orientation of the exocyclic bonds relative to ring D is axial with C(14), equatorial with C(1) and H(9), pseudoaxial with S, and pseudoequatorial with C(4). Ring D has a trans linkage (the linkage of rings B and C can be called "pseudocis") with cyclohexane ring A. The benzene rings (D in I and C in II) are planar.

LITERATURE CITED

1. V. G. Kharchenko, S. K. Klimenko, and T. I. Krupina, Khim. Geterotsikl. Soed., No. 3, 76 (1971).
2. V. G. Kharchenko and A. A. Rassudova, Zh. Org. Khim., 9, 2177 (1972).
3. I. A. Gillean, D. W. Phelps, and A. W. Cordes, Acta Crystallogr., 29, Sect. B, 2296 (1973).
4. S. S. Chu, Acta Crystallogr., Sect. B, 29, 1690 (1973).
5. S. S. Chu, Acta Crystallogr., Sect. B, 28, 3625 (1972).
6. S. S. Chu and M. Mangion, Acta Crystallogr., Sect. B, 31, 2135 (1975).
7. O. Kennard and A. S. Horn, Acta Crystallogr., Sect. B, 30, 1644 (1974).
8. A. Smith, R. Kalish, and E. I. Smutny, Acta Crystallogr., Sect. B, 28, 3494 (1972).
9. L. E. Sutton (ed.), Tables of Interatomic Distances and Configuration in Molecules and Ions, Suppl. 1956-1959, London (1968).
10. V. A. Naumov, in: Problems in Stereochemistry [in Russian], No. 1, Kiev University Publishing House, Kiev (1971).

HETEROATOMIC AZIRIDINE DERIVATIVES.

10*. NEW MACROHETEROCYCLIC SYSTEMS — DERIVATIVES OF 1,2-BENZO-4,13-DIAZA-7,10-DITHIACYCLOTETRADECA-1-ENE AND 1,4-DIAZA-7,10,11,14-TETRATHIACYCLOHEXADECANE

M. G. Voronkov, V. I. Knutov, V. A. Usov,
M. K. Butin, and O. B. Bannikova

UDC 547.717'897

Recently the chemistry of macrocyclic compounds has produced a new development. The synthesis of catenanes and rotaxanes, the invention of crown ethers, the syntheses of cyclophanes, ansa compounds, etc. [2-5] are broadly well-known results in this field.

The cyclization of linear bifunctional compounds is one of the methods of synthesizing macrocycles. In order to obtain linear diamines we reacted aziridine and N-(carbomethoxyethyl)aziridine with 1,2-ethanedithiol in various solvents. 1,2-Ethanedithiol in methanol at 60°C reacts with 2 moles of aziridine or N-(carbomethoxyethyl)aziridine forming the diamino-3,6-dithiaoctanes I, II. In an aprotic solvent (benzene) 1,2-ethanedithiol yields sulfide III with aziridine, which is easily oxidized by atmospheric oxygen to disulfide IV (see Scheme 1).

Diamines I and II easily react with phthalic dichloroanhydride in dry benzene or toluene at 5°C in the presence of triethylamine under conditions of high dilution [6]. The yields of the derivatives of 1,2-benzo-4,13-diaza-7,10-dithiacyclotetradeca-1-ene V, VI come to 66 and 70%, respectively.

The reaction of disulfide IV with oxalyl chloride proceeds similarly in dry benzene forming 1,2-dioxo-3,16-diaza-6,9,10,13-tetrathiacyclohexadecane (VII) with an 80% yield.

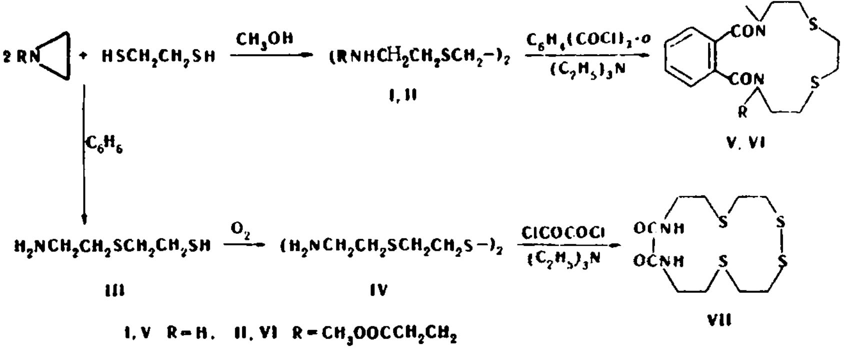
---

[*] See [1] for Communication 9.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1474-1475, November, 1979. Original article submitted August 11, 1978; revision submitted May 17, 1979.

0009-3122/79/1511-1183$07.50

Scheme 1



EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument. The PMR spectra were run on a Tesla BS 487C spectrometer (80 MHz); the solvent for compounds I, V was DMSO-d_6, for II, VI $CDCl_3$. The chemical shifts are given on the δ scale in relation to TMS.

1,8-Diamino-3,6-dithiaoctane (I). A mixture of 4.3 g (0.1 mole) of aziridine and 4.7 g (0.05 mole) of 1,2-ethanedithiol in 80 ml of methanol was heated for 6 h at 55-60°C. The methanol was evaporated and the residue recrystallized from benzene. The yield of I was 7.6 g (84%). mp 45°C. IR spectrum: 3320, 1590 (NH_2); 760 cm^{-1} (CH_2SCH_2) PMR spectrum: 2.75-3.24 ppm (12H, m, NCH_2, SCH_2). Found %: C 40.9; H 8.8; N 15.4; S 35.0. $C_6H_{16}N_2S_2$. Calculated %: C 40.0; H 8.8; N 15.5; S 35.5. Dihydrochloride, mp 175-176°C. Literature data [7]: mp 186-188°C. Found%: N 11.0. $C_6H_{16}N_2S_2 \cdot 2HCl$. Calculated %: N 11.1.

1,8-Bis(N-carbomethoxyethylamino)-3,6-dithiaoctane (II) was obtained similarly from 9.0 g (0.07 mole) of N-(carbomethoxyethyl)aziridine and 3.3 g (0.033 mole) of 1,2-ethanedithiol. The yield was 9.3 g (75%). Oil. IR spectrum: 3320 (NH), 1740 ($COOCH_3$), 760 cm^{-1} (CH_2SCH_2). PMR spectrum: 2.53-2.67 (16H, m, NCH_2, SCH_2), 3.57 ppm (6H, s, OCH_3). Dihydrochloride, mp 145-146°C. Found %: Cl 16.5%. $C_{14}H_{28}N_2O_4S_2 \cdot 2HCl$. Calculated %: Cl 16.7.

2-Aminoethyl 2-Mercaptoethyl Sulfide (III). A mixture of 8.6 g (0.2 mole) of aziridine and 9.4 g (0.1 mole) of 1,2-ethanedithiol in 120 ml of benzene was heated for 12 h at 55-60°C. The benzene was evaporated and the residue was vacuum distilled. The yield of sulfide III was 8.9 g (65%). bp 155-157°C (6 mm). IR spectrum: 3300, 3360, 1600 (NH_2), 2550 cm^{-1} (SH). Found %: N 10.3. $C_4H_{11}NS_2$. Calculated %: N 10.2.

Bis[2-(2-aminoethylthio)ethyl] Disulfide (IV). Sulfide III, 6.8 g (0.05 mole), was allowed to stand in air for 72 h. Compound IV which formed was crystallized from benzene. Yield 5.2 g, mp 105°C. Found %: C 35.7; H 6.8; N 9.8. $C_8H_{20}N_2S_4$. Calculated %: C 35.3; H 7.3; N 10.3.

3,14-Dioxo-1,2-benzo-4,13-diaza-7,10-dithiacyclotetradeca-1-ene (V). To a solution of 1.0 g (5.5 mmole) of diamine I and 1.12 g (0.011 mole) of triethylamine in 1 liter of dry toluene with cooling to 5°C and intense agitation was slowly added a solution of 1.12 g (5.5 mmole) of phthalic dichloroanhydride in 20 ml of dry toluene. It was agitated for 30 min, the precipitate was filtered off, and the solvent evaporated under reduced pressure. The residue was dissolved in dimethylformamide and precipitated with diethyl ether. Yield 1.15 g (66%), mp 181-182°C. IR spectrum: 3270 (NH), 1640 (CO), 765 cm^{-1} (CH_2SCH_2). PMR spectrum: 2.99-3.56 (12H, m, NCH_2, SCH_2), 7.70 ppm (4H, m, C_6H_4). Found %: C 54.5; H 5.6; N 9.1; mol. wt. (cryoscopically) 295. $C_{14}H_{18}N_2O_2S_2$. Calculated %: C 54.2; H 5.8; N 9.1; mol. wt. 310.

2,14-Dioxo-4,13-bis(2-carbomethoxyethyl)-1,2-benzo-4,13-diaza-7,10-dithiacyclotetradeca-1-ene (VI). This compound was similarly obtained from 1.0 g (2.8 mmole) of compound II and 0.57 g (2.8 mmole) of phthalic dichloroanhydride. Yield 0.96 g (70%). Oil. IR spectrum: 1735 ($COOCH_3$), 1640 (CO), 760 cm^{-1} (CH_2SCH_2). PMR spectrum: 2.62-3.53 (16H, m, NCH_2, SCH_2), 3.62 (6H, s, OCH3), 7.29 ppm (4H, m, C_6H_4). Found %: C 54.7; H 6.5; N 5.1; mol. wt. 501. $C_{22}H_{32}N_2O_6S_2$. Calculated %: C 54.8; H 6.2; N 5.5; mol. wt. 482.

1,2-Dioxo-3,16-diaza-6,9,10,13-tetrathiacyclohexadecane (VII). This compound was similarly obtained from 0.6 g (3.0 mmole) of disulfide IV and 0.38 g (3.0 mmole) of oxalyl chloride. The yield was 0.58 g (80%), mp 135°C. IR spectrum: 3290 (NH), 1650 (CO), 730

cm^{-1} (CH_2SCH_2). Found %: N 8.4; S 40.3; mol. wt. 302. $C_{10}H_{18}N_2O_2S_4$. Calculated %: N 8.6; S 39.6; mol. wt. 326.

LITERATURE CITED

1. M. G. Voronkov, V. I. Knutov, L. M. Chudesova, and O. B. Bannikova, Khim. Geterotsiklich. Soed., No. 1, 55 (1979).
2. G. Schill, Catenanes, Rotaxanes, and Knots, Academic Press (1971).
3. J. J. Christensen, D. J. Eatough, and R. M. Izatt, Chem. Rev., 74, 351 (1974).
4. J. S. Bradshaw and I. K. Hui, J. Heterocycl. Chem., 11, 649 (1974).
5. G. R. Newkome, J. D. Sauer, J. M. Roper, and D. C. Hager, Chem. Rev., 74, 513 (1977).
6. Ya. L. Gol'dfarb, S. Z. Taits, and L. I. Belen'kii, Zh. Org. Khim., 29, 3564 (1959).
7. F. P. J. Dwyer and F. Lions, J. Am. Chem. Soc., 69, 2917 (1947).

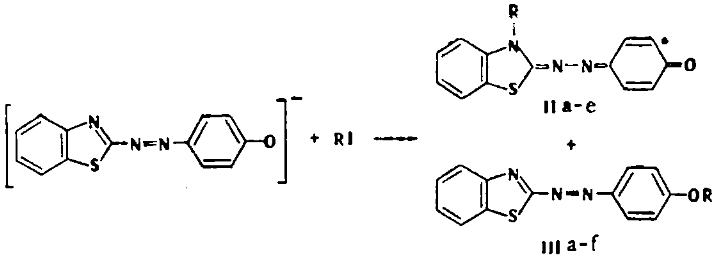
ALKYLATION OF THE 2-BENZOTHIAZOLYLAZOPHENOL ANION

A. Yu. Ermishov and I. L. Shegal

UDC 547.789.5.6:542.953

The alkylation of benzothiazolylazophenol (I) has not been sufficiently studied. There is a report on the methylation of I resulting in the formation of (3-methylbenzothiazolyl)-2-azino-4-(1,4-dihydro)-1-oxobenzene [1] (IIa).

We established that the anion of azophenol I is alkylated with a satisfactory yield by various alkyl halides in an ethanolic sodium ethylate solution at two reaction centers forming N- and O-substitution products (Table 1). The structure of methyl derivatives IIa and IIIa was demonstrated on the basis of the IR spectra and by comparison with stabilized quinoneazine and hydroxyazoid forms obtained according to [2-4]. A mixture of isomers IIa and IIIa was also isolated by methylating anion I with diazomethane.



IIa-e

IIIa-f

a $R=CH_3$; b $R=C_2H_5$; c $R=i\text{-}C_3H_7$; d $R=n\text{-}C_4H_9$; e $R=n\text{-}C_8H_{17}$; f $R=CH_2C_6H_5$

A nonsynchronous accumulation of the methylation products was noted in separate experiments: in the first hours isomer IIa is formed, the portion of which decreases during the reaction through the accumulation of isomer IIIa (Table 2); in connection with this the reaction in which compounds IIa and IIIa are formed can be assigned to a thermodynamically controlled one.

An increase in the length of the carbon chain and degree to which the alkyl is branched, as the Stuart–Briegleb model shows, leads to an increase in the steric hindrances for the N-alkylated product, which leads to a decrease in the portion of the N-isomer. The possibility of a transition of isomer IIa to isomer IIIa during boiling in the ethanolic sodium ethylate solution, dimethylformamide, and mesitylene should be mentioned. At this time anion I is not detected. Evidently polar compound IIa [2] can exist as a charge-transfer type of associated dimer During heating in a solvent the synchronous transfer of the methyl groups from the nitrogen to the oxygen atom takes place. Thus the accumulation of the thermodynamically more stable compound IIIa does not proceed through the dealkylation of isomer IIa forming anion I but through the intermolecular transfer of the methyl groups. The following fact points to the lesser stability of the N-alkyl bond in going from methyl derivative IIa to ethyl derivative

---

N. P. Ogarev Mordov State University, Saransk 430000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1476-1478, November, 1979. Original article submitted December 12, 1977; revision submitted October 17, 1978.

0009-3122/79/1511-1185$07.50