Chemistry of Heterocyclic Compounds, Vol. 46, No. 9, 2010

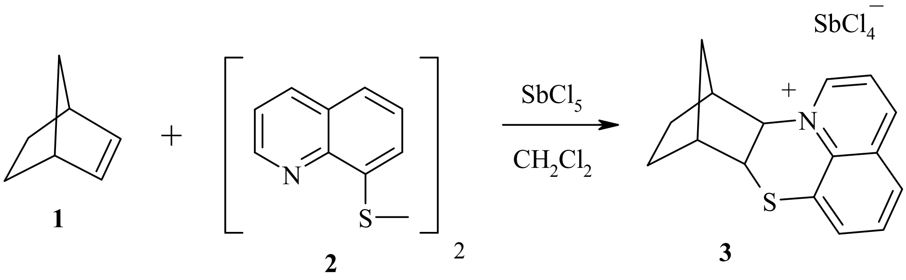
UNUSUAL REACTION OF DI(8-QUINOLYL) DISULFIDE WITH NORBORNENE

A. V. Borisov[1]*, Zh. V. Matsulevich[1], V. K. Osmanov[1], G. N. Borisova[1], G. K. Fukin[2], and E. V. Baranov[2]

Keywords: di(8-quinolyl) disulfide, norbornene, heterocyclization.

Lewis acids facilitate the addition of disubstituted organic disulfides to alkenes. This addition usually gives the disulfenylation products, namely, dithioesters [1-4].

In the present work, we report a new direction for the reaction of an alkene with a dihetaryl disulfide containing a potentially nucleophilic nitrogen atom in the hetaryl fragment. We found that the reaction of norbornene (**1**) with di(8-quinolyl) disulfide (**2**) in methylene chloride in the presence of $SbCl_5$ at about 0°C gives *peri*-annelated system **3** in 85% yield.



The molecular structure of this product was determined by X-ray diffraction crystallographic analysis and shown in the Figure 1.

The IR spectra were taken on a Shimadzu IR-Prestige-21 spectrometer, KBr pellets. The ^1H NMR spectra were taken on a Bruker DRX-500 spectrometer at 500 MHz in DMSO-d_6 with TMS as the internal standard.

---

* To whom correspondence should be addressed, e-mail: avb1955@rambler.ru.

[1]R. E. Alekseev Nizhnii Novgorod State Technical University, Nizhnii Novgorod 603950, Russia.
[2]G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhnii Novgorod 603950, Russia.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1423-1425, September, 2010. Original article submitted April 21, 2010.

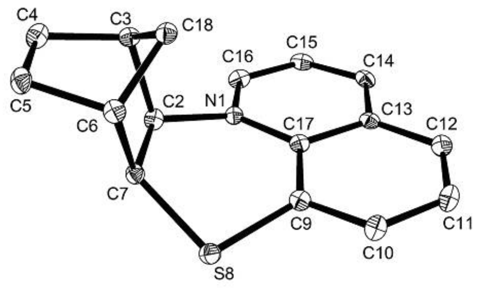


Fig. 1. Structure of the cation of salt **3** (the hydrogen atoms are not shown).

TABLE 1. Main Bond Lengths (l) and Valence Angles (ω) in the Cation of Salt **3**

Bond	l, Å	Angle	ω, deg
N(1)–C(2)	1.504(4)	C(16)–N(1)–C(17)	119.8(3)
N(1)–C(16)	1.336(4)	C(16)–N(1)–C(2)	114.7(3)
N(1)–C(17)	1.381(4)	C(17)–N(1)–C(2)	125.2(3)
S(8)–C(7)	1.793(3)	C(9)–S(8)–C(7)	101.27(15)
S(8)–C(9)	1.744(3)		

8-Thia-1-azoniumpentacyclo[7.7.1^{3,6}.0^{2,7}.0^{13,17}]octatdeca-1(17),9,11,13,15-pentaene Tetrachlorantimonite (3). A solution of $SbCl_5$ (1.80 g, 6 mmol) in methylene chloride (50 ml) and a solution of alkene **1** (0.38 g, 4 mmol) in methylene chloride (10 ml) were added to a solution of disulfide **2** (1.92 g, 6 mmol) in methylene chloride (200 ml) at ~0°C. After 12 h, 1.35 g (65%) precipitated salt **3** was filtered off and the filtrate was evaporated in vacuum. Recrystallization of the residue from methylene chloride gave an additional 0.41 g (20%) salt **3**; mp 163-165°C. IR spectrum, ν, cm^{-1}: 1612, 1585, 1523, 1404, 1367, 1300, 1226, 1078, 1031, 823, 752. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.40, 1.51 (2H, two m, 2H-5); 1.46 (1H, d, $^3J = 10.4$, H-18 *syn*); 1.68 (2H, m, 2H-4); 1.83 (1H, d, $^3J = 10.4$, H-18 *anti*); 2.53 (1H, br. s, H-6); 2.57 (1H, br. s, H-3); 3.96 (1H, d, $^3J = 8.0$, H-7); 5.45 (1H, d, $^3J = 8.0$, H-2); 8.03 (1H, t, $^3J = 8.0$, H-11); 8.21 (1H, m, H-15); 8.20 (1H, d, $^3J = 9.0$, H-12); 8.28 (1H, d, $^3J = 8.2$, H-10); 9.28 (1H, d, $^3J = 9.4$, H-14); 9.78 (1H, d, $^3J = 5.4$, H-16). Found, %: C 36.96; H 3.04. $C_{16}H_{16}Cl_4NSSb$. Calculated, %: C 37.11; H 3.11.

X-ray Diffraction Structural Analysis of Salt 3. The experimental set of intensities was measured on a Smart APEX automatic diffractometer equipped with a graphite monochromator using MoKα radiation and ω-θ-scanning.The structure was solved by the direct method and refined by the method of least squares relative to F^2_{hkl} anisotropically for all the non-hydrogen atoms. The hydrogen atoms were placed in geometrically calculated positions and refined in the horse rider model. All the calculations were carried out using the *SHELXTL* program package v.6.12 [5]. The unit cell parameters of monoclinic crystals of $C_{16}H_{16}Cl_4NSSb$ at 100K were as follows: $a = 9.7599(5)$, $b = 10.1019(6)$, $c = 18.9310(10)$ Å, $\beta = 95.1380(10)°$, $V = 1858.97(18)$ Å^3, $Z = 4$, space group $P2(1)/c$, $d_{\mathrm{calc}} = 1.850$ g/cm^3, $\mu = 2.168$ mm^{-1}, $2.10 \leq \theta \leq 26.0°$. A total of 15315 reflections were measured, of which 3640 reflections [$R_{\mathrm{int}} = 0.0400$] were independent, $GOOF = 1.017$, $R_1 = 0.0363$, $wR_2 = 0.0860$, ($I > 2\sigma(I)$), $R_1 = 0.0490$, $wR_2 = 0.0900$ (over all the data). The residual electron density 1.949-1.319 e. Å^{-3}. The crystallographic data for salt **3** were deposited at the Cambridge Crystallographic Data Center (CCDC 771314) (http://www.ccdc.cam.ac.uk/data_request/cif).

This work was carried out with the financial support of the Russian Basic Research Fund (Project 09-03-97034-p-povolzh'e-a).

REFERENCES

1. M. C. Caserio, C. L. Fisher, and J. K. Kim, *J. Org. Chem.*, **50**, 4390 (1985).
2. S. I. Usugi, H. Yorimitsu, H. Shinokubo, and K. Oshima, *Org. Lett.*, **6**, 601 (2004).
3. A. V. Martynov, A. R. Zhinkin, and S. V. Amosova, *Zh. Org. Khim.*, **42**, 207 (2006).
4. N. Yamagiwa, Y. Suto, and Y. Torisawa, *Bioorg. Med. Chem. Lett.*, 6197 (2007).
5. G. M. Sheldrick, *SHELTXTL, v. 6.12, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA (2000).