Silylation of γ,γ-bis(alkoxycarbonyl)-substituted aliphatic nitro compounds: synthesis of *N*,*N*-bis(trimethylsilyloxy)aminocyclopropanes*

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Silylation of γ,γ-bis(alkyloxycarbonyl)-β-aryl- and γ,γ-bis(alkyloxycarbonyl)-β-alkyl-substituted aliphatic nitro compounds proceeds stereoselectively to give the corresponding *N*,*N*-bis(trimethylsilyloxy)aminocyclopropanes in high yields. These compounds can be used as synthetic equivalents of nitrosocyclopropanes.

Key words: aliphatic nitro compounds, silylation, *N*,*N*-bis(trimethylsilyloxy)aminocyclopropanes, nitrones.

Silylation of aliphatic nitro compounds (ANC) opens up new possibilities for their utilization in organic synthesis.[2] Thus it has been demonstrated that ANC containing electron-withdrawing substituents in the γ-position can be transformed into oximes of α,β-unsaturated carbonyl compounds,[3,4] *N*,*N*-bis(trialkylsilyloxy)enamines,[5,6] *N*,*N*-divinylhydroxylamines,[7,8] and some other products.[9]

In the reactions studied, silyl nitronates **A** or *N*,*N*-bis(silyloxy)enamines **B** served as the key intermediates (Scheme 1). However, the transition of silyl nitronates **A** into *N*,*N*-bis(silyloxy)enamines **B** in the course of silylation of ANC can be accompanied by the formation of stabilized cationic intermediates of the type **C** or **C′**.** Intramolecular cyclization of these cations can afford dihydrofurans **D** or cyclopropanes **E**, respectively. Activation of protons at the C_γ atom of ANC should favor enolization of the carbonyl group and, consequently, the formation of products of the type **E**.

The previously unknown *N*,*N*-bis(silyloxy)aminocyclopropanes **E** are of interest as promising precursors of presumably potent biologically active β-aminocyclopropanecarboxylic acids,[11,12] which have not been described in the literature.

In the present study, silylation of γ,γ-bis(alkoxycarbonyl)-substituted ANC (**1**) aimed at the synthesis of the corresponding *N*,*N*-bis(silyloxy)aminocyclopropanes was examined in detail. From the aforesaid, it is compounds **1** that can be considered as the most promising starting compounds in the synthesis of cyclopropanes **2**.

* This article is dedicated to Academician M. G. Voronkov on the occasion of his 80th birthday. For the preliminary communication, see Ref. 1.

** The formation of analogous bicyclic cations has been discussed in the literature.[10]

Results and Discussion

The principal results of silylation of ANC **1** under the action of Me_3SiBr in the presence of Et_3N are presented in Scheme 2 and Table 1.

The nature of silylation products depends substantially on the character of the substituents in the β-position of the starting ANC **1**. Thus the reactions of ANC **1** containing the methyl or an aryl substituent in the β-position afforded stereoselectively only the *trans* isomers of the target cyclopropanes **2**; the structures were

Table 1. Silylation of $(MeO_2C)_2CHCR^1R^2CH_2NO_2$ (**1**) under the action of Me_3SiBr/Et_3N

Starting ANC **1**	R^1	R^2	Time/days (at −30 °C)	Product	Yield (%)[a]
1a	C_6H_5	H	3	**2a**	97
1b	2-$MeOC_6H_4$	H	7	**2b**	90
1c	3-$MeOC_6H_4$	H	3	**2c**	90
1d	4-$MeOC_6H_4$	H	3	**2d**	85
1e	3-$NO_2C_6H_4$	H	3	**2e**	95
1f	4-$NO_2C_6H_4$	H	5	**2f**	95
			1	**3f**	33[b]
			3	**3f**	21[c]
				2f	45
1g	4-ClC_6H_4	H	3	**2g**	80
1h	4-MeC_6H_4	H	3	**2h**	95
1i	Me	H	4	**2i**	76
1j[d]	Me	Me	8[e]	**3j**	65
1k	H	H	3	**4**	90[f]

[a] The yields were determined with the use of the quantitative standard ($ClCH_2CH_2Cl$) from the ^1H NMR spectroscopic data.
[b] The conversion **1f** → **3f** was 35%.
[c] The conversion **3f** → **2f** was 69%.
[d] $(EtOOC)_2CHCMe_2CH_2NO_2$.
[e] At 0 °C.
[f] With respect to the product distilled.

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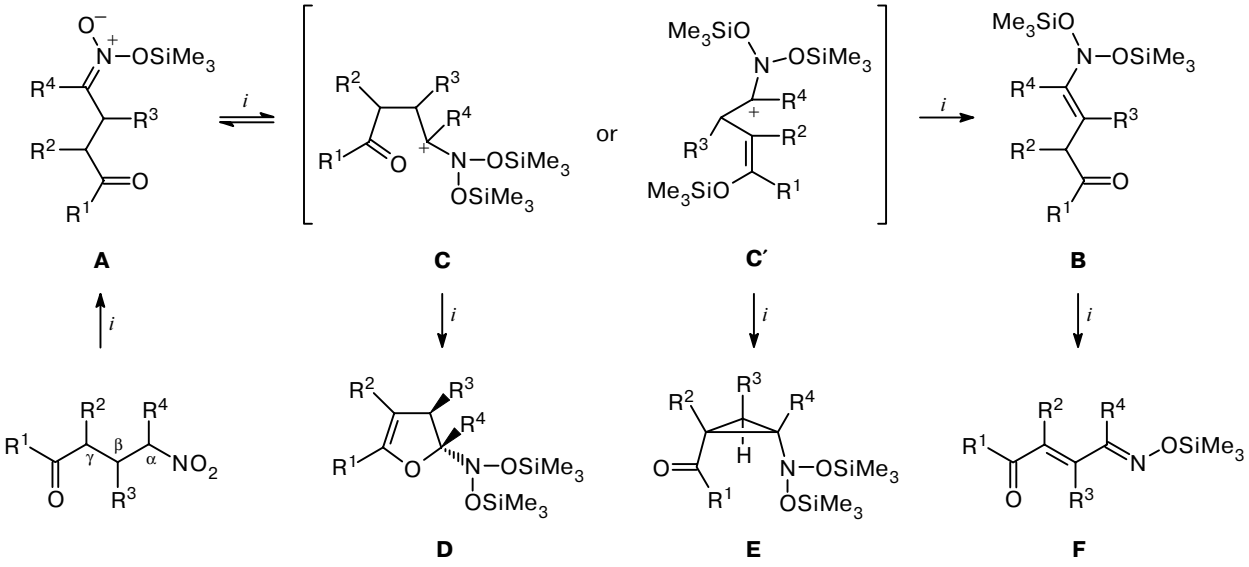
Scheme 1



i. Silylation.

elucidated as described below. Silylation of ANC containing two methyl groups in the β-position with respect to the nitro group (**1j**) proceeded much more slowly and yielded only silyl nitronate **3j** (at −30 °C). Under more drastic conditions (Me_3SiOTf/Et_3N, 20 °C), silylation of **1j** gave rise to a mixture of unidentified products.

We also did not observe the formation of the target cyclopropane **2k** upon silylation of ANC **1k** devoid of substituents in the β-position. The latter reaction yielded silylated conjugated enoxime **4** as the only product, which underwent desilylation to give enoxime **5**. Previously, we have obtained an analogous result[4] when performing silylation of methyl γ-nitrobutyrate under similar conditions.

Thus, silylation of ANC bearing two methoxycarbonyl groups in the γ-position affords either cyclopropanes **2** or silylated α,β-unsaturated oxime **4**; the process can also be terminated at the stage of formation of silyl nitronate **3** (see Table 1).

The most probable mechanism of the formation of these compounds is shown in Scheme 2. The first stage involves generation of silyl nitronates **3** as evidenced by the facts that silylation of ANC **1f** (under conditions of incomplete conversion of **1f**) afforded compound **3f** and that silylation of sterically crowded ANC **1j** gave rise to compound **3j**.

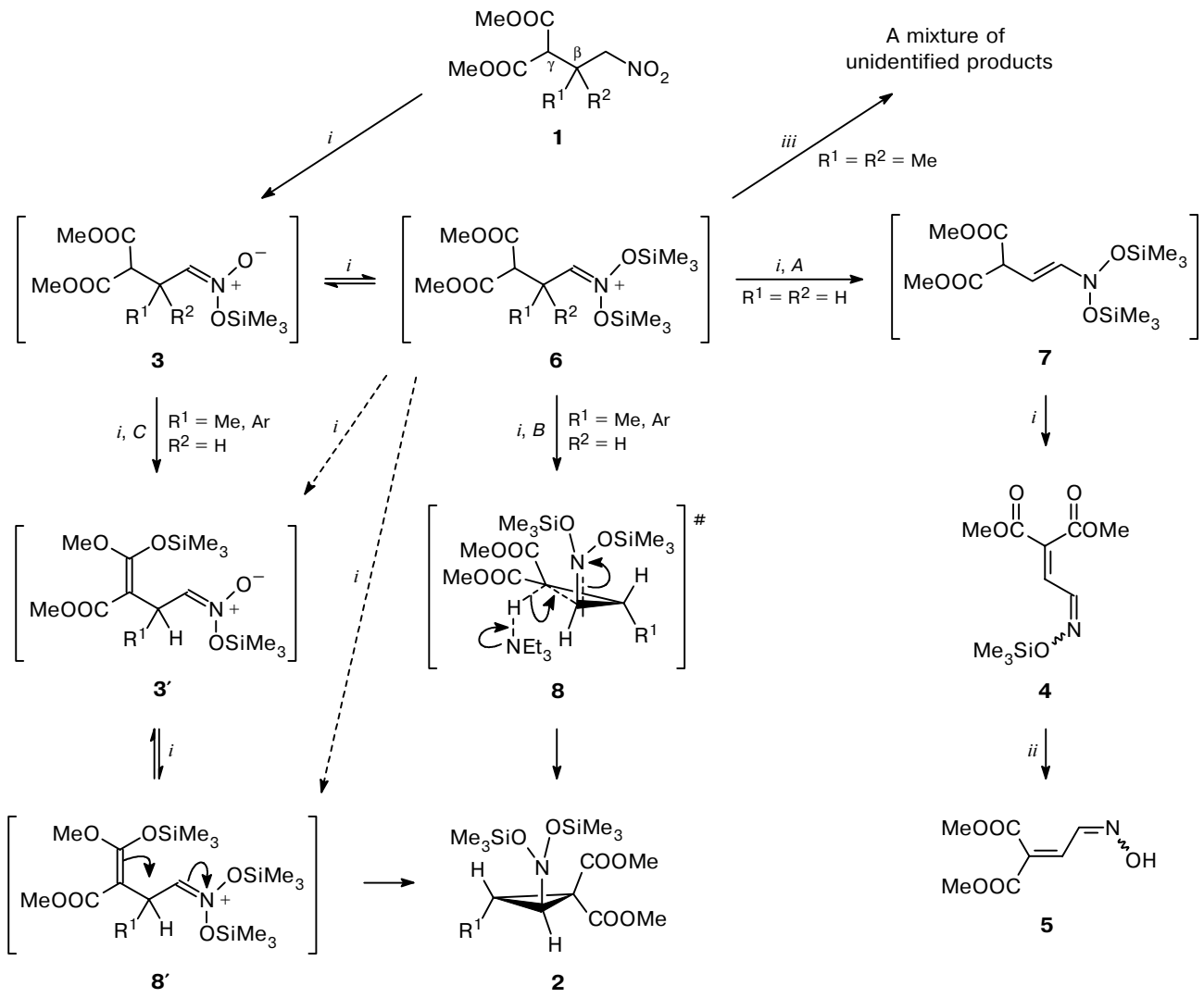
Silyl nitronates **2** can exist in equilibrium with carboimmonium cations **6**, which are typically stabilized through the proton abstraction giving rise to *N*,*N*-bis(silyloxy)enamines of the type **7** (the reaction **A** → **B**, see Scheme 1). Silylation of γ-functionalized ANC **1k**, which contains no substituents at the C_β atom, follows the same pathway (path *A*, see Scheme 2). Apparently, substituents at the C_β atom of ANC create steric hindrances to the approach of Et_3N to the β-proton thus slowing down the formation of *N*,*N*-bis(silyloxy)enamines of the type **7** by the path *A* and facilitating the formation of *N*,*N*-bis(silyloxy)aminocyclopropanes **2**.

The formation of cyclopropanes **2** from carboimmonium cations of the type **6** can follow two pathways. Thus cyclization of cation **6** *via* intermediate **8** is highly probable (path *B*). In this case, assuming that the stages **1** → **3** and **3** → **6** are fast, the rate of formation of cyclopropane **2** should depend on the concentration of Et_3N. This was the case in the silylation of ANC **1a**. At the concentration of Et_3N of 0.38 mol L^{-1}, the conversion **1a** → **2a** was 33%, whereas this reached 87% as the concentration of Et_3N was increased to 0.53 mol L^{-1} (in both cases, $T = -28$ °C, $t = 20$ h, the concentrations of Me_3SiBr and **1a** were 0.45 and 0.134 mol L^{-1}, respectively). The formation of a mixture of **2f** and **3f** in the case of incomplete conversion of ANC **1f** under the conditions of silylation is also a circumstantial evidence that the synthesis of cyclopropane **2** proceeded by the path *B*.

However, based on the above-mentioned facts, the possibility of the formation of cyclopropanes **2** by the path *C* cannot be ruled out. In the latter case, cation **8′** is a kinetically independent intermediate. The probable pathways of the formation of cation **8′** are shown in Scheme 2. However, malonates are generally transformed into the corresponding silylketene acetals under more drastic conditions, *viz.*, in the presence of the stronger silylating reagent ($Me_3SiOSO_2CF_3/Et_3N$) at 20 °C.[13]

It should be noted that cyclopropanes **2** are hydrolytically unstable. In air, pure crystalline or oily products

Scheme 2



2 are gradually transformed into the starting ANC **1**. The same process was observed upon dissolution of cyclopropanes **2** in methanol, the conversion into the starting ANC **1** being virtually quantitative (Scheme 3).

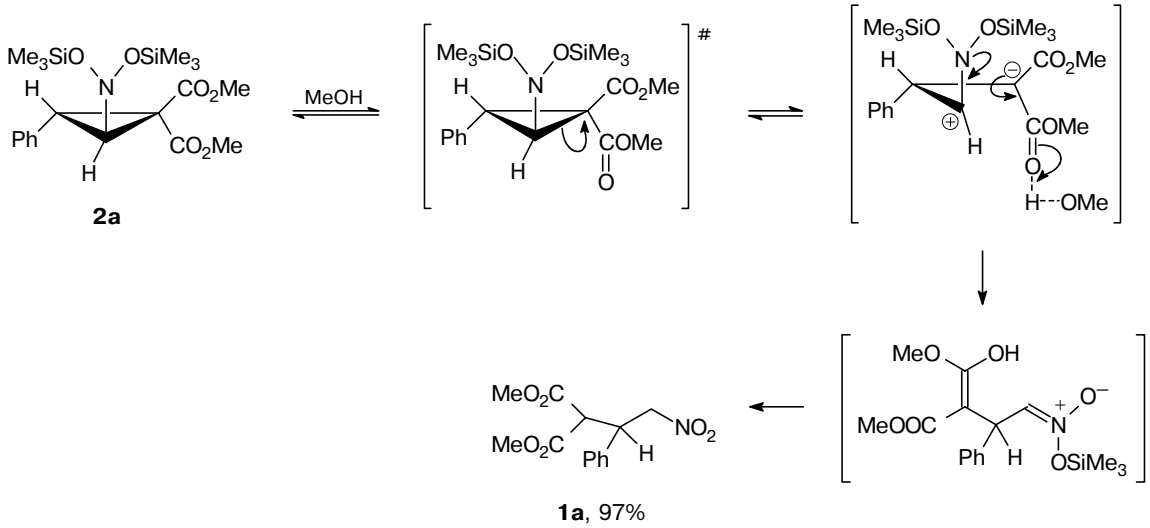
Apparently, the hydrolytic instability of compounds **2** is associated with the fact that the strained endocyclic C—C bond readily undergoes heterolytic cleavage due to stabilization of the resulting charges by two MeOOC groups and the $(Me_3SiO)_2N$ fragment. At the same time, cyclopropanes **2** dissolved in light petroleum withstand treatment with water, which substantially facilitates their isolation.

Cyclopropanes **2** can be considered as synthetic equivalents of nitrosocyclopropanes **9**, which are still poorly studied[14—19] (Scheme 4).

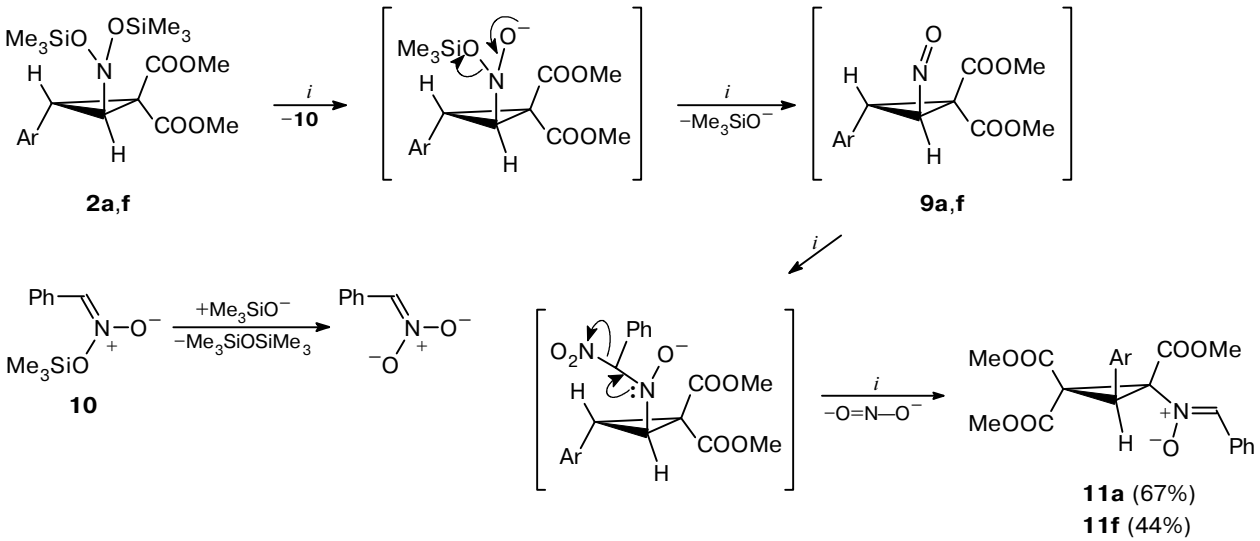
Treatment of compounds **2** with nucleophilic reagents which are able to desilylate the $(Me_3SiO)_2N$ fragment (for example, with the $PhCH(NO_2)^-$ anion) afforded nitrosocyclopropanes **9**; under the reaction conditions, the nucleophile is regenerated upon the reaction of the resulting silyl nitronate **10** with the Me_3SiO^- anion. Nitrosocyclopropanes **9a**,**f** thus formed were captured by the same $PhCH(NO_2)^-$ anion giving rise to the *trans-Z*-isomers of nitrones **11a** (67%) and **11f** (44%), respectively.[20] Nitrones **11** are thermally labile and virtually completely decompose on storage in solutions at room temperature for two days to give a mixture of unidentified products.

Cyclopropanes **2a—k** contain a new structural fragment, *viz.*, the $(Me_3SiO)_2N$ group bound to the sp^3-hybridized C atom. Hence, their structures call for

Scheme 3



Scheme 4



Ar = Ph (**a**), 4-$NO_2C_6H_4$ (**f**)
i. $PhCH_2NO_2$/DBU, CH_2Cl_2, −30 °C.

further investigation. The compositions of crystalline products **2a**,**f**—**h** were confirmed by the data from elemental analysis.* The presence of the main fragments in cyclopropanes **2** was proved based on the NMR spectroscopic data. Thus the presence of the three-membered ring in products **2** was established employing the INADEQUATE procedure (using **2a** as an example). We observed all three small spin-spin coupling constants $^1J_{C,C}$ (9.8, 13.8, and 19.5 Hz) characteristic of cyclopropanes.[21] The presence of the cyclopropane fragment in products **2** is additionally confirmed by high values of $^1J_{H,C}$ (162.3 and 182.1 Hz for compound **2a**) and the upfield chemical shifts of the corresponding signals in the ^1H and ^{13}C NMR spectra (Table 2).[22] The *trans* configuration of the stereoisomers of cyclopropanes **2** was supported by the NOE experiment performed for compound **2a** (Fig. 1).

The fact that the ^1H, ^{13}C, and ^{29}Si NMR spectra of all cyclopropanes **2** have two signals of the Me_3SiO groups indicates that these groups are diastereotopic. Taking into account that no coalescence of these signals

* According to the NMR spectroscopic data, the content of the major compound in oils **2b**—**e**,**i** was no less than 90%. These compounds cannot be purified by chromatography and fractionation because of their instability.

Table 2. ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data for the silylation products of ANC **1**

Compound	δ (*J*/Hz)		
	^{1}H	^{13}C	^{29}Si
2a	0.15, 0.16 (both s, 9 H each, $OSiMe_3$); 3.34 (s, 3 H, OMe); 3.56 (d, 1 H, C<u>H</u>Ph, ^{3}J = 7.4); 3.78 (s, 3 H, OMe); 4.30 (d, 1 H, CHN, ^{3}J = 7.4); 7.21 (br.s, 5 H, Ph)	0.2, 0.5 ($OSiMe_3$); 35.4 (<u>C</u>HAr); 44.1 (<u>C</u>$(CO_2Me)_2$); 52.2, 52.8 (OMe); 62.1 (CHN); 127.5 (*p*-CH_{Ph}); 128.3, 128.6 (*o*- and *m*-CH_{Ar}); 132.8 (C_{Ar}); 165.7, 165.9 (C=O)	24.48; 24.82
2b	0.14, 0.17 (both s, 9 H each, $OSiMe_3$); 3.32 (s, 3 H, OMe); 3.61 (d, 1 H, C<u>H</u>Ar, ^{3}J = 7.3); 3.77, 3.79 (both s, 3 H each, OMe); 4.61 (d, 1 H, CHN, ^{3}J = 7.3); 6.76 (d, 1 H, Ar, ^{3}J = 8.6); 6.83 (m, 1 H, Ar); 7.16 (m, 2 H, Ar)	0.2, 0.4 ($OSiMe_3$); 31.8 (<u>C</u>HAr); 43.3 (<u>C</u>$(CO_2Me)_2$); 51.9, 52.5, 55.4 (OMe); 62.1 (CHN); 110.0, 120.0, 128.8, 129.1 (CH_{Ar}); 121.4, 158.5 (C_{Ar}); 165.8, 166.0 (C=O)	24.13; 24.48
2c	0.16 (br.s, 18 H, $OSiMe_3$); 3.40 (s, 3 H, OMe); 3.55 (d, 1 H, C<u>H</u>Ar, ^{3}J = 6.9); 3.74 (s, 3 H, OMe); 3.79 (s, 3 H, OMe); 4.29 (d, 1 H, CHN, ^{3}J = 6.9); 6.71—6.82 (m, 3 H, Ar); 7.14 (t, 1 H, Ar, ^{3}J = 7.6)	0.1, 0.4 ($OSiMe_3$); 35.3 (<u>C</u>HAr); 44.0 (<u>C</u>$(CO_2Me)_2$); 52.1, 52.7, 55.0 (OMe); 62.1 (CHN); 113.4, 113.7, 120.8, 129.2 (CH_{Ar}); 134.3, 159.4 (C_{Ar}); 165.6, 165.7 (C=O)	24.47; 24.78
2d	0.09, 0.10 (both s, 9 H each, $OSiMe_3$); 3.30 (s, 3 H, OMe); 3.48 (d, 1 H, C<u>H</u>Ar, ^{3}J = 6.7); 3.64, 3.71 (both s, 3 H each, OMe); 4.22 (d, 1 H, CHN, ^{3}J = 6.7); 6.69 (d, 2 H, Ar, ^{3}J = 8.7); 7.08 (d, 2 H, Ar, ^{3}J = 8.7)	0.0, 0.3 ($OSiMe_3$); 34.7 (<u>C</u>HAr); 43.9 (<u>C</u>$(CO_2Me)_2$); 51.9, 52.4, 54.8 (OMe); 62.1 (CHN); 113.5, 129.5 (CH_{Ar}); 124.5, 158.8 (C_{Ar}); 165.6, 165.7 (C=O)	24.26; 24.55
2e	0.18, 0.19 (both s, 9 H each, $OSiMe_3$); 3.46 (s, 3 H, OMe); 3.64 (d, 1 H, C<u>H</u>Ar, ^{3}J = 7.0); 3.83 (s, 3 H, OMe); 4.34 (d, 1 H, CHN, ^{3}J = 7.0); 7.46 (t, 1 H, Ar, ^{3}J = 7.9); 7.58 (br.d, 1 H, Ar, ^{3}J = 7.7); 7.58 (m, 2 H, Ar)	0.1, 0.2 ($OSiMe_3$); 33.9 (<u>C</u>HAr); 43.8 (<u>C</u>$(CO_2Me)_2$); 52.3, 52.7 (OMe); 61.8 (CHN); 122.4, 123.4, 129.2, 134.5 (CH_{Ar}); 135.0, 147.9 (C_{Ar}); 164.9, 165.0 (C=O)	24.95; 25.24
2f	0.15, 0.17 (both s, 9 H each, $OSiMe_3$); 3.42 (s, 3 H, OMe); 3.63 (d, 1 H, C<u>H</u>Ar, ^{3}J = 7.4); 3.81 (s, 3 H, OMe); 4.34 (d, 1 H, CHN, ^{3}J = 7.4); 7.42 (d, 2 H, Ar, ^{3}J = 8.1); 8.13 (d, 2 H, Ar, ^{3}J = 8.1)	0.2, 0.4 ($OSiMe_3$); 34.5 (<u>C</u>HAr); 44.4 (<u>C</u>$(CO_2Me)_2$); 52.6, 53.0 (OMe); 62.0 (CHN); 123.5, 129.6 (CH_{Ar}); 140.6, 147.3 (C_{Ar}); 165.2 (2 C=O)	24.98; 25.32
2g	0.16, 0.18 (both s, 9 H each, $OSiMe_3$); 3.41 (s, 3 H, OMe); 3.55 (d, 1 H, CHAr, ^{3}J = 7.0); 3.81 (s, 3 H, OMe); 4.30 (d, 1 H, CHN, ^{3}J = 7.0); 7.18 (d, 2 H, Ar, ^{3}J = 8.6); 7.23 (d, 2 H, Ar, ^{3}J = 8.6)	0.2, 0.5 ($OSiMe_3$); 34.6 (<u>C</u>HAr); 44.1 (<u>C</u>$(CO_2Me)_2$); 52.4, 52.9 (OMe); 62.1 (CHN); 128.5, 130.0 (CH_{Ar}), 131.4, 133.5 (C_{Ar}); 165.6, 165.7 (C=O)	24.67; 25.00
2h	0.15, 0.19 (both s, 9 H each, $OSiMe_3$); 2.25 (s, 3 H, Me); 3.36 (s, 3 H, OMe); 3.51 (d, 1 H, C<u>H</u>Ar, ^{3}J = 7.5); 3.76 (s, 3 H, OMe); 4.26 (d, 1 H, CHN, ^{3}J = 7.3); 7.02 (d, 2 H, Ar, ^{3}J = 11.6); 7.11 (d, 2 H, Ar, ^{3}J = 11.8)	0.2, 0.5 ($OSiMe_3$); 21.1 (Me); 35.2 (<u>C</u>HAr); 44.1 (<u>C</u>$(CO_2Me)_2$); 52.2, 52.7 (OMe); 62.2 (CHN); 128.5, 129.0 (CH_{Ar}); 129.8, 137.1 (C_{Ar}); 165.8, 165.9 (C=O)	24.31; 24.62
2i	0.07, 0.13 (both s, 9 H each, $OSiMe_3$); 1.01 (d, 3 H, Me, ^{3}J = 6.5); 2.25 (dq, 1 H, C<u>H</u>Me, $^{3}J_1 = {}^{3}J_2$ = 6.5); 3.55 (d, 1 H, CHN, ^{3}J = 6.5); 3.66, 3.68 (both s, 3 H each, OMe)	0.1, 0.3 ($OSiMe_3$); 11.0 (Me); 25.8 (<u>C</u>HMe); 41.7 (<u>C</u>$(CO_2Me)_2$); 52.3, 52.4 (OMe); 64.4 (CHN); 166.2, 167.0 (C=O)	23.73; 24.00
3f	0.22 (s, 9 H, $OSiMe_3$); 3.60 (s, 3 H, OMe); 3.70 (s, 3 H, OCH_3); 4.04 (d, 1 H, C<u>H</u>$(COOMe)_2$, ^{3}J = 9.2); 4.58 (dd, 1 H, C<u>H</u>Ar, ^{3}J = 7.2, ^{3}J = 9.2); 6.63 (d, 1 H, CH=N, ^{3}J = 9.2); 7.52 (d, 2 H, Ar, ^{3}J = 8.7); 8.18 (d, 2 H, Ar, ^{3}J = 8.5)	−0.3 ($OSiMe_3$); 42.4 (<u>C</u>HAr); 53.0, 54.2 (OMe); 53.1 (<u>C</u>H$(COOMe)_2$); 114.7 (CH=N); 123.9, 129.3 (CH_{Ar}); 144.5, 147.4 (C_{Ar}); 167.3 (C=O)	28.34
3j	0.19 (s, 9 H, $OSiMe_3$); 1.17 (t, 6 H, CH_2CH_3, ^{3}J = 7.1); 1.28 (s, 6 H, $C(CH_3)_2$); 4.09 (q, 4 H, 2 OCH_2, ^{3}J = 7.1); 4.18 (s, 1 H, C<u>H</u>$(COOEt)_2$); 6.17 (s, 1 H, CH=N)	−0.4 ($OSiMe_3$); 13.9 ($OCH_2\underline{C}H_3$); 22.0 ($C(\underline{C}H_3)_2$); 36.2 (<u>C</u>$(CH_3)_2$); 55.5 (<u>C</u>H$(COOEt)_2$); 61.0 (2 $O\underline{C}H_2CH_3$); 122.6 (CH=N); 167.8 (C=O)	26.94

(*to be continued*)

Table 2 (*continued*)

Compound	δ (*J*/Hz)		
	^{1}H	^{13}C	^{29}Si
4 [a]	*anti* Isomer: 0.19 (s, 9 H, $OSiMe_3$); 3.77, 3.80 (both s, 3 H each, OMe); 7.33 (d, 1 H, CH=C, ^3J = 10.6); 8.14 (d, 1 H, CH=N, ^3J = 10.6) *syn* Isomer: 0.20 (s, 9 H, $OSiMe_3$); 3.65, 3.81 (both s, 3 H each, OMe); 7.69 (d, 1 H, CH=N, ^3J = 9.8); 7.79 (d, 1 H, CH=C, ^3J = 9.8)	*anti* Isomer: −0.6 ($OSiMe_3$); 52.9 (OMe); 53.0 (OMe); 130.1 (CH=C); 138.8 (CH=C); 151.7 (CH=N); 164.4, 164.7 (C=O) *syn* Isomer: −0.5 ($OSiMe_3$); 53.0 (OMe); 53.2 (OMe); 128.7 (CH=C); 131.0 (CH=C); 146.9 (CH=N); 164.7, 164.8 (C=O)	*anti* Isomer: 20.23 *syn* Isomer: 19.72
5	*anti* Isomer: 3.83, 3.86 (both s, 3 H each, OMe); 7.41 (d, 1 H, CH=C, ^3J = 10.5); 8.19 (d, 1 H, CH=N, ^3J = 10.5); 9.02 (br.s, 1 H, OH) *syn* Isomer: 3.76, 3.87 (both s, 3 H each, OMe); 7.63 (d, 1 H, CH=N, ^3J = 10.0); 7.91 (d, 1 H, CH=C, ^3J = 10.0); 9.02 (br.s, 1 H, OH)	*anti* Isomer: 53.0 (OMe); 53.1 (OMe); 139.7 (CH=C); 138.6 (CH=C), 147.7 (CH=N), 164.0, 164.6 (C=O)[b]	—
11a [c]	3.52, 3.79 (both s, 3 H each, OMe); 4.34 (d, 1 H, CHAr, ^3J = 6.2); 4.96 (d, 1 H, CHN, ^3J = 6.2); 7.30 (br.s, 5 H, Ph); 7.41 (br.s, 3 H, Ph); 7.73 (s, 1 H, CH=N); 8.22 (br.s, 2 H, Ph)	34.1 (CHPh); 43.1 ($C(CO_2Me)_2$); 52.9, 53.3 (MeO); 59.4 (CHN); 127.9, 130.8 (p-CH_{Ph}); 128.5, 128.8, 128.8, 128.8 (o-CH_{Ph} and m-CH_{Ph}); 130.1, 132.1 (C_{Ph}); 136.1 (CH=N); 165.48, 165.54 (C=O)	—
11f [d]	3.56, 3.79 (both s, 3 H each, OMe); 4.41 (d, 1 H, CHAr, ^3J = 6.0); 4.99 (d, 1 H, CHN, ^3J = 6.0); 7.42 (м, 3 H, Ph); 7.49 (d, 2 H, 4-$NO_2C_6H_4$, ^3J = 8.2); 7.80 (s, 1 H, CH=N); 8.15 (d, 2 H, 4-$NO_2C_6H_4$, ^3J = 8.3); 8.21 (br.s, 2 H, Ph)	33.1 (CHPh); 43.0 ($C(CO_2Me)_2$); 53.3, 53.6 (MeO); 59.2 (CHN); 123.7, 129.7 (CH_{Ar}); 139.8, 147.5 (C_{Ar}); 128.6, 129.0 (o-CH_{Ph} and m-CH_{Ph}); 129.9 (C_{Ph}); 131.1 (p-CH_{Ph}); 136.7 (CH=N); 165.0, 165.3 (C=O)	—

[a] ^{15}N NMR, δ: *anti* isomer, 26.5 ($^2J_{H,N}$ = 4.5 Hz); *syn* isomer, 12.2 ($^2J_{H,N}$ = 13.5 Hz).
[b] The ^{13}C NMR spectrum of the *syn* isomer was not recorded because of its low concentration.
[c] ^{14}N NMR, δ: −110 (CH=N(O), $\Delta\nu_{1/2} \approx 700$ Hz).
[d] ^{14}N NMR, δ: −15 (NO_2, $\Delta\nu_{1/2} \approx 850$ Hz); −110 (CH=N(O), $\Delta\nu_{1/2} \approx 750$ Hz).

was observed in the spectra measured at temperatures up to 60 °C, it can be concluded that the inversion of the N atom in molecules **2** is hindered due to the high barrier.

The structures of oximes **4** and **5** were confirmed by the data from NMR spectroscopy and elemental analysis. The *syn* and *anti* configurations were assigned to the stereoisomers of products **4** and **5** based on the chemical shifts of the protons of the CH=N fragment and the spin-spin coupling constants $^2J_{H,N}$ using criteria described previously.[23] (Eneoxime **5** has been mentioned in the literature;[24] however, the specimen obtained in the present study differs from that obtained earlier in the spectral characteristics and the melting point. It is most likely that the inconsistency between our data and the earlier results is merely due to the error that appeared in the preparation of the paper.[24])

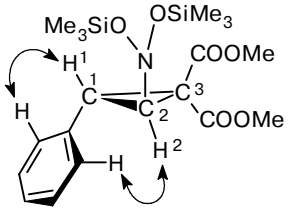


Fig. 1. Determination of the configuration of cyclopropane **2a** by NOE experiments (irradiation of protons of the phenyl group).

Thus, we have demonstrated that silylation of ANC **1** bearing two methoxycarbonyl groups in the γ-position and the aryl or alkyl substituent in the β-position proceeds smoothly to form *trans* isomers of the corresponding *N*,*N*-bis(silyloxy)aminocyclopropanes **2**, which are chemical equivalents of nitrosocyclopropanes **9**.

Base-catalyzed intramolecular nucleophilic substitution of the Br atom in (1-aryl-2-bromo-2-nitro)ethylmalonates giving rise to the corresponding nitrocyclopropanes[25] most closely resembles the cyclization under consideration.

Apparently, variations in the substituents in the γ-position of ANC **1** call for further investigation. Preliminary NMR analysis demonstrated that silylation of ethyl 2-benzoyl-4-nitro-3-phenylbutyrate under the action of Me_3SiBr/Et_3N at −30 °C afforded a mixture of the corresponding *N*,*N*-bis(silyloxy)aminocyclopropane **E** (one stereoisomer with the configuration shown in Scheme 1; 31%), 2-[*N*,*N*-bis(silyloxy)amino]-2,3-dihydrofuran **D** (one stereoisomer with the configuration shown in Scheme 1; 29%), and α,β-unsaturated oxime **F** (see Scheme 1, one isomer; 30%),* *i.e.*, competing carbocyclization, heterocyclization, and double silylation followed by elimination of Me_3SiOH take place.

* For **D**, **E**, and **F**, $R^1 = R^3$ = Ph, R^2 = COOEt, and R^4 = H.

Experimental

The NMR spectra were recorded on a Bruker AM-300 instrument in $CDCl_3$. The chemical shifts were measured relative to the residual signal of the solvent (^1H, δ 7.26; ^{13}C, δ 77.16),[26] Me_4Si (^{29}Si, δ 0) as the internal standard, and $MeNO_2$ (^{14}N and ^{15}N, δ 0) as the external standard. The ^{29}Si and ^{15}N signals were observed using the INEPT pulse sequence.[27]

All operations were carried out under an atmosphere of dry argon using freshly distilled CH_2Cl_2. The starting ANC **1a—d,f—h**,[28] **1e**,[29] **1i**,[30] **1j**,[31] and **1k** [32] were synthesized according to known procedures.

Synthesis of cyclopropanes 2 (general procedure). Triethylamine (0.27 mL, 1.92 mmol) was added to a solution of ANC **1** (0.60 mmol) in CH_2Cl_2 (3 mL) at −30 °C and then a solution of Me_3SiBr (0.24 mL, 1.80 mmol) in CH_2Cl_2 (1 mL) was added dropwise during 5 min. The reaction mixture was kept with intermittent stirring for 1—8 days (see Table 1), diluted with light petroleum (10 mL), and poured with stirring into a mixture of water (10 mL) and light petroleum (15 mL). The organic layer was separated, washed with water (10 mL) and brine (5 mL), and dried with Na_2SO_4. The solvents were evaporated *in vacuo*. The yields of the reaction products were determined by NMR spectroscopy using $ClCH_2CH_2Cl$ as the internal standard.

Compound 2a, the yield was 0.25 g, yellowish crystals, m.p. 54—57 °C (light petroleum). Found (%): C, 52.89; H, 7.20; N, 3.27; Si, 13.44. $C_{19}H_{31}NO_6Si_2$. Calculated (%): C, 53.62; H, 7.34; N, 3.29; Si, 13.20. **Compound 2b**, the yield was 0.24 g, yellowish oil. **Compound 2c**, the yield was 0.25 g, yellowish oil. **Compound 2d**, the yield was 0.23 g, yellowish oil. **Compound 2e**, the yield was 0.27 g, greenish oil. **Compound 2f**, the yield was 0.27 g, yellowish crystals, m.p. 129—133 °C (light petroleum). Found (%): C, 48.55; H, 6.40; N, 6.03; Si, 12.04. $C_{19}H_{30}N_2O_8Si_2$. Calculated (%): C, 48.49; H, 6.43; N, 5.95; Si, 11.94. **Compound 2g**, the yield was 0.22 g, yellowish crystals, m.p. 121—124 °C (light petroleum). Found (%): C, 49.82; H, 6.67; Cl, 7.86; N, 3.12; Si, 12.54. $C_{19}H_{30}ClNO_6Si_2$. Calculated (%): C, 49.60; H, 6.57; Cl, 7.71; N, 3.04; Si, 12.21. **Compound 2h**, the yield was 0.25 g, yellowish crystals, m.p. 72—75 °C (light petroleum). Found (%): C, 54.53; H, 7.43; N, 3.10; Si, 12.90. $C_{20}H_{33}NO_6Si_2$. Calculated (%): C, 54.64; H, 7.57; N, 3.19; Si, 12.78. **Compound 2i**, the yield was 0.17 g, greenish oil.

Analogously, derivative **4** was obtained from compound **1k**; the ratio of the *syn* and *anti* isomers was 1 : 2.7, the yield was 0.14 g, colorless oil, b.p. 110—115 °C (0.07 Torr). Found (%): C, 46.25; H, 6.57; N, 5.35; Si, 10.90. $C_{10}H_{17}NO_5Si$. Calculated (%): C, 46.31; H, 6.61; N, 5.40; Si, 10.83.

Silyl nitronates 3f,j. Silylation of compounds **1f,j** was carried out according to the above-described procedure under conditions indicated in Table 1. The reaction mixture was diluted with dry toluene and the precipitate of $[Et_3NH]^+Br^-$ was filtered off in an inert atmosphere. The mother liquor was concentrated *in vacuo* and the residue was analyzed by ^1H NMR spectroscopy using $ClCH_2CH_2Cl$ as the internal standard.

Nitrones 11a,f. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.30 mL, 2 mmol) was added to a solution of $PhCH_2NO_2$ (0.276 g, 2 mmol) in CH_2Cl_2 (9 mL) at −30 °C and the reaction mixture was kept for 5 min. Then a solution of cyclopropane **2** (2 mmol) in CH_2Cl_2 (6 mL) was added dropwise at the same temperature over 10 min. The reaction mixture was kept with stirring at −30 °C for 1.5 h and then diluted with anhydrous Et_2O (25 mL). The precipitate was filtered off in an inert atmosphere. The mother liquor was concentrated *in vacuo* and the crude product was purified by column chromatography (a 1 : 3 EtOAc—light petroleum mixture as the eluent, 20 g of silica gel Silica Woelm 32-63).

Nitrone 11a, the yield was 0.47 g (67%), white crystals, m.p. 132—133 °C, R_f = 0.16 (EtOAc—light petroleum, 1 : 3, Merck 60 F_{254}). Found (%): C, 67.30; H, 5.34; N, 4.31. $C_{20}H_{19}NO_5$. Calculated (%): C, 67.98; H, 5.42; N, 3.96. **Nitrone 11f**, the yield was 0.35 г (44%), yellow crystals, m.p. 158—161 °C, R_f = 0.16 (EtOAc—light petroleum, 1 : 3, Merck 60 F_{254}). Found (%): C, 60.43; H, 4.60; N, 7.24. $C_{20}H_{18}N_2O_7$. Calculated (%): C, 60.30; H, 4.55; N, 7.03.

Enoxime 5. Distilled compound **4** (0.12 г, 0.46 mmol, *syn*-**4** : *anti*-**4** = 1 : 2.7) was dissolved in MeOH (5 mL). Then 40% HF (0.03 mL) was added. The mixture was kept at ~20 °C for 2 h and then concentrated *in vacuo*. The residue was recrystallized from a 7 : 1 light petroleum (b.p. 64 °C)—CH_2Cl_2 mixture to give 0.053 g (62%) of compound **5**, *syn*-**5** : *anti*-**5** = 1 : 21, white crystals, m.p. 83—85 °C (*cf.* lit. data[24]: m.p. 71 °C). Found (%): C, 44.87; H, 4.83; N, 7.45. $C_7H_9NO_5$. Calculated (%): C, 44.92; H, 4.85; N, 7.48.

Methanolysis of cyclopropane 2a. Compound **2a** (0.08 g, 0.19 mmol) was dissolved in CH_2Cl_2 (1 mL). Then MeOH (0.5 mL) was added at 0 °C. The reaction mixture was kept at ~20 °C for 1 h and concentrated *in vacuo*. The crystalline residue was pure ANC **1a** obtained in a yield of 0.05 g (97%).

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