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Me_3SiBr-Mediated Intramolecular Cyclization of γ-Functionalized Trimethylsilyl Nitronates.

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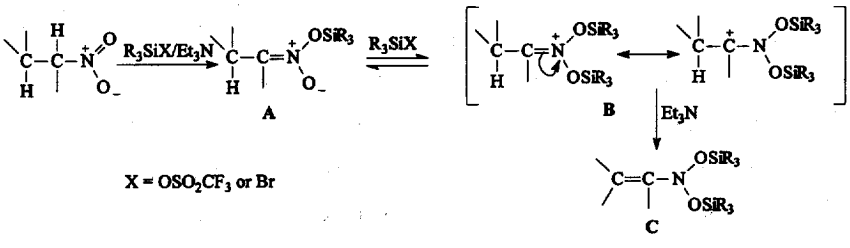
Abstract: The silylation of nitro compounds of general formula $X^1X^2CHCH(Ar)CH_2NO_2$ with Me_3SiBr/Et_3N at –30°C leads to hitherto unknown 2-(*N,N*-bis(trimethylsilyloxy)amino-2,3-dihydrofurans (X^1=PhCO, X^2=H) or to *N,N*-bis(trimethylsilyloxy)aminocyclopropanes (X^1=X^2=COOMe). *N,N*-Bis(trimethylsilyloxy)immonium cations appear to be the key intermediates in this process.

The silylation of aliphatic nitro compounds is known to lead to trialkylsilyl nitronates **A** or bis(trialkylsilyloxy)enamines (BSENA) **C** (Scheme 1).[1]

The trialkylsilyl nitronates **A** have been well investigated and widely used as versatile synthetic intermediates.[2] On the other hand, the chemical reactivity of BSENA **C** is not yet clearly understood. However, they reveal the promising ability to be good equivalents of α-carbonylcarbenium ions in reactions with N-[2,3] and C-nucleophiles.[4] γ-Functionalized BSENA may be good precursors for stereoselective synthesis of trans-α,β-unsaturated oximes.[5]



Scheme 1.

Recently we have developed a simple procedure for the preparation of BSENA **C**, which undoubtedly increases their attractiveness as reagents for organic synthesis.[6] The apparent precursor of BSENA, carboimmonium ion **B**, that is formed upon reversible transfer of the Me_3Si-group to nitronate oxygen has not

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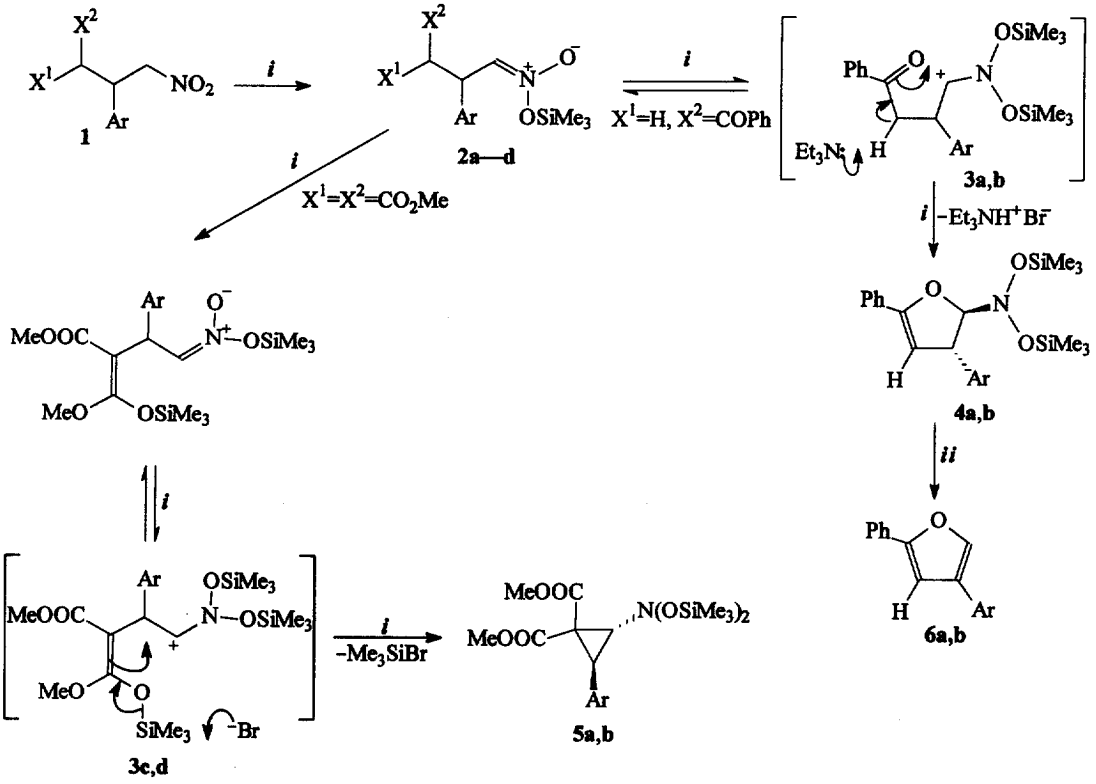
attracted the attention of chemists.[7] However, during attempts to synthesize β,β-disubstituted BSENA bearing electron-withdrawing substituents in the γ-position, we encountered two unanticipated transformations of the starting γ-functionalized-β-aryl nitro compounds **1** (Scheme 2).[8] The expected BSENA products were not isolated, but cyclic products — 3-aryldihydrofuranes **4a,b** and arylcyclopropanes **5a,b**[9] — were isolated instead.



Scheme 2. *i*: Me_3SiBr/Et_3N in CH_2Cl_2 at –30°C; *ii*: NH_4F/MeOH

nitro compound **1**	Ar	X^1	X^2	Product, (Yield, %)†
1a	Ph	H	COPh	**4a**, (83)†
1b	p-ClPh	H	COPh	**4b**, (87)†
1c	Ph	COOMe	COOMe	**5a**, (61)
1d	p-MeO	COOMe	COOMe	**5b**, (88)

†The yield was determined by NMR with internal standard.

The proposed mechanisms of these reactions include the intramolecular interception of cationic intermediates **3** with nucleophilic moieties as the key step followed by deprotonation or elimination of the Me_3Si-group. The participation of silyl nitronates **2** in these cyclizations was supported by an independent experiment.[10] The immonium cations **3** undergo either base-induced deprotonation or intramolecular cyclization. *A priori*, it could be anticipated that, the bulky β-aryl group would hinder the approach of the base;

as the result, the cyclization rate would be higher than that of the usual β-*C*-deprotonation to give BSENA (Schemes 1 and 2).

The structures of the 4-aryldihydrofurans **4** and arylcyclopropanes **5** were determined by NMR spectroscopy and additionally by elemental analysis (for **5**).[9,11] The structure of **4** was confirmed by their transformations into known 3,5-diarylfurans **6** upon treatment with NH_4F/MeOH (Scheme 2).[12] The presence of a three-membered ring in **5** unambiguously follows from the three characteristically small spin-spin coupling constants $^1J(^{13}C—^{13}C)$ (9.8, 13.8 and 19.5 Hz, defined by INADEQUATE) and from the large $^1J(^1H—^{13}C)$ coupling constants for the cyclic protons and the carbon atoms as well as by their upfield chemical shifts (NMR-data for cyclic atoms are marked by boldface characters).[9,13] The evidence in favour of a *trans*-arrangement of substituents both in the arylcyclopropanes **5** and the 3-aryldihydrofurans **4** results from the observation of a NOE between the ortho-protons of the aryl substituent and all cyclic protons. The ^{15}N-chemical shift of the $N(OSiMe_3)_2$-group in **4** and **5** (see[9]) ressembles the corresponding data for known BSENA.[6]

In conclusion, two new transformations of γ-functionalized aliphatic nitro compounds, leading to arylcyclopropanes and 3-aryldihydrofurans bearing the new $N(OSiMe_3)_2$-moiety attached to the sp^3-carbon atom, have been found. Further investigations of these cyclizations interconnected by a common reaction intermediate — a carboimmonium ion — are being pursued in our group.

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7. The cyclic analogue of cation **B** had already been considered convincingly as the reaction intermediate (see Chlenov, I. E.; Morozova, N. S.; Tartakovsky, V. A. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1983**, 1889 — 1891, 1713 — 1714 (Engl.)).
8. The starting nitro compounds were prepared by known procedures; **1a**: Bergbreiter, D. E.; Lalonde, J.J. *J. Org. Chem.* **1987**, *52*, 1601 — 1603; **1b**: Kohler, E. P.; Smith, L. I. *J. Amer. Chem. Soc.* **1922**, *44*, 624 — 634; **1c**: Kohler, E. P.; Engelbrecht, H. *J. Amer. Chem. Soc.* **1919**, *41*, 764 — 770; **1d**: Perekalin, V. V.; Zobacheva, M. M. *Zh. Obshch. Khim.* **1959**, 2905 — 2910 (Russ.), 2865 — 2867 (Engl.).

9. *Typical procedure.* To a stirred solution of nitro compounds **1a—d** (2.4 mmol) and Et_3N (0.83 g, 8.2 mmol) in CH_2Cl_2 (3.5 mL) a solution of Me_3SiBr (1.22g, 8.0 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise at –40°C. The mixture was kept for 60 h at –30°C with occasional stirring, diluted with petroleum ether (b.p. 40—70°C) and poured into ice-cooled water. The organic layer was separated, washed with brine, dried (Na_2SO_4) and evaporated *in vacuo* to give compound **4a** as a viscous oil. NMR ($CDCl_3$): δ (^1H) 0.17 (s, 9 H, $SiMe_3$), 0.19 (s, 9 H, $SiMe_3$), 4.75 (dd, 1 H, C*H*Ph, ^3J = 3.0 and 3.8 Hz), 5.05 (d, 1 H, C*H*N), 5.58 (d, 1 H, C*H*=C), 7.18—7.39 (m, 8 H, CH_{Ph}), 7.65 (m, 2 H, ortho-C*H* at 5-Ph); δ (^{13}C) 0.2 ($SiMe_3$), 0.3 ($SiMe_3$), 48.6 (*C*HPh), 99.8 (*C*H=C), 106.9 (*C*HN), 125.1 (ortho-*C*H at 5-Ph), 126.6, 127.9, 128.2 and 128.4 (all CH_{Ph}), 130.2 and 143.3 (both C_{Ph}), 155.1 (*C*=CH); δ (^{15}N) –145.00 (d, J = 9.7 Hz); δ (^{29}Si) 24.54, 26.19. Compound **4b**, viscous oil, NMR ($CDCl_3$): δ (^1H) 0.21 (s, 9 H, $SiMe_3$), 0.22 (s, 9 H, $SiMe_3$), 4.81 (dd, 1 H, C*H*Ar, ^3J = 4.0 and 3.4 Hz), 5.04 (d, 1 H, C*H*N), 5.56 (d, 1 H, C*H*=C), 7.29 (m, 3 H, CH_{Ph}), 7.34 (d, 2 H, CH_{Ar}, ^3J = 7.4 Hz), 7.34 (d, 2 H, CH_{Ar}), 7.68 (d, 2 H, ortho-CH_{Ph}, ^3J = 8.0 Hz); δ (^{13}C) 0.3 ($SiMe_3$), 0.4 ($SiMe_3$), 48.1 (*C*HAr), 99.3 (*C*H=C), 106.9 (*C*HN), 125.3, 128.3, 128.5, 129.5 (CH_{Ar}+CH_{Ph}), 128.4 (p-CH_{Ph}), 130.1 and 142.1 (C_{Ar}+C_{Ph}), 155.6 (*C*=CH); δ (^{29}Si) 24.71, 26.42. Compound **5a**, white crystals; m.p. 53 — 57°C (from petroleum ether, b.p. 30 — 40°C). NMR ($CDCl_3$): δ (^1H) 0.18 (s, 9 H, $SiMe_3$), 0.20 (s, 9 H, $SiMe_3$), 3.38 (s, 3 H, OMe), **3.63** (d, 1 H, C*H*Ph, ^3J = 7.0 Hz), 3.82 (s, 3 H, OMe), **4.36** (d, 1 H, C*H*N), 7.25 (m, 5 H, CH_{Ar}); δ (^{13}C) 0.3 (q, $SiMe_3$, ^1J = 118.9 Hz), 0.5 (q, $SiMe_3$, ^1J = 119.4 Hz), **35.4** (dm, *C*HPh, ^1J = **162.3 Hz**), **44.2** (dd, $C(CO_2Me)_2$, ^2J = 1.7 and 3.8 Hz), 52.2 (q, OMe, ^1J = 147.6 Hz), 52.8 (q, OMe, ^1J = 147.3 Hz), **62.2** (dd, *C*HN, ^1J = **182.1 Hz**, ^2J = 4.2 Hz), 127.5 (dm, CH_p, ^1J = 160.2 Hz), 128.2 (^1J = 160.4 Hz) and 128.6 (^1J = 156.0 Hz) (both dm, CH_o and CH_m), 132.9 (m, C_{Ar}), 165.7 (m, C=O), 165.9 (m, C=O); δ (^{15}N) –146.81 (d, J = 2.9 Hz); δ (^{29}Si) 24.39, 24.68. Anal. Calcd. for $C_{19}H_{31}NO_6Si_2$: C, 53.62; H, 7.34; N, 3.29; Si, 13.20. Found: C, 53.57; H, 7.30; N, 3.25; Si, 13.23. Compound **5b**, viscous oil, NMR ($CDCl_3$): δ (^1H) 0.18 (s, 9 H, $SiMe_3$), 0.19 (s, 9 H, $SiMe_3$), 3.39 (s, 3 H, OMe), **3.57** (d, 1 H, C*H*Ar, ^3J = 6.7 Hz), 3.73 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), **4.32** (d, 1 H, C*H*N), 6.78 (d, 2 H, CH_{Ar}, ^3J = 8.4 Hz), 7.18 (d, 2 H, CH_{Ar}); δ (^{13}C) 0.1 ($SiMe_3$), 0.4 ($SiMe_3$), **34.8** (*C*HAr), **44.1** ($C(CO_2Me)_2$), 52.1 (OMe), 52.6 (OMe), 54.9 (OMe), **62.3** (*C*HN), 113.7 (CH_{Ar}), 124.7 (C_{Ar}), 129.7 (CH_{Ar}), 158.9 (C_{Ar}), 165.7 (C=O), 165.8 (C=O); δ (^{29}Si) 24.25, 24.54. Anal. Calcd. for $C_{20}H_{33}NO_7Si_2$: C, 52.72; H, 7.30; N, 3.07; Si, 12.33. Found: C, 52.59; H, 7.35; N, 3.08; Si, 12.42.

10. Trimethylsilyl nitronate **2a** was prepared according to Aizpurua, J.M.; Oiarbide, M.; Palomo, C. *Tet. Lett.* **1987**, *28*, 5361 — 5364 and employed in silylation with Me_3SiBr/Et_3N (see typical procedure[9]) giving rise to 3-aryldihydrofuran **4a** with the yield 65%.

11. Similar dihydrofurans were considered as reaction intermediates in the synthesis of furans from nitroalkenes and 1,3-dicarbonyl compounds (see Yoshikoshi, A; Miyashita, M. *Acc. Chem. Res.* **1985**, *18*, 284 — 290).

12. The treatment of 3-aryldihydrofuran **4** with catalytic amount of NH_4F in MeOH at 20°C leads to 3-aryl-5-phenylfurans **6**. Melting points and NMR-spectra of **6** correspond to literature data; **6a**: Kel'in, A.V.; Kulinkovich, O.G. *Zh. Org. Khim.* **1994**, *30*, 197 — 200 (Russ.); *Russ. J. Org. Chem.* **1994**, *30*, 202 — 206 (Engl.); **6b**: Molina, P; Lorenzo, A; Fresenda, P.M. *Synthesis* **1983**, 49 — 50; Padmanabhan, S.; Ogawa, T, Suzuki, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2114 — 2116.

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