46 °C (*cf.* Ref. 7: m.p. 45 °C). Found (%): Si, 44.80. $C_8H_{24}OSi_4$. Calculated (%): Si, 45.19. IR (KBr), ν/cm^{-1}: 1050 (SiOSi). UV (hexane), λ_{max}/nm: 236.

The reaction of dichlorooligosilane **1** (3 g, 10 mmol) with anhydrous $Ni(OH)_2$ [5] (0.92 g, 10 mmol) and Py (3.2 g, 40 mmol) was performed in a similar way. Green crystalline product **4** (64% yield, 1.43 g) corresponds in composition to the complex described previously.[8] Found (%): Cl, 16.21; N, 11.97; Ni, 13.80. $C_{20}H_{20}Cl_2N_4Ni$. Calculated (%): Cl, 15.89; N, 12.56; Ni, 13.15. Heterocycle **2** (1.61 g, 65%) was obtained after product **4** was separated from the reaction mixture and the solvents were removed. Compound **5** (0.66 g, 57%) was isolated by aqueous extraction from the remained solid residue. IR (KBr), ν/cm^{-1}: 2600 (≡N · HCl).

The reaction of dichlorodisilane **6** (1.87 g, 10 mmol) with $Ni(OH)_2$ (0.93 g, 10 mmol) and Py (3.2 g, 40 mmol) gave compound **4** (1.95 g, 87.4%), heterocycle **7** (0.91 g, 69%), and compound **5** (0.82 g, 70.6%). The compounds were isolated from the reaction mixture by a similar scheme. Found (%): C, 35.80; H, 8.92; Si, 41.93. $C_8H_{24}O_2Si_4$. Calculated (%): C, 36.30; H, 9.14; Si, 42.45. IR (KBr), ν/cm^{-1}: 1050 (SiOSi). UV (hexane), λ_{max}/nm: 200.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-33724 and 97-03-32689).

References

1. M. G. Voronkov, E. A. Maletina, and V. K. Roman, *Geterosiloksany* [*Heterosiloxanes*], Nauka, Sibirskoe Otdelenie, Novosibirsk, 1984, 143 pp. (in Russian).
2. R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359.
3. M. M. Levitskii and A. L. Buchachenko, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1432 [*Russ. Chem. Bull.*, 1997, **46**, 1367 (Engl. Transl.)].
4. A. I. Chernyavskii and B. G. Zavin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1513 [*Russ. Chem. Bull.*, 1997, **46**, 1449 (Engl. Transl.)].
5. *Handbook of Preparative Inorganic Chemistry*, Ed. G. Brauer, Academic Press, New York—London, 1954, 805 pp.
6. R. Shavio, C. B. Lowe, J. A. Zota, C. B. Aakeroy, P. B. Hitchcock, K. R. Seddon, and R. L. Carlin, *Inorg. Chim. Acta*, 1992, **198**, 613.
7. M. Kumada, M. Ishikawa, and B. Murai, *J. Chem. Soc. Jpn.*, 1963, **66**, 637; *Chem. Abstrs.*, 1963, **59**, 15303.
8. A. S. Antsyshkina and M. A. Porai-Koshits, *Kristallografiya* [*Crystallography*], 1958, **3**, 676 (in Russian).

Received December 19, 1997;
in revised form March 17, 1998

Reaction of 5-allyl-2,5-dichloro-4,4-dimethoxy-3-morpholinocyclopent-2-enone with Me_3SiI

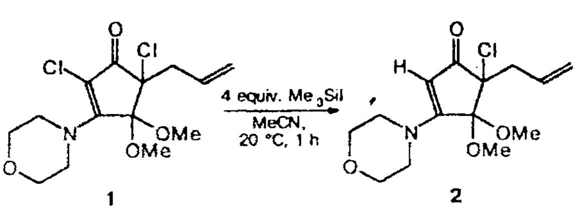
F. A. Akbutina, S. A. Torosyan, and M. S. Miftakhov*

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

5-Allyl-2,5-dichloro-4,4-dimethoxy-3-morpholinocyclopent-2-enone reacts with Me_3SiI in MeCN to give the corresponding product of reductive vinylic monodechlorination.

Key words: α,α′-dichlorocyclopentenone, iodotrimethylsilane, reductive monodechlorination.

The reaction of dichloroenamineketone (**1**)[1] with Me_3SiI in a solution of MeCN occurs as reductive dechlorination to form compound **2** in ~80% yield.



1 **2**

Note that the chloroenaminoketone fragment in compound **1** and related cyclopentenones differs from that in the corresponding systems devoid of Cl by its pronounced chemical "inertness." Among the transformations studied of this class of compounds,[2—9] transformation **1**→**2** is the first example of the reaction involving the vinylic Cl atom. It is of interest to study the mechanism of formation of **2**. This reaction extends the synthetic potentialities of Me_3SiI as the reagent. The known variants of application of Me_3SiI in the synthesis include the cleavage of ethers and esters, ketals, preparation of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1660—1661, August, 1998.

silyl ethers of enols (see Refs. 10 and 11), reductive debromination of α-bromoketones,[12] *etc.*

Experimental

IR spectra were obtained on a UR-20 spectrophotometer in a thin layer. NMR spectra were recorded on a Bruker AM-300 spectrometer (^{1}H, 300 and ^{13}C, 75.47 MHz) in $CDCl_3$ using $SiMe_4$ as the internal standard. Commercial Me_3SiI (Aldrich) was used.

5-Allyl-5-chloro-4,4-dimethoxy-3-morpholinocyclopent-2-enone (2). A solution of compound **1** (0.1 g, 0.3 mmol) and Me_3SiI (0.25 mL, 1.2 mmol) in MeCN (5 mL) was stirred at 20 °C for 1 h in an argon atmosphere. Then the reaction mixture was treated with a saturated solution of $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (4×10 mL). The combined extracts were washed with a saturated solution of $Na_2S_2O_3$ (5 mL), dried with $MgSO_4$, and concentrated *in vacuo*, and the residue was chromatographed on SiO_2 (ethyl acetate—hexane (2 : 1) as the eluent). Compound **2** was obtained as an oil in 83% yield (75 mg). IR, ν/cm^{-1}: 1600, 1700. ^{1}H NMR, δ: 2.70 (m, 2 H, CH_2); 3.25 and 3.55 (both s, 6 H, OMe); 3.75 (m, 8 H, NCH_2CH_2O); 5.05 (m, 2 H, $=CH_2$); 5.15 (s, 1 H, HC(2)); 5.80—5.90 (m, 1 H, CH=). ^{13}C NMR, δ: 44.12 (CH_2); 47.81 (CH_2N); 51.52 and 53.44 (OMe); 66.66 (CH_2O); 76.46 (C(5)); 100.38 (C(2)); 105.23 (C(4)); 118.40 ($CH_2=$); 132.79 (CH=); 165.02 (C(3)); 192.05 (C=O). Found (%): C, 55.98; H, 6.60; N, 4.40. $C_{14}H_{20}ClNO_4$. Calculated (%): C, 55.81; H, 6.64; N, 4.65. MS, *m/z*: 303 $[M+2]^+$ (2.6), 301 $[M]^+$ (7.5), 288 (18), 286 $[M-Me]^+$ (52), 276 (9.3), 274 $[M-HCN]^+$ (28), 272 (6), 270 $[M-OMe]^+$ (18), 268 (35), 266 $[M-Cl]^+$ (100).

References

1. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2334 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
2. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2539 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
3. G. A. Tolstikov, S. A. Ismailov, L. M. Khalilov, and M. S. Miftakhov, *Zh. Org. Khim.*, 1992, **28**, 438 [*J. Org. Chem. USSR*, 1992, **28** (Engl. Transl.)].
4. S. A. Ismailov, M. S. Miftakhov, and G. A. Tolstikov, *Mendeleev Commun.*, 1991, 149.
5. M. S. Miftakhov, R. M. Khalikov, R. R. Akhmetvaleev, and G. A. Tolstikov, *Zh. Org. Khim.*, 1995, **31**, 207 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
6. M. S. Miftakhov, N. A. Ivanova, S. A. Yumagulova, S. A. Torosyan, and N. S. Vostrikov, *Zh. Org. Khim.*, 1995, **31**, 1639 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
7. M. S. Miftakhov, R. M. Khalikov, A. A. Fatykhov, and R. R. Akhmetvaleev, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1169 [*Russ. Chem. Bull.*, 1995, **44**, 1129 (Engl. Transl.)].
8. F. A. Akbutina, S. A. Torosyan, N. S. Vostrikov, L. V. Spirikhin, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2961 [*Russ. Chem. Bull.*, 1996, **45**, 2813 (Engl. Transl.)].
9. F. A. Akbutina, S. A. Torosyan, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1646 [*Russ. Chem. Bull.*, 1997, **46**, 1569 (Engl. Transl.)].
10. W. C. Grontas and D. Felker, *Synthesis*, 1980, 861.
11. M. Fieser and L. Fieser, in *Reagents for Organic Synthesis*, Wiley, New York, 1980, **8**, 261; 1982, **10**, 216; 1984, **11**, 271.
12. Tse-Lok Ho, *Synth. Commun.*, 1981, **11**, 101.

Received December 29, 1997;
in revised form February 24, 1998

Reactions of arensulfenamides with olefins in the presence of picric acid

N. V. Zyk, E. K. Beloglazkina, and A. V. Mamaeva*

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0290. E-mail: bel@org.chem.msu.su

N-(2- and 4-Nitrophenylthio)morpholines in the presence of equimolar amounts of picric acid enter into the reaction of electrophilic sulfenylation of the C=C norbornene bond to give bi- and tricyclic sulfides. With cyclohexene, *trans*-2-arylthiocyclohexanol are formed.

Key words: arensulfenamides, picric acid, sulfenylation.

Several examples of activation of electrophilic reactions of sulfenamides by protic acids are known. For example, *N*-(4-nitrophenylthio)acetimide in the presence of CF_3COOH reacts with alkenes to give trifluoroacetates of the corresponding β-arylthioalkanols.[1] The activation of arenesulfenamides by trifluoromethane-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1661—1663, August, 1998.

1066-5285/98/4708-1617 $20.00 © 1998 Plenum Publishing Corporation