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NEW ASPECTS OF NITROSATION OF ARYLCYCLOPROPANES: NITROSATION OF PHENYLCYCLOPROPANES WITH BULKY ALKYL SUBSTITUENTS IN THE SMALL RING

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It has been shown for the first time that nitrosation of phenylcyclopropanes with bulky alkyl substituents in the small ring proceeds predominantly with attack of the nitrosonium cation on the benzyl carbon atom of the cyclopropane ring with intermediate formation of an alkyl carbocation. In addition to isoxazolines, 1,2-oxazines and Δ^1-pyrroline N-oxide are formed, formation of the latter is preceded by skeletal rearrangement.

Keywords: 1-alky-2-phenylcyclopropanes, isoxazolines, 1,2-oxazines, Δ^1-pyrroline N-oxide, nitrosation, skeletal rearrangement.

The synthesis of isoxazolines and isoxazoles by the nitrosation of arylcyclopropanes is the most established method for the construction of these heterocycles, to a large extent facilitated by the search for available and effective nitrosating reagents [1, 2]. Widening the range of nitrosating agents in these reactions provided a new contribution to our ideas of the process of nitrosation and the conversion of such cyclopropanes.

Particular attention has been paid to the regiochemistry of the nitrosation of alkylcyclopropanes, directly connected to the spatial interactions of substituents in the small ring.

It is known that in most cases nitrosation of 1,2-disubstituted cyclopropanes leads to the formation of a mixture of isomeric isoxazolines [1, 3]. Thus on nitrosation of 1-methyl-2-phenylcyclopropane the basic reaction product is 3-methyl-5-phenylisoxazoline, formed as a result of opening the C(1)–C(2) bond, while a second isomer appeared, 4-methyl-5-phenylisoxazoline, formed by opening of the C(1)–C(3) bond, probably caused by the formation of steric hindrance on introducing the nitroso group into the small ring. In this connection we were interested in studying the nitrosation of a number of cyclopropanes containing bulky substituents in the small ring. We chose 1-cyclohexyl- (**1**), 1-isopropyl- (**2**), and 1-*tert*-butyl-2-phenylcyclopropanes (**3**) as model substrates.

* Dedicated to Academician of the Russian Academy of Sciences B. A. Trofimov on his 70th jubilee.

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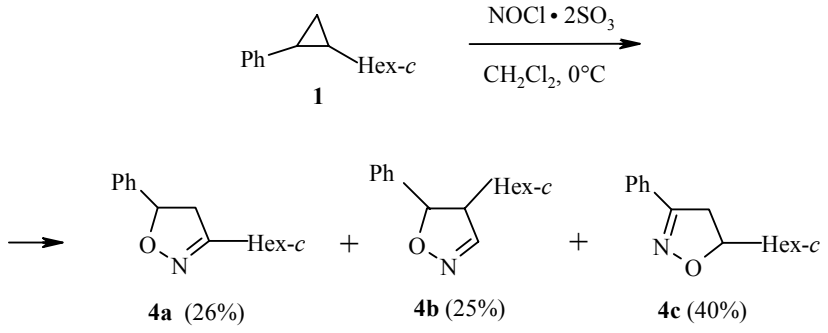
It was suggested that the large volume of the substituent at position 2 of the cyclopropane ring led to a decrease in the fraction of the 3,5-disubstituted isoxazoline, the product of opening the C(1)–C(2) bond, and on increase in the fraction of the corresponding 4,5-isomer, product of opening the C(1)–C(3) bond.

The results we have obtained were unexpected: an increase in the size of the substituent in the small ring led not only to an increase in the content of the 4,5-disubstituted isoxazoline in the reaction mixture, but also to the appearance of atypical products of nitrosation of arylcyclopropanes with opening of the 1,2-disubstituted bond and attack of the nitrosonium cation at the benzyl carbon atom.

For example, in the case of cyclopropane **1** the isomeric isoxazolines **4a-c** were isolated from the reaction mixture, compound **4c** being as the main product. It should be noted that products of nitrosation of arylcylopropanes resulting from attack of the nitrosonium cation on the benzyl carbon atom of the small ring has not been reported in the literature before.

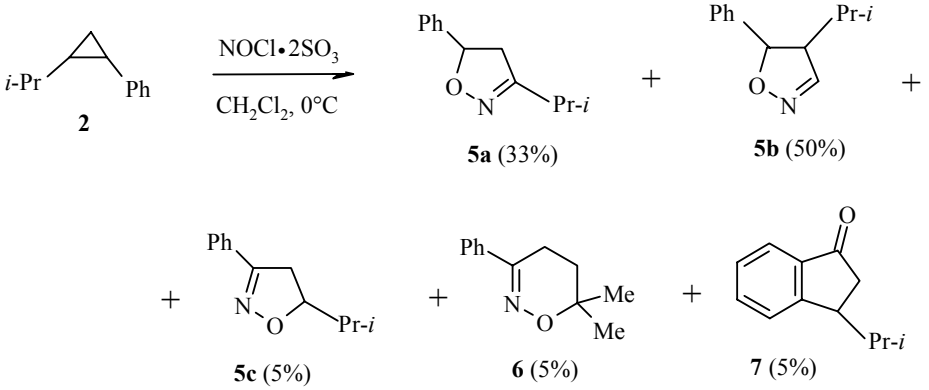


1

4a (26%) **4b** (25%) **4c** (40%)

The structures of compounds **4a-c** were determined from the chemical shifts and multiplicities of the signals in the ^{1}H NMR spectra.

In the spectra of compounds **4a,c** and **4b** a set of signals of the isoxazoline ring were present as ABM and AMX systems respectively. The signals of the CHO proton in the 5.0-6.0 ppm field are characteristic for each isomer. For isomers **4a** and **4c** it appears as a doublet of doublets with two vicinal constants of the order of 8-10 Hz. In isomer **4c** a complication of the signal of the CHO proton is observed as a result of interaction with the protons of the alkyl substituent (an additional coupling constant of 6.8 Hz), while in the isomer **4b** the signal of the CHO appears as a doublet. In addition in the spectrum of isomer **4b** there is a signal of the CH=N proton at weak field which is absent for isomers **4a** and **4c**. The chemical shifts and multiplicities of the remaining signals correspond to the proposed structures (Table 1).



2

5a (33%) **5b** (50%) **5c** (5%) **6** (5%) **7** (5%)

Table 1. ^{1}H NMR Spectra of Alkylarylisoxazolines **4a-c, 5a-c, 8a,b**

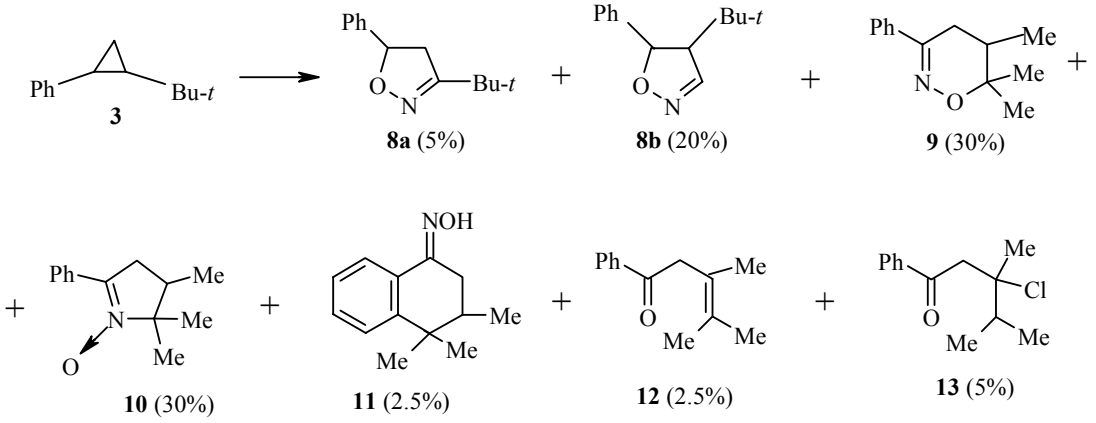
Com-pound	Chemical shifts, δ, ppm (*J*, Hz)					Other signals
	H-4	H-4'	HCO	HC=N	H of the aromatic ring	
4a	2.84 (dd, ^2J = 16.5, ^3J = 7.8)	3.33 (dd, ^2J = 16.5, ^3J = 10.8)	5.46 (dd, ^3J = 10.8, ^3J = 7.8)	—	7.29-7.40 (5H, m)	2.47 (1H, m); 1.6-1.9 (m) and 1.0-1.4 (10H, m)
5a	2.93 (dd, ^2J = 16.8, ^3J = 8.2)	3.39 (dd, ^2J = 16.8, ^3J = 10.8)	5.55 (dd, ^3J = 10.8, ^3J= 8.2)	—	7.31-7.40 (5H, m)	1.21 (3H, d, *J* = 6.8, CH_3); 1.22 (3H, d, *J* = 6.8, CH_3); 2.78 (1H, pent, *J* = 6.8, C<u>H</u>$(CH_3)_2$)
8a	2.93 (ddm, ^3J = 8.0, ^2J = 16.8)	3.38 (ddm, ^3J = 10.9, ^2J = 16.8)	5.58 (dd, ^3J = 8.0, ^3J = 10.9)	—	7.37 (5H, m)	1.61 (9H, s, $3CH_3$)
4b	—	3.10 (td, ^3J = 6.5, ^3J = 1.9)	5.26 (d, ^3J = 6.5)	7.15 (d, ^3J = 1.9)	7.30 (3H, m); 7.37 (2H, m)	1.00-1.18 (3H, m); 1.20-1.30 (3H, m); 1.60-1.90 (5H, m)
5b	—	3.12 (dd, ^3J = 6.3, ^3J = 1.6)	5.24 (d, ^3J = 6.3)	7.14 (d, ^3J = 1.6)	7.28-7.40 (5H, m)	1.07 (3H, d, *J* = 6.8, CH_3); 1.04 (3H, d, *J* = 6.8, CH_3); 1.97 (1H, sext, *J* = 6.5, C<u>H</u>$(CH_3)_2$)
8b	—	3.03 (dd, ^3J = 5.3, ^3J = 1.9)	5.28 (d, ^3J = 5.3)	7.11 (d, ^3J = 1.9)	7.27 (3H, t), 7.36 (2H, m)	1.05 (9H, s, $3CH_3$)
4c	3.07 (dd, ^2J = 16.4, ^3J = 8.8)	3.30 (dd, ^2J = 16.4, ^3J = 10.6)	4.50 (ddd, ^3J = 10.6, ^3J = 8.8; ^3J = 6.8)	—	7.37 (3H, m); 7.64 (2H, m)	1.96 (1H, m); 1.00-1.30 (m) and 1.50-1.80 (m, 10H)
5c	3.05 (dd, ^2J = 16.6, ^3J = 8.8)	3.33 (dd, ^2J = 16.6, ^3J = 10.6)	4.52 (ddd, ^3J = 10.6, ^3J = 8.8, ^3J = 6.7)	—	7.40 (3H, m) 7.69 (2H, m)	0.99 (3H, d, *J* = 6.6, CH_3); 1.05 (3H, d, *J* = 6.6, CH_3); 1.95 (1H, m, C<u>H</u>$(CH_3)_2$)

Table 2. ^{13}C NMR Spectra of Isoxazolines **4a-c, 5a-c, 8b**

Compound	Chemical shifts, δ, ppm							
	CH_2 CHR	CHO	C=N	Aromatic carbon atoms				Other atoms
				C-1	C(2)H, C(6)H	C(3)H, C(5)H	C-4	
4a		81.0	157.5	141.4	128.5	125.5	127.7	25.8 ($3CH_2$), 26.0, 30.4, 37.25 (CH)
5a	43.3	81.3	163.1	141.4	128.7	125.7	128.0	20.1 ($2CH_3$), 27.9 ($\underline{C}H(CH_3)_2$)
4b	63.9	83.4	147.8	141.7	128.7	125.6	127.9	26.01, 26.04, 26.20, 30.7, 31.0, 40.1 (CH)
5b	64.7	83.5	147.8	141.6	128.7	125.5	128.0	19.9 (CH_3), 20.3 (CH_3), 30.3 ($\underline{C}H(CH_3)_2$)
8b	69.2	81.5	145.5	142.4	125.1	128.6	127.6	27.5 ($3CH_3$), 33.1 (C_{quat}),
4c	42.5	85.8	156.4	126.2	128.7	126.6	129.9	25.7, 25.9, 26.3, 28.6, 31.9 (CH), 37.4

More complex mixtures of reaction products were obtained from the nitrosation of 1-isopropyl- and 1-*tert*-butyl-2-phenylcyclopropanes. In the case of hydrocarbon **2** the isoxazolines **5a** and **5b** were isolated as the main components, with the amount of **5b** exceeding that of **5a** by a half. Small quantities of the isoxazoline **5c,** the oxazine **6**, and 3-isopropylindanone-1(**7**) were also formed.

In the case of hydrocarbon **3** only 5% of the isoxazoline **8a** was isolated, the amount of isoxazoline **8b** isolated corresponded to 20% of the initial cyclopropane, 5-*tert*-butyl-3-phenylisoxazoline was not observed among the reaction products. The main reaction products were the corresponding oxazine **9** (30%) and the pyrroline N-oxide **10** (30%). Small quantities of a fraction consisting of a mixture of the oxime **11** and the ketones **12, 13** were also isolated.



The composition and structures of compounds **6**, **7**, **9-13** were established on the basis of NMR and IR spectroscopy, mass spectrometry, and elemental analyses.

Oxazine **9** was isolated in the pure state, while compound **6** was characterized in a mixture with isoxazoline **5b**. The *m/z* molecular ion values of compounds **6** and **9** are respectively 189 and 203, i.e., these compounds are structural isomers of the corresponding isoxazolines **5** and **8**. Analysis of the chemical shifts and

multiplicities of the signals of the aliphatic portion of the ^{1}H NMR spectra shows the change in structure of the alkyl substituent which in this case can only arise if the reaction center is the carbon atom bonded to the substituent. Fragmentation of the molecular ions corresponds to the structures **6** and **9**.

In the case of cyclopropane **3** a single compound with a molecular ion $[M]^+$ 203 and a small value of R_f was isolated in pure form. The character and multiplicity of the proton signals were identical with those of oxazine **9**, but were shifted by 0.3-0.5 ppm to weak field. We assigned structure **10** to this compound. The data of the ^{1}H NMR spectrum of the isolated compound did not disagree with the proposed structure **10**.

The ketone **7** was isolated in pure form, while oxime **11** was characterized in a mixture with compounds **12** and **13**. A carbonyl absorption at 1690 cm^{-1} appears in the IR spectrum of compound **7**. The signal of the C=O carbon appears at 198.2 ppm in its ^{13}C NMR spectrum.

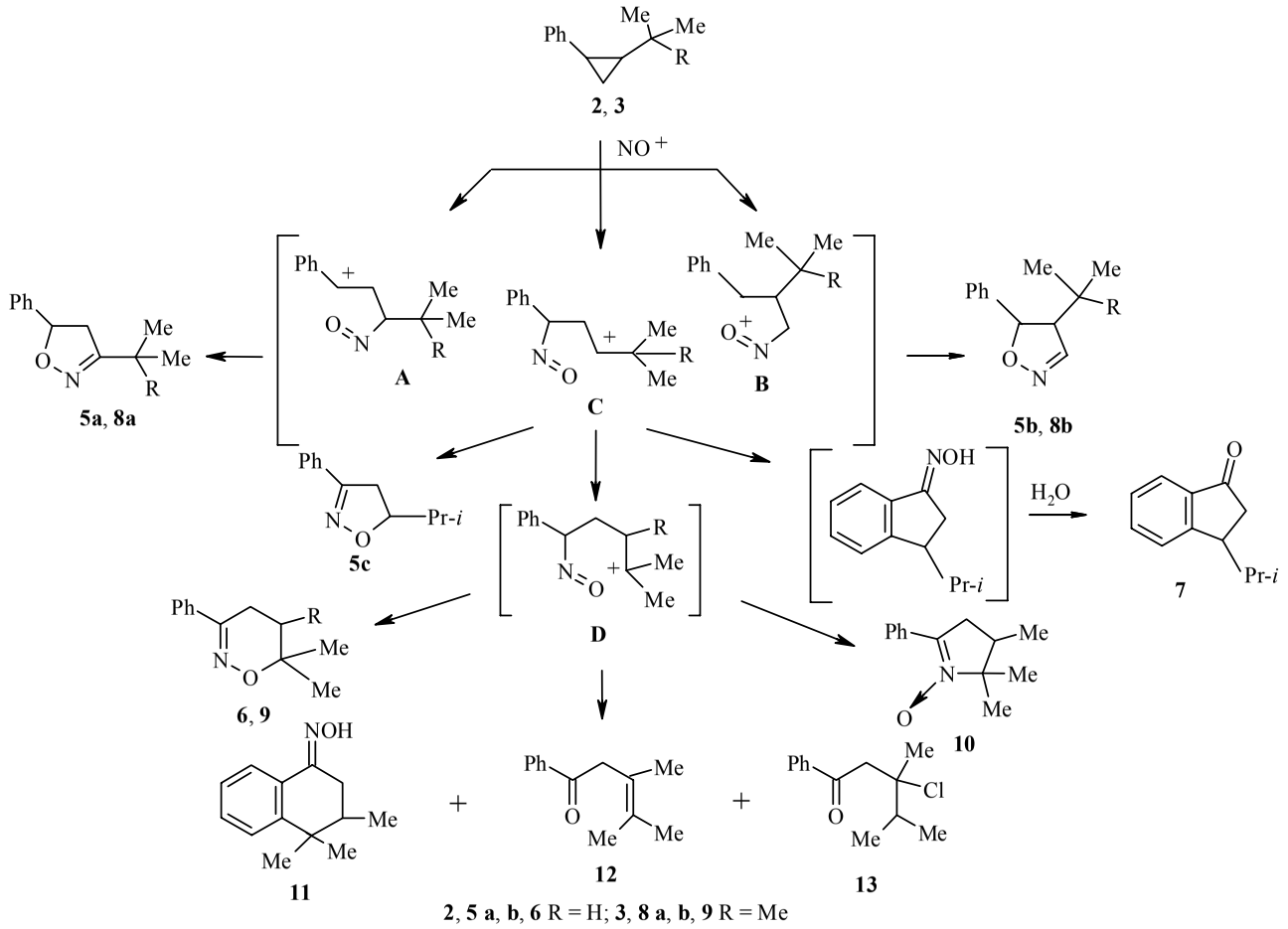
The IR spectrum of the first fraction isolated from the reaction mixture obtained from the nitrosation of hydrocarbon **3** showed the presence of an oxime unit and a carbonyl group (1690, 3300-3500 cm^{-1}). Chromato-mass spectroscopic analysis of the mixture of these compounds, taking into account the multiplicities and integrated intensities of the proton signal in the ^{1}H NMR spectrum permitted the assignments of structures **11-13** to these compounds.

In their ^{1}H NMR spectra the signals of the protons of the CH_2 group of compounds **7** and **11** appear as doublets of doublets with large geminal couplings of ~ 17 Hz and vicinal couplings within the limits of 4.5 and 9.5 Hz. The signal of the H-3 proton for ketone **7** and oxime **11** are multiplets appearing at 2.83 and 2.22 ppm respectively. In the indanone **7** it is shifted to lower field because it is found in the benzyl position relative to the aromatic ring. The isopropyl fragment is retained in ketone **7**, whereas in the spectrum of compound **9** signals of three different methyl groups are observed which indicated the rearrangement of the hydrocarbon skeleton. The character of the signals of the aromatic region in the ^{1}H and ^{13}C NMR spectra indicate the presence of an *ortho* substituent in the aromatic ring.

Despite the various structures of compounds **6**, **7**, and **9-13 ,** they are all formed as a result of an initial attack of the nitrosonium cation at the benzyl carbon atom of the small ring with subsequent opening of the 1,2-disubstituted bond of the cyclopropane ring and formation of a carbocation center (**C**). Subsequently different stabilization of the intermediate is possible: by participation of an internal nucleophile (the oxygen of the nitroso group – the 1,2-oxazines **6** and **9**, the nitrogen atom of the nitroso group – the Δ^1-pyrroline N-oxide **10**), an external nucleophile (a chlorine atom – ketone **12**), elimination of a proton (unsaturated ketone **13**), or electrophilic attack of a carbocation on the aromatic ring (ketone **7**, oxime **11**). We note that, in the case of the *tert*-butyl radical, all of the following conversions precede skeletal rearrangement with participation of the substituent with formation of a stable tertiary carbocation **D**, which is analogous to the hydride shift which precedes the cyclization for the formation of oxazine **6**.

Thus the whole range of compounds obtained as a result of nitrosation of hydrocarbons **2** and **3**, including isoxazolines **5a,b** and **8a,b**, are formed from the carbocations **A** and **B** respectively, can be described by the scheme on the p. 1280.

It follows from these studies that with increasing size of the alkyl substituent in 1-alkyl-2-phenyl-cyclopropanes spatial factors play role and the attack of the nucleophile predominates at the unsubstantiated carbon on the small ring (the yield of the 4,5-disubstituted isoxazoline is equal to or exceeds the yield of the 3,5-disubstituted isomer in the case of hydrocarbons **1** and **2, 3** respectively). In the isopropyl, cyclohexyl, and *tert*-butyl series of substituents the preference for the attack of the nitrosonium cation at the benzyl carbon atom of the smaller ring with opening of the C(1)–C(2) bond increases: the overall yield of products formed as a result of this reaction is 10, 40, and 74% respectively. The solution to the question whether this is connected only with the size of the substituent or is associated with the influence of other factors requires further investigation.


2, 3
NO+
A
B
C
D
5a, 8a
5b, 8b
5c
6, 9
7
10
11
12
13
H2O
2, 5 a, b, 6 R = H; 3, 8 a, b, 9 R = Me

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions with HMDS (δ 0.05 ppm) as internal standard were recorded on a Bruker Avance 400 instrument (400 and 100 MHz respectively). IR spectra of nujol mulls or thin films were recorded on UR-20 spectrometer, mass spectra were recorded on Finnigan MAT SSQ 7000 chromato-mass spectrometer, ionization energy 70 eV, quartz capillary column OV-1 (25 m), temperature regime: 70 (2 min) -20 (1 min) -280°C (10 min). Elemental analyses of the compounds synthesized were determined on a Carlo-Erba CHN-analyzer. Melting points were determined on a block in open capillaries. R_f values were determined on Silufol plates in 1:10 ethyl acetate–petroleum ether (compounds **4-9**, **11-13**) or 2:1 ethyl acetate–petroleum ether (compound **10**).

The phenylcyclopropanes **1-3** were synthesized by a known method by decomposition of the corresponding pyrazolines [4] and were used in reactions as a mixture of the *cis* and *trans* isomers.

Syntheses of Isoxazolines from Arylcyclopropanes and NOCl·2SO$_3$ (General Method). An equimolar quantity of an arylcyclopropane in methylene chloride (2ml) was added to a suspension of $NOCl·2SO_3$ (1 mmol) in methylene chloride (10 ml) at 0°C. The solid dissolved partially and the solution became colored. At the end of the reaction (monitored by TLC) the reaction mixture was neutralized with sodium carbonate solution and washed with water. The water layer was extracted with methylene chloride (3×10 ml), the extract was dried with Na_2SO_4, the solvent was evaporated, and the reaction products were isolated chromatographically.

Compounds 4a-c were prepared by the reaction of 2-cyclohexyl-1-phenylcyclopropane (**1**) (400 mg, 2 mmol) and $NOCl·2SO_3$ (450 mg, 2 mmol) for 2 h at 0°C after standard treatment of the reaction mixture and chromatographic isolation on a column (SiO_2 40/100, 1:10 ethyl acetate–petroleum ether).

3-Cyclohexyl-5-phenylisoxazoline (4a). Yield 134 mg (26%). R_f 0.40. Mass spectrum, *m/z* (I_{rel}, %): 229 $[M]^+$ (37), 161 (89), 117 (14), 104 (100), 91 (17), 83 (8), 77 (13), 55 (13).

4-Cyclohexyl-5-phenylisoxazoline (4b). Yield 129 mg (25%). R_f 0.42. Mass spectrum, *m/z* (I_{rel}, %): 229 $[M]^+$ (77), 186 $[M\text{-}HCNO]^+$ (35), 146 $[M\text{-}C_6H_{11}]^+$ (100), 130 (97), 117 (28), 107 (88), 104 (85), 91 (42), 83 (40), 55 (62).

5-Cyclohexyl-3-phenylisoxazoline (4c). Yield 206 mg (40%). R_f 0.44. IR spectrum, ν, cm^{-1}: 1675 (C=N), 1600. Mass spectrum, *m/z* (I_{rel}, %): 229 $[M]^+$ (44), 146 $[M\text{-}C_6H_{11}]^+$ (100), 118 (62), 104 (16), 91 (42), 77 (33), 55 (18).

Compounds 5a-c, 6, and **7** were obtained as a result of the reaction of 1-isopropyl-2-phenylcyclopropane (**2**) (473 mg, 3 mmol) and $NOCl·2SO_3$ (677 mg, 3 mmol) for 2 h at 0°C after standard work-up of the reaction mixture and chromatographic separation on a column (SiO_2 40/100, 1:10 ethyl acetate–petroleum ether).

3-Isopropyl-5-phenylisoxazoline (5a). Yield 180 mg (33%). R_f 0.25. Found, %: C 76.25; H 8.10; N 7.26. $C_{12}H_{15}NO$. Calculated, %: C 76.19; H 7.94; N 7.41.

4-Isopropyl-5-phenylisoxazoline (5b). Yield 280 mg (50%). R_f 0.31. Mass spectrum, *m/z* (I_{rel}, %): 189 $[M]^+$ (55), 146 $[M\text{-}HCNO]^+$ (55), 131 $[M\text{-}HCNO\text{-}CH_3]^+$ (100), 115 (27), 107 (51), 91 (52), 77 (36), 51 (12). Found, %: C 76.29; H 7.75; N 7.65. $C_{12}H_{15}NO$. Calculated, %: C 76.19; H 7.94; N 7.41.

6,6-Dimethyl-3-phenyl-5,6-dihydro-4H-1,2-oxazine (6) (isolated and characterized in a mixture with isoxazoline **5b**). Yield 28 mg (5%). R_f 0.29. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (6H, s, $2CH_3$); 1.90 (2H, t, *J* = 7.0, CH_2); 2.60 (2H, t, *J* = 7.0, CH_2); 7.40 (3H arom, m); 7.74 (2H arom, m). ^{13}C NMR spectrum, δ, ppm: 15.6 ($2CH_3$); 19.7 (CH_2); 29.6 (CH_2); 73.83 (CO); 125.2, 128.4, 129.2 (C- 4); 136.09 (C-1); 152.87 (C=N). Mass spectrum, *m/z* (I_{rel}, %): 189 $[M]^+$ (100), 174 $[M–CH_3]^+$, (72), 130 $[M\text{-}CH_3\text{-}CH_3CHO]^+$ (44), 117 $[PhCNCH_2]^+$ (19), 103 $[PhC=N]^+$ (63), 77 (54).

5-Isopropyl-3-phenylisoxazoline (5c). Yield 25 mg (5%) (separated and characterized in a mixture with ketone **7**). R_f 0.40, Mass spectrum, *m/z* (I_{rel}, %): 189 $[M]^+$ (33), 146 $[M\text{-}i\text{-}Pr]^+$ (22), 118 (100), 104 (17), 91 (39), 77 (74), 51 (46).

3-Isopropylindanone-1 (7). Yield 26 mg (5%). R_f 0.42. IR spectrum, ν, cm^{-1}: 2970-2890, 1690 (C=O), 1605, 1460, 1310, 1290, 775. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 (3H, d, *J* = 6.9, CH_3); 1.43 (3H, d, *J* = 7.0, CH_3); 2.18 (1H, m, $\underline{H}C(CH_3)_2$); 2.43 (1H, dd, *J* = 17.0, *J* = 7.0, CH_2); 2.83 (1H, m, *i*-Pr-C$\underline{H}$); 2.89 (1H, dd, *J* = 17.0, *J* = 4.5, CH_2); 7.32 (1H, dt, *J* = 7.8, *J* = 0.6, H-6 arom); 7.36 (1H, d, *J* = 7.8, H-4 arom); 7.53 (1H, dt, *J* = 7.8, *J* = 1.4, H-5 arom); 8.03 (1H, dd, *J* = 7.8, *J* = 1.4, H-7 arom). ^{13}C NMR spectrum, δ, ppm: 20.3 (CH_3); 20.6 (CH_3); 35.4 ($\underline{C}(CH_3)_2$); 39.9 (*i*-Pr-$\underline{C}$); 43.4 (CH_2); 126.4, 126.7, 128.3, 131.6 (C_{quat}); 133.9, 147.7 (C_{quat}); 198.2 (C=O). Mass spectrum, *m/z* ($I_{rel,}$ %): 174 $[M]^+$ (50), 159 $[M\text{-}CH_3]^+$ (43), 132 (100). 131 (74), 115 (30),104 (84), 91 (27), 78 (47), 51 (41). Found, %: C 82.89; H 8.20. $C_{12}H_{14}O$. Calculated, %: C 82.76; H 8.05.

Compounds 8a,b, 9-13 were obtained as a result of the reaction of 1-*tert*-butyl-2-phenylcyclopropane (**3**) (470 mg, 2.7 mmol) and $NOCl{\cdot}2SO_3$ (677 mg, 3 mmol) for 2 h at 0°C after standard work-up of the reaction mixture and column chromatographic separation (SiO_2, 40/100, 1:10 ethyl acetate–petroleum ether). R_f 0.54.

3-*tert*-Butyl-5-phenylisoxazoline (8a). Yield 25 mg (5%). R_f 0.30.

4-*tert*-Butyl-5-phenylisoxazoline (8b). Yield 110 mg (20%). R_f 0.36. IR spectrum, ν, cm^{-1}: 1680 (C=N), 1600. Mass spectrum: *m/z* (I_{rel}, %): 203 $[M]^+$ (40), 147 $[M - t\text{-}Bu]^+$ (87), 130 (100), 115 (19), 105 (15), 77 (18), 57 (*t*-Bu) (75).

5,6,6-Trimethyl-3-phenyl-5,6-dihydro-4H-1,2-oxazine (9). Yield 160 mg (30%). R_f 0.32. IR spectrum, ν, cm^{-1}: 1660 (C=N), 1595. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 (3H, d, ^3J = 6.8, CH_3); 1.15 (3H, s, CH_3); 1.38 (3H, s, CH_3); 2.00 (1H, m, C$\underline{H}CH_3$); 2.15 (1H, dd, ^3J = 9.9, ^2J = 18.2, CH_2); 2.62 (1H, dd, ^3J = 5.9, ^2J = 18.2, CH_2); 7.34 (3H arom); 7.70 (2H arom). ^{13}C NMR spectrum, δ, ppm: 16.76 (CH_3); 18.82 (CH_3); 25.74 (CH_3); 27.80 (CH_2); 32.82 (CH); 77.18 ($CO(CH_3)_2$); 125.04 (C-2,3 arom); 128.17 (C-2,3 arom); 128.91 (C-4 arom); 136.02 (C-1 arom); 153.50 (C=N). Mass spectrum, *m/z* (I_{rel}, %): 203 $[M]^+$ (70), 188 $[M\text{-}CH_3]^+$ (5), 160 (10), 144 (36), 130 (100), 118 (84), 104 (65), 103 (58), 77 (40), 59 (28), 43 (21).

4,5,5-Trimethyl-2-phenyl-Δ^1-pyrroline N-Oxide (10). Yield 160 mg (30%). R_f 0.41. IR spectrum, ν, cm^{-1}: 2980-2940, 2860, 1540, 1450, 1370, 1220. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.17 (3H, d, ^3J = 6.9, CH_3); 1.28 (3H, s, CH_3); 1.47 (3H, s, CH_3); 2.31 (1H, m, C$\underline{H}CH_3$); 2.62 (1H, dd, ^3J = 9.2, ^2J = 16.3, CH_2); 3.15 (1H, dd, ^3J = 8.0, ^2J = 16.3, CH_2); 7.41 (3H arom); 8.83 (2H arom). ^{13}C NMR spectrum, δ, ppm: 14.81 (CH_3); 19.49 (CH_3); 25.15 (CH_3); 35.17 (CH_2); 37.34 (CH); 77.59 ($N\underline{C}(CH_3)_2$); 127.01 (C-2,3 arom); 128.13 (C-2,3 arom); 129.43 (C-4 arom); 129.92 (C-1 arom); 136.19 (C=N). Mass spectrum, *m/z* (I_{rel}, %): 203 $[M]^+$ (90), 188 $[M\text{-}CH_3]^+$ (26), 171 (12), 118 (41), 103 (100), 91 (19), 83 (45), 77 (59), 55 (31), 41 (49).

3,4,4-Trimethyl-3,4-dihydronaphthalin-1(2H)-one Oxime (11) (separated and characterized in a mixture with ketones **12** and **13**). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, d, ^3J = 6.9, CH_3); 1.44 (6H, s, $2CH_3$); 2.22 (1H, m, C$\underline{H}CH_3$); 2.55 (1H, dd, ^3J = 9.5, ^2J = 17.4, CH_2); 2.79 (1H, dd, ^3J = 4.5, ^2J = 17.4, CH_2); 7.31 (1H arom); 7.47 (1H arom); 7.55 (1H arom); 8.04 (1H arom). Mass spectrum, *m/z* (I_{rel}, %): 203 $[M]^+$ (33), 170 (60), 160 (19), 141 (56), 118 (100), 105 (40), 83 (34), 57 (20).

3,4,4-Trimethyl-1-phenylbuten-3-one (12) (separated and characterized in a mixture with ketone **13** and oxime **11**). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.29 (6H, s, $2CH_3$); 1.59 (3H, s, CH_3); 3.13 (1H, d, ^3J = 16.5, CH_2); 3.38 (1H, d, ^3J = 16.5, CH_2); 7.41 ($3H_{arom}$); 7.68 ($2H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 188 $[M]^+$ (5), 173 (9), 147 (81), 146 (50), 130 (100), 117 (11), 115 (24), 77 (25), 83 (43), 57 (66).

3-Chloro-3,4,4-trimethyl-1-phenylbutanone (13) (isolated and characterized in a mixture with ketone **12** and oxime **11**). ^{1}H NMR spectrum, δ ppm (*J*, Hz): 0.99 (3H, d, ^3J = 6.84, CH_3); 1.04 (3H, d, ^3J = 6.75, CH_3); 1.40 (3H, s, CH_3); 2.93 (1H, d, ^2J = 16.6, CH_2); 3.21 (1H, d, ^2J = 16.6, CH_2); 7.41 (3H arom); 7.68 (2H arom). Mass spectrum, *m/z* (I_{rel}, %): 224 $[M]^+$ (5),188 (53), 173 (100), 145 (61), 131 (81), 117 (26), 105 (11), 103 (11), 77 (11).

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