Available online at www.sciencedirect.com
ScienceDirect
*Mendeleev Commun.*, 1994, **4(4)**, 135
Mendeleev Communications

# Substitution of the Nitro Group in Chloronitrofuroxan by *N*- and *O*-Trimethylsilyl Derivatives

**Olga V. Zavarzina, Oleg A. Rakitin* and Lenor I. Khmel'nitskii**

*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328*

A method for the substitution of the nitro group in 3-chloro-4-nitrofuroxan by trimethylsilyl derivatives of secondary amines and amidoximes is proposed.

The nitro group is known to be substituted in nitrofuroxans by the action of various nucleophilic agents.[1–3] This method is broadly used for the synthesis of functionally substituted furoxans.

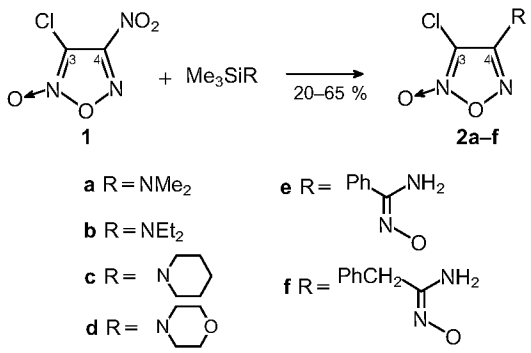
The action of nucleophiles on some nitro- as well as halogenofuroxans, however, results not only in substitution but also in furoxan ring opening.[4,5] One such substrate is chloronitrofuroxan **1**.[5] Our investigations have shown that the substitution products could not be obtained when **1** was treated with nucleophilic reagents. So, primary and secondary aliphatic amines decomposed it, and amidoximes did not react with **1**. At the same time, trimethylsilyl derivatives are known to be more active than the corresponding amines.[6] Therefore, we decided to use them for the substitution of the nitro group in **1**. Previous substitutions of the nitro and other groups by action of *N*- and *O*-trimethylsilyl derivatives in heterocyclic series are not known.

We have established that reaction of **1** with *N*-trimethylsilyl derivatives of secondary amines and *O*-derivatives of amidoximes affords compounds hitherto practically inaccessible – the corresponding 3-chlorofuroxans **2a–f**.†

The substituent positions in the furoxan ring were established by $^{13}C$ NMR spectroscopy, the signals being assigned in accordance with ref. 7.

Trimethylsilyl derivatives of alcohols, primary aliphatic and aromatic amines, as well as trimethylsilyl cyanide, gave no substitution products in their reactions with **1**.

Chloronitrofuroxan **1** is known to exist as a mixture of two isomers: 3-chloro-4-nitrofuroxan (70%) and 4-chloro-3-nitrofuroxan (30%).[7] We have found that only the former underwent the substitution reaction, whereas the latter remained intact, or decomposed under more severe conditions. This may be associated with the fact that the chlorine atom at position 4 is less susceptible to substitution than the nitro group.




**Scheme 1** *Conditions:* **a**, $CH_2Cl_2$, 18 °C, 2 h; **b–d**, MeCN, 18 °C, 2 h; **e–f**, MeCN, boiled 3 h. In all cases a 1.5–2.5 fold excess of silyl derivative was used.

Evidently this method may also be used for other heterocyclic compounds which are susceptible to undesired transformations by the action of nucleophiles.

† All new compounds prepared had satisfactory elemental analysis data and were characterized by $^1H$, $^{13}C$ and mass spectroscopy.

**2a** M.p. 46 °C, decomposing on storage, $^1H$ NMR ($CDCl_3$) 2.99 s (6H, $Me_2$), $^{13}C$ NMR ($CDCl_3$) 104.99 (C–Cl), 156.62 (*C*–$NMe_2$), 38.60 ($Me_2$).

**2b** Oil, decomposing on storage, $^1H$ NMR ($CDCl_3$) 1.19 t (6H, Me), 3.41 q (4H, $CH_2$), $^{13}C$ NMR ($CDCl_3$) 104.66 (C–Cl), 154.94 (*C*–$NEt_2$), 43.00 ($CH_2$), 13.24 (Me).

**2c** M.p. 48–50 °C, $^1H$ NMR ($CDCl_3$) 1.64 m (6H, $CH_2$–C), 3.33 d (4H, $CH_2$–N), $^{13}C$ NMR ($CDCl_3$) 105.63 (C–Cl), 156.92 (O–N=C–N), 47.74 ($CH_2$–N), 24.69 and 23.65 [$(CH_2)_2$–C].

**2d** M.p. 112–114 °C, $^1H$ NMR ($CDCl_3$) 3.37 s (4H, $CH_2$–N), 3.78 s (4H, $CH_2$–O), $^{13}C$ NMR ($CDCl_3$) 105.17 (C–Cl), 156.51 (O–N=C–N), 65.81 ($CH_2$–O), 46.73 ($CH_2$–N).

**2e** M.p. 148 °C (decomp.), $^1H$ NMR [$(CD_3)_2SO$] 7.23 s (2H, $NH_2$), 7.52 m (3H, Ph), 7.70 m (2H, Ph), $^{13}C$ NMR [$(CD_3)_2SO$] 104.90 (C–Cl), 161.54 (O–N=C–O), 158.95 (Ph–*C*=N–O), 127.13, 128.74, 130.47 and 131.22 (Ph).

**2f** M.p. 81–83 °C, $^1H$ NMR ($CDCl_3$) 3.60 s (2H, $CH_2$), 5.00 s (2H, $NH_2$), 7.33 m (5H, Ph), $^{13}C$ NMR ($CDCl_3$) 104.60 (C–Cl), 161.10 (O–N=C–O), 158.49 ($CH_2$–*C*=N–O), 127.71, 128.75, 128.99 and 133.94 (Ph), 36.53 ($CH_2$).

## References

1 R. Calvino, A. Gasco and A. Serafino, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1240.
2 A. Gasco, V. Mortarini, Y. Rua and A. Serafino, *J. Heterocycl. Chem.*, 1973, **10**, 587.
3 T. I. Godovikova, O. A. Rakitin, S. P. Golova, S. A. Vozchikova and L. I. Khmel'nitskii, *Mendeleev Commun.*, 1993, 209 and references cited therein.
4 H. Wieland, *Ber.*, 1901, **42**, 4192.
5 O. A. Rakitin, T. I. Godovikova, Yu. A. Strelenko and L. I. Khmel'nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2398 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, 2198).
6 J. F. Klebe, in *Advances in Organic Chemistry*, ed. E. C. Taylor, 1972, vol. 8, p. 101.
7 O. A. Rakitin, V. A. Ogurtsov, Yu. A. Strelenko and L. I. Khmel'nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1020 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, 909).

*Received: Moscow, 15th March 1994*
*Cambridge, 10th May 1994; Com. 4/01756K*