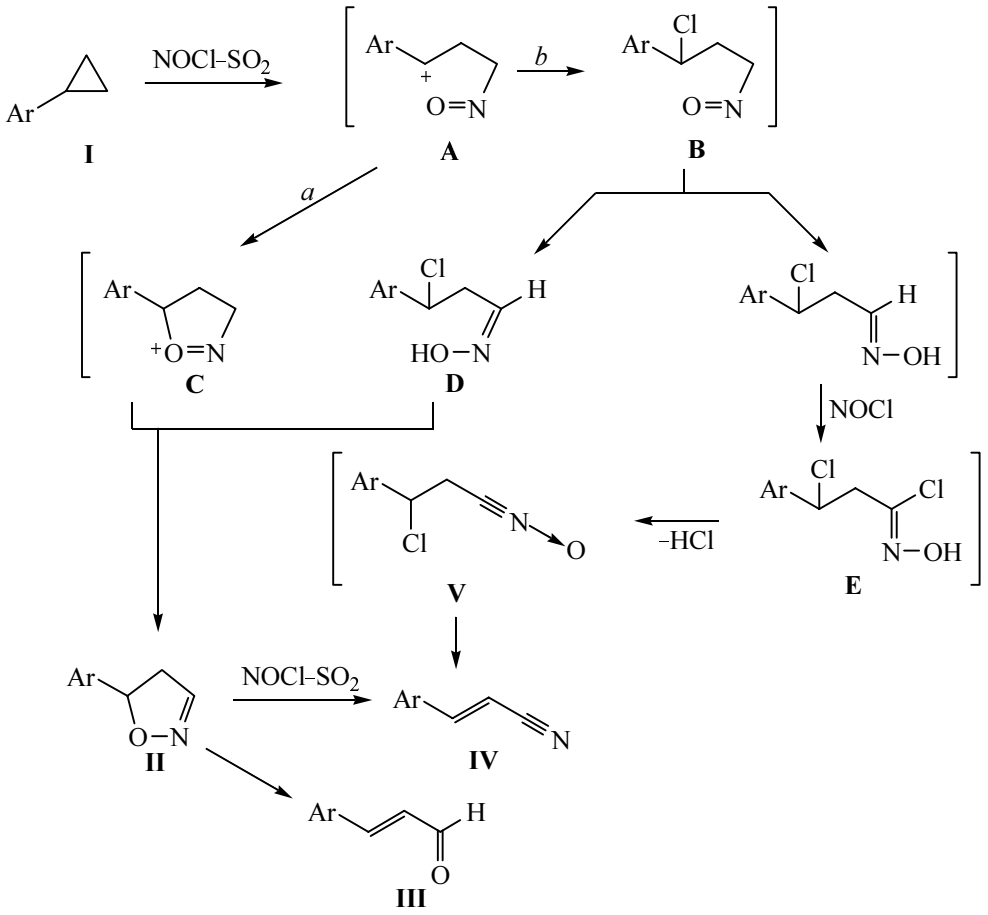
The ^{1}H NMR spectrum of the aliphatic part of this compound comprises a system of tree coupled protons (Table 2). A large geminal constant ^3J 15.2 Hz observed for two protons indicates the presence of a methylene group.

We analysed the ^{13}C NMR spectrum of the reaction mixture and by subtracting the signals belonging to cyclopropane **Id** and isoxazoline **IId** we determined the signals corresponding to the third compound (Table 3). The assignment of the aromatic carbons signals was performed with accounting for the related structures **Id** and **IId**. The lack of signals in the region 150–160 ppm in the ^{13}C NMR spectrum, and also of the third coupling constant by the protons of the methylene group in the ^{1}H NMR spectrum permits the exclusion of oxime from the possible structures (structure **D**, see the Scheme). In addition the fragmentation character of the molecular ion [*M*]$^+$ 259 in the initial stage is not characteristic of oximes but analogous to the decomposition pattern of known nitrile oxides ArCN–O [4].

All the above stated made it possible to suggest that the unknown compound possessed structure **V** (see the Scheme. The ^{1}H NMR spectrum of the aliphatic part of the molecule does not contradict the assumed structured **V**. In the ^{13}C NMR spectrum we assigned to the carbon of the nitrile oxide fragment in **Vd** the signal with the chemical shift 136 ppm. The scanty published data on the chemical shifts of carbon in nitrile oxide fragments are not uniform [5] for this carbon atom in the structures described occurs in quite different environments. Therefore we could not find any correlation of the values obtained with the published data. The calculation of carbon chemical shifts for structures **Va, Vc**, and **Vd** performed applying database of the program ACDLab provided values close to the experimental findings (Table 3).

Compound **Vd** obtained from initial 4-bromo-phenylcyclopropane (**Id**) was stable at storage in chloroform solution for 2 months at –20°C.Compound **Va** obtained from phenylcyclopropane (**Ia**) under similar conditions suffered partial decomposition as revealed by ^{1}H NMR spectrum: In the spectrum of the mixture appeared signals corresponding to 3-phenylacrylonitrile (**IVa**). In the chromato-mass spectrum of a sample obtained from compound **Ia** and stored for 2 months in $CDCl_3$ solution

Scheme.



at –20°C were found the molecular ions of initial cyclopropane **Ia** ([*M*]$^+$ 118), 3-phenylacrylonitrile (**IVa**) ([*M*]$^+$ 129), 5-phenylisoxazoline (**IIa**) ([*M*]$^+$ 147), and also of compound **Va** ([*M*]$^+$ 181).

From the study of the composition and structure of the reaction products, and from investigation of the effect of substituents attached to the aromatic ring of arylcyclopropanes the scheme of transformation of the latter compounds treated with nitrosyl chloride may be suggested.

We believe that at the nitrosation of arylcyclopropanes in the liquid sulfur dioxide first arises a benzyl type cation **A** (see the scheme) that can be stabilized by adding a nucleophile. Note that the role of a nucleophile may play both a chloride anion formed as a result of nitrosonium cation addition to the cyclopropane (path *b*) and an oxygen of the nitroso group (path *a*). In the latter case from the cationoid intermediate **C** forms the isoxazoline by a proton elimination.

Nitroso compound **B** may undergo isomerization into the corresponding oxime. The conversion of γ-substituted oximes of *syn*-configuration **D** into isoxazolines is a known method of the synthesis of these compounds [6]. Therefore this pathway may contribute to the main direction of the reaction.

It is known at the same time that the nitrosyl chloride is a mild chlorinating reagent for preparation of hydroximoyl chlorides **E** from aldoximes [7]. *Z*-Isomers of the latter easily transform into the corresponding nitrile oxides eliminating a hydrogen chloride molecule [8]. In reactions carried out at excess nitrosyl chloride this side product may be the source of compound **V**; the yield of the latter grows at growing concentration of nirtosyl chloride as show the ^{1}H NMR spectra, and the yield of compound **V** may reach 25%.

Aldehydes **III** may result from the hydrolysis of oximes or decomposition of isoxazolines, and nitriles **IV** may originate from decomposition of nitrileoxides **V** and isoxazolines.

Hence, monoarylcyclopropanes easily react with nitrosyl chloride activated by sulfur(IV) oxide to furnish 5-arylisoxazolines in good yield, and the reaction under

Table 3. Chemical shifts of carbon atoms, δ, ppm ($CDCl_3$) of compounds **Ia, Ic, Id, IIa, IIc, IId, Va, Vc**, and **Vd** established from the ^{13}C NMR spectra, and also calculated for compounds **Va, Vc**, and **Vd** using database of the program ACDLab

Compd. no.	CH_2	ArCH	CNO	C of the aromatic ring			
				C^4R	C^2H	C^3H	C^1
Ia	9.08	15.29	–	125.26	125.57	128.17	143.85
IIa	43.59	79.87	145.64	128.08	125.68	128.65	140.73
Va	46.37	58.54	136.39	129.50	126.93	128.75	139.63
Va (calcd.)	23.84	59.76	120.11	129.78	127.99	128.05	139.71
Ic[a]	9.13	15.23	–	134.95	125.82	129.16	141.02
IIc[a]	43.64	80.11	146.05	137.81	125.92	129.0.4	138.03
Vc[a]	46.44	58.81	136.70	139.05	127.02	129.56	138.79
Vc (calcd.)	23.84	59.76	120.11	138.85	128.96	129.25	137.31
Id	9.37	15.08	–	118.89	127.51	131.29	143.09
IId	43.75	79.16	145.39	122.06	127.43	131.87	140.00
Vd	46.38	57.73	136.66	122.87	128.79	132.03	138.74
Vd (calcd.)	23.84	59.76	120.11	122.92	130.78	131.70	138.83

[a] Carbon chemical shifts of CH_3 groups: 21.01 (**Ic**), 21.20 (**IIc**), 21.20 (**Vc**) established from the ^{13}C NMR spectra.

consideration is a convenient metod of isoxazolines synthesis. The reaction occurs the most selectively between –55 and –60°C. With arylcyclopropanes containing electron-donor substituents a complete conversion of the initial compound is attained already at the double excess of the nitrosyl chloride, whereas the conversion rate of the aryl-cyclopropanes with nonactivated aromatic rings sig-nificantly increases at enhances molar ratio NOCl : aryl-cyclopropane. However the too large excess of the nitrosyl chloride results in a side process due to the chlorination of intermediate compounds. The optimum excess of the nitrosyl chloride with respect to cyclo-propane is fivefold.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered from solutions of compounds in $CDCl_3$ on spectrometers Varian XR-400 and Avance-400 at operating frequency 400 MHz (internal reference HMDS). IR spectra were taken on a spectrophotometer UR-20 from mulls in mineral oil or from thin films. Mass spectra were recorded on a GC-MS instrument Finnigan MAT SSQ 7000 [ionizing electrons energy 70eV, quartz capillary column OV-1 (25 m), temperature programming: from 70 (2 min) to 280°C (10 min), heating rate 20 deg/min]. Melting points were measured on a block in an open capillary.

Initial arylcyclopropanes **Ia–Il** were prepared by known procedures: **Ia** by reduction of 1,1-dichloro-2-phenylcyclopropane [9]; **Ib** and **Ic** by decomposing the corresponding pyrazolines [10] obtained from the Mannich bases; **Id, Ie**, and **Ih** by direct halogenation [11, 12] and acylation of **Ia** [11] respectively at low temperature; nitro derivatives **Ik** and **Il** by nitration of phenylcyclopropane with subsequent separation of the isomer mixture by chromatography [13]; **Ig** by replacement of bromine atom in compound **Id** by a cyano group [14]; **If** by iodination of the corresponding amino derivative [15]; **Ij** by substitution of iodine with a benzylthio group followed by oxidation [16]; in the same way as compound **Ij** was prepared sulfone **Ii**, mp 138–140°C, mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 272 (91), 165 (69), 139 (73), 133 (100), 117 (71), 115 (71), 105 (18), 91 (50), 77 (17), 65 (28).

General procedure of isoxazolines synthesis from arylcyclopropanes and nitrosyl chloride in the liquid sulfur dioxide. Into a test tube was charged 3 mmol of arylcyclopropane and on cooling to –60°C was added the desired amount of NOCl as a solution in dichloromethane and 5 ml of liquid SO_2. The test tude was tightly stoppered, warmed to the required temperature, shaken till the mixture became homogeneous, and kept for the required time at the desired temperature (at temperature higher than –20°C the reaction was carried out in sealed ampules).

Workup of the reaction mixture. *a.* At the end of the required reaction time 20 ml of cold dichloromethane was added to the reaction mixture, the content of the test tube was warmed to 0°C, and the organic layer was neutralized with a water solution of sodium carbonate and then washed with water. The water layer was extracted with dichloromethane, the combined organic

solutions were dried over sodium sulfate. On evaporating the solvent the residue was subjected to chromatography on silica gel (eluent ethyl acetate–petroleum ether, 1:3).

The yields of compounds obtained are given in Table 1. Physical constants of separated aldehydes and acrylonitriles were consistent with the published data [17].

b. At the end of the required reaction time 5 ml of dichloromethane cooled to the reaction temperature was added to the reaction mixture, and the solution was quickly evaporated on a rotary evaporator.

Conversion of 4-cyanophenylcyclopropane (Ig). After the reaction of 0.07g (0.5 mmol) cyclopropane **Ig** and 0.18 g (2.5 mmol) of nitrosyl chloride for 24 h at 20°C the workup of the reaction mixture by procedure *a* afforded 0.06 g of products mixture. The chromatographic separation on plates with SiO_2, (eluent ethyl acetate–petroleum ether, 1:3) gave the following compounds: 0.005 g (7%) of **3-(4-cyanophenyl)acrylonitrile (IVg)** (mixture of isomers *cis:trans* = 1:2). Oily substance, R_f 0.45. IR spectrum (mull in mineral oil), cm^{-1}: 2230–2220 (CN). Mass spectrum, *m/z* (I_{rel}, %), ***cis*-(IVg)**: $[M]^+$ 154 (100), 127 (50), 100 (10), 76 (10), 50 (10); ***trans*-(IVg)**: $[M]^+$ 154 (100), 127 (50), 100 (10), 75 (10), 57 (10), 50 (10); 0.008 g (10%) of ***trans*-4-cyanocinnamic aldehyde (IIIg)**, R_f 0.33. IR spectrum (film), cm^{-1}: 2235 (CN), 1690 (C=O), 1130; 0.04 g (46%) **5-(4-cyanophenyl)isoxazoline (IIg)**. Colorless oily substance, R_f 0.17. IR spectrum (film), cm^{-1}: 3085, 2940, 2860, 2240 (CN), 1615, 1510, 1440, 1420, 1290, 855. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.95 d.d.d (1H, CH_2, ^2J 17.6, ^3J 7.5, ^3J 1.8), 3.53 d.d.d (1H, CH_2, ^2J 17.6, ^3J 11.4, ^3J 1.8), 5.60 d.d (1H, CHO, ^3J 11.4, ^3J 7.5), 7.23 t (1H, CHN, ^3J 1.8), 7.45 d ($2H_{arom}$, ^3J 8.3) 7.68 d ($2H_{arom}$,^3J 8.3). ^{13}C NMR spectrum, δ, ppm: 43.89, 78.77, 112.01 ($\underline{C}^4_{ap}$-CN), 118.50 (CN), 126.35, 132.62, 146.30, 145.26 (HC=N). Found, %: C 69.83; H 4.77; N 16.11. $C_{10}H_8N_2O$. Calculated, %: C 69.77; H 4.65; N 16.28.

Conversion of 4-tosylphenylcyclopropane (Ii). After the reaction of 0.11g (0.4 mmol) of cyclopropane **Ii** and 0.13 g (2.0 mmol) of NOCl at –20°C for 96 h the workup of the reaction mixture by procedure *a* and chromatographic separation on a plate (SiO_2, ethyl acetate–petroleum ether, 1:1) afforded 0.06 g (59%) **4-tosylphenylcyclopropane (Ii)** and 0.02 g (17%) **5-(4-tosylphenyl)isoxazoline (IIi)**, R_f 0.39, mp 122–123°C (ethyl acetate–petroleum ether). IR spectrum (film), cm^{-1}: 3070, 2930, 2860, 1600, 1500, 1320 (SO_2), 1310, 1290, 1160 (SO_2), 1115, 750. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.30 s (3H, CH_3), 2.90 d.d (1H, CH_2, ^2J 17.4, ^3J 7.5), 3.46 d.d (1H, CH_2, ^2J 17.4, ^3J 11.3), 5.55 d.d (1H, CHO, ^3J 7.5, ^3J 11.3), 7.18 br.s (1H, CHN), 7.29 d ($2H_{arom}$, ^3J 7.8), 7.44 d ($2H_{arom}$, ^3J 8.2), 7.80 d ($2H_{arom}$, ^3J 7.8), 7.91 d ($2H_{arom}$, ^3J 8.2). ^{13}C NMR spectrum, δ, ppm: 21.43 (CH_3), 43.75, 78.63, 126.35, 127.57, 127.89, 129.85, 138.33, 141.57, 144.22, 145.22, 146.36. Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 301 (40), 258 (14) $[M - HCNO]^+$, 233 (23), 151 (25), 139 (100), 91 (34), 77 (14).

Conversion of 2-benzylsulfophenylcyclopropane (Ij). After the reaction of 0.12 g (0.45 mmol) of cyclopropane **Ij** and 0.14 g (2.2 mmol) of NOCl at –20°C for 96 h the workup of the reaction mixture by procedure *a* and chromatographic separation on a plate (SiO_2, ethyl acetate–petroleum ether, 1:1) afforded 0.10 g (85%) of **2-benzylsulfophenylcyclopropane (Ij)** and 0.016 g (12%) of **5-(2-benzylsulfophenyl)isoxazoline (IIj)**, R_f 0.75, mp 121–122°C (ethyl acetate–petroleum ether). IR spectrum (film), cm^{-1}: 3070, 3040, 2985, 2930, 2860, 1600, 1500, 1320 (SO_2), 1290, 1160 (SO_2), 1125, 780. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.77 d.d.d (1H, CH_2, ^2J 18.4, ^3J 7.1, ^3J 1.8), 3.54 d.d.d (1H, CH_2, ^2J 18.4, ^3J 11.4, ^3J 1.5), 4.30 s (2H, CH_2), 5.78 d.d (1H, CHO, ^3J 7.1, ^3J 11.4), 7.11 br.s (1H, CHN), 7.05 d ($2H_{arom}$, ^3J 7.25), 7.23–7.74 ($7H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 45.53, 63.51, 76.26, 126.80, 127.32, 128.26, 128.62, 128.99, 130.73, 130.88, 134.14, 134.40, 142.34, 145.65. Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 301 (1.25), 146 (15) $[M - SO_2CH_2Ph]^+$, 116 (34) $[M - SO_2CH_2Ph - NO]^+$, 91 (100), 65 (10).

Conversion of 4-bromophenylcyclopropane (Id). After the reaction of cyclopropane **Id** with a 7-fold excess of NOCl in the liquid sulfur dioxide at –55 to –60°C for 2 h the workup of the reaction mixture by procedure *b* furnished an oily blue substance containing compounds **Id, IId**, and **Vd** in a ratio 8:10:8 (according to ^{1}H NMR data). Mass spectrum of compound **Vd**, *m/z* (I_{rel}, %): $[M]^+$ 261/259 (8), 245/243 (10), 233/231 (3), 205/203 (100), 129 (16), 124 (11), 117 (10), 102 (26), 89 (59), 63 (41), 51 (25), 32 (71).

Conversion of phenylcyclopropane (Ia). After the reaction of cyclopropane **Ia** with a 5-fold excess of NOCl in the liquid sulfur dioxide at –55...–60°C for 2 h the workup of the reaction mixture by procedure *b* furnished an oily blue substance containing compounds **Ia**, **IIa**, and **Va** in a ratio 2:1:1 (according to ^{1}H NMR data). Mass spectrum of compound **Va**, *m/z* (I_{rel}, %): $[M]^+$ 181 (10), 165 (10), 138 (3), 125 (100), 103 (10), 89 (8), 40 (30).

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REFERENCES

1. Kozikowski, A.P., *Acc. Chem. Res.,* 1984, vol. 17, p. 410; Lipshuts, B.H., *Chem. Res.,* 1986, vol. 86, p. 795; Lakhvich, F.A., Koroleva, E.V., and Akhrem, A.A., *Khim. Geterotsikl. Soedin.,* 1989, p. 435; Koroleva, E.V. and Lakhvich, F.A., *Usp. Khim*., 1997, vol. 66, p. 31.
2. Bondarenko, O.B., Gavrilova, A.Yu., Saginova, L.G., and Zyk, N.V., *Zh. Org. Khim.,* 2003, vol. 39, p. 1084.
3. Bondarenko, O.B., Gavrilova, A.Yu., Saginova, L.G., Zyk, N.V., and Zefirov, N.S., *Izv. Akad. Nauk, Ser. Khim.,* 2003, p. 741; Gazzaeva, R.A., Shabarov, Yu.S., and Saginova, L.G., *Khim. Geterotsikl. Soedin.,* 1984, p. 309.
4. Krayushkin, M.M., Kalik, M.A., Zav'yalova, V.K., Loktionov, A.A., and Bogdanov, V.S., *Khim. Geterotsikl. Soedin.,* 1989, p. 1620.
5. Rai, K.M.L. and Hassner, A., *Indian J. Chem*., 1997, vol. 36B, p. 242; Krayushkin, M.M., Loktionov, A.A., and Belen'kii, L.I., *Khim. Geterotsikl. Soedin.,* 1988, p. 1034; Zyablikova, T.A., Buzykin, B.I., Dokuchaev, A.S., Sokolov, M.P., Gainullin, R.M., and Petrov, M.V., Abstracts of Papers, *Fiz.-Khim. met. issl. strukturno-dinamicheskikh molekulyarnykh sistem. Vseross. soveshch.* (All-Russian Meeting on Physicochemical Methods of Investigating of Structurally Flexible Molecular System), 1994, ch. 1, p. 94.
6. Park, K.P., Shiue, C.-Y., and Clapp, L.B., *J. Org. Chem.,* 1970, vol. 35, p. 2065.
7. Rheinboldt, R., Dewald, M., Jansen, F., and Schmitz-Dumont, O., *Lieb. Ann*., 1927, vol. 451, p. 161; Iwakura, Y., Uno, K., Shiraishi, S., and Hougu, T., *Bull. Chem. Soc. Jpn*., 1968, vol. 41, p. 2954; Torssell, K.B.G., *Nitrile, Oxides, Nitrones, and, Nitronates in Organic Synthesis*, New York: VCH, Publ, 1988.
8. Hegarty, A.F. and Mullane, M., *J. Chem. Soc., Chem. Commun.,* 1984, p. 229.
9. Mochalov, S.S., Kosynkin, D.V., Yudin, I.D., Zavodskikh, K.A., Shabarov, Yu.S., and Zefirov, N.S., *Khim. Geterotsikl. Soedin.,* 1994, p. 472.
10. Kost, A. and Ershov, V.V., *Zh. Obshch. Khim.,* 1957, vol. 11, p. 3874.
11. Levina, R.Ya. and Gembitskii, P.A., *Zh. Obshch. Khim.,* 1961, vol. 31, p. 3480.
12. Saginova, L.G., Bondarenko, O.B., Shabarov, Yu.S, and Gazzaeva, R.A., *Zh. Org. Khim.,* 1984, vol. 20, p. 2124.
13. Shabarov, Yu.S., Potapov, V.K., and Levina, R.Ya., *Zh. Obshch. Khim.,* 1964, vol. 34, p. 1964.
14. Applequist, D. and McKenzie, F., *J. Org. Chem*., 1976, vol. 41, p. 2264.
15. Shabarov, Yu.S., Mochalov, S.S., Novokreshchennykh, V.D., Volkov, E.M., and Ermishkina, S.A., *Zh. Org. Khim.,* 1975, vol. 11, p. 1907.
16. Veselovskaya, S.V., Saginova, L.G., and Shabarov, Yu.S., *Zh. Org. Khim.,* 1987, vol. 23, p. 129.