SYNTHESIS OF PERHYDRO-1,4-SELENAZINES AND PERHYDRO-1,4-TELLURAZINES CONTAINING A SULFAMIDE GROUP*

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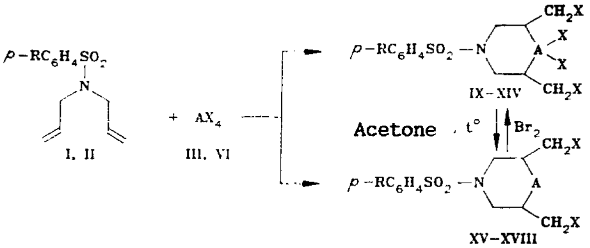
Dehalogenation products were obtained under conditions for the two-phase selenohalogenation of N,N-diallylarylsulfamides in addition to the major products, 1,1-dihalo-2,6-dihalomethyl-4-arylsulfonylperhydro-1,4-selenazines. Phenylselenium trihalides form derivatives of perhydro-1,4-azaselenonium halides. Tellurohalogenation gives analogous results but tetrabromotellurium partially forms intermolecular complexes.

Selenium-containing heterocyclic compounds have recently attracted attention as possible antiparasitic [2, 3] and antibacterial agents [4, 5]. In this regard, definite interest is found in previously unreported perhydro-1,4-selenazines and perhydro-1,4-tellurazines containing an arylsulfamide group. For the synthesis of these compounds, we used our method for two-phase seleno- and tellurohalogenation [6] of N,N-diallylarylsulfamides (I) and (II) by tetrabromoselenium (III), tetrachloroselenium (IV), tetrabromotellurium (V), tetrachlorotellurium (VI), phenylselenium tribromide (VII), and phenylselenium tribromide (VIII) [7].

Dehalogenation products XV-XVIII were obtained from the mother liquor in the case of selenium tetrahalides under the reaction conditions in addition to the major products, perhydro-1,4-selenazines IX-XIV.

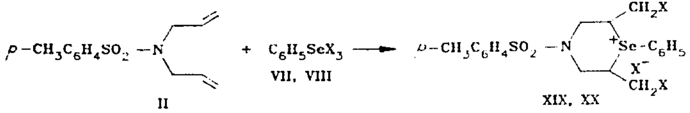


I, IX, X, XIII, XV, XVI R=H; II, XI, XII, XIV, XVII, XVIII R=CH₃; III, IV, IX, XI, XII, XV, XVI A=Se; V, VI, XIII, XIV A=Te; III, V, IX, XI, XIV, XV, XVII X=Br; IV, VI, X, XII, XIII, XVI, XVIII X=Cl

Signals for the CH_2—halogen, CH—Se, CH—Te, and CH—N protons are clearly seen in the PMR spectra of IX-XVIII (Table 1) but there are no signals for protons at carbon-carbon multiple bonds.

Azines IX-XII readily undergo dehalogenation even upon heating in acetone at reflux to give XV-XVIII, which, in turn, give IX-XII upon halogenation.

Phenylselenium trihalides VII and VIII react with diallylsulfamide II in diethyl ethyl ether at −30°C to give perhydro-1,4-azaselenonium halides XIX and XX. The spectral characteristics of these compounds are close to those reported for XI and XII.



VII, XIX X=Br; VIII, XX X=Cl

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TABLE 1. Characteristics of Compounds Synthesized

Compound	Chemical formula	mp, °C (dec.)	IR spectrum cm^{-1}	PMR spectrum, δ (ppm), J (Hz)	Yield, %
IX	$C_{12}H_{15}Br_4NO_2SSe$	146...148	1160, 770, 570	3,52...3,94 (4H, m, $2CH_2N$); 3,98 (4H, d, $2CH_2Br$); 4,02...4,88 (2H, m, 2CHSe); 7,85...8,46 (5H, m, C_6H_5)	61
X	$C_{12}H_{15}Cl_4NO_2SSe$	139...141	1160, 760, 680	3,70 (4H, m, $2CH_2N$); 4,33 (4H, m, $2CH_2Cl$); 4,72 (2H, m, 2CHSe); 7,7...7,9 (5H, m, C_6H_5)	46
XI	$C_{13}H_{17}Br_4NO_2SSe$	142...144	1165, 765, 575	2,46 (3H, s, CH_3); 3,38...3,95 (4H, m, $2CH_2N$); 3,95...4,38 (4H, m, $2CH_2Br$), 4,38...4,88 (2H, m, 2CHSe); 7,74 (2H, d, 2CH); 7,91 (2H, d, $J=10,0$ Hz, 2CH)	76
XII	$C_{13}H_{17}Cl_4NO_2SSe$	155...156	1160, 760, 655	2,60 (3H, s, CH_3); 2,98...3,66 (4H, m, $2CH_2N$); 4,23...4,53 (4H, m, $2CH_2Cl$); 4,73...5,23 (2H, m, 2CHSe); 7,66 (2H, d, $J=8,0$ Hz, 2CH)	44
XIII	$C_{12}H_{15}Cl_4NO_2SSe$	148...150	1160, 690	3,30...3,78 (4H, m, $J=11,25$ Hz. $2CH_2N$); 4,02...4,48 (4H, m, $2CH_2Cl$); 4,48...5,20 (2H, m, 2CHTe), 7,60...7,98 (5H, m, C_6H_5)	27
XIV	$C_{13}H_{17}Br_4NO_2STe$	134...135	1155, 570	2,45 (3H, s. CH_3); 3,03...3,45 (4H, m. $2CH_2N$); 4,05 (4H, m, $J=11,25$ Hz $2CH_2Br$); 4,18...4,80 (2H, м, 2CHTe); 7,35 (2H, d, $J=10,0$ Hz 2CH)	32
XV	$C_{12}H_{15}Br_2NO_2SSe$	154...155	1150, 770, 575	3,35...3,88 (4H, m, $2CH_2N$); 3,90 (4H, d. $2CH_2Br$); 3,98...4,58 (2H, m, 2CHSe); 7,92...8,46 (5H, m, C_6H_5) (in$CDCl_3$)	52
XVI	$C_{12}H_{15}Cl_2NO_2SSe$	149	1160, 780, 680	3,36...3,49 (4H, m, $2CH_2N$); 3,69 (4H, s, $2CH_2Cl$); 3.90 (2H, m, 2CHSe); 7,5...7,8 (5H, m, C_6H_5)	50
XVII	$C_{13}H_{17}Br_2NO_2SSe$	179...181	1160, 770, 570	2,37 (3H, s, CH_3); 3,0...3,6 (4H, m, $2CH_2N$); 3,76 (4H, d. $2CH_2Br$); 3,90 (2H, m. 2CHSe); 7,67 (2H, d, $J=10,0$ Hz, 2CH); 7,85 (2H, d 2CH)	74
XVIII	$C_{13}H_{17}Cl_2NO_2SSe$	168...169	—	—	49

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*IX-XII were crystallized from $CHCl_3$, while XIII was crystallized from $C_2H_4Cl_2$ and XIV was crystallized from CCl_4.

The decrease in electron affinity upon descending in the series S, Se, Te and the increase in the availability of valence orbitals lead to diffferent properties for organotellurium compounds, which permit their use to obtain derivatives not characteristic for organosulfur and organoselenium compounds. Thus, the great capacity of tellurium compounds to form stable complexes with electron-donor ligands is well known [8]. Tetrabromotellurium, for example, forms monomolecular complexes XXI and XXII with I and II in addition to cyclic perhydro-1,4-tellurazine (XIV):

$$p\text{-}RC_6H_4SO_2\text{-}N\text{-}(\text{-}CH_2\text{-}CH{=}CH_2)_2\cdot TeBr_4$$

XXI, XXII

XXI R=H; XXII R=CH_3

The IR spectrum of XXI has a C═C stretching band at 1610 cm^{-1}. The PMR spectrum of the CH_2 group protons appear as a doublet at 3.89 ppm, while the CH_2═CH proton multiplet appears at 5.1-6.0 ppm.

Thus, selenium and tellurium tetrahalides and phenylselenium trihalides undergo selective anti-Markovnikov addition to 1,6-heterodienes to give largely derivatives of perhydro-1,4-selenazine and perhydro-1,4-tellurazine. Tetrabromotellurium partially form intramolecular complexes.

EXPERIMENTAL

The IR spectra were taken on an IKS-29 spectrometer for KBr pellets. The PMR spectra were taken on a Tesla BS-487C spectrometer at 80 MHz and WS-200SY spectrometer in DMSO-d_6 with HMDS as the internal standard. The purity of the compounds and composition of the reaction mixtures were monitored by thin-layer chromatography on Silufol plates with iodine as the developer. The elemental analysis data for C, H, N, and Hal corresponded to the calculated values.

Samples of N,N-diallylphenylsulfamide, N,N-diallyl(p-tolylsulfamide), and the phenylselenium trihalides were obtained according to reported procedures [9, 10].

1,1-Dihalo-2,6-dihalomethyl-4-arylsulfonylperhydro-1,4-selenazines and -tellurazines (IX-XIV). A sample of 30 mmoles selenium or tellurium tetrahalide obtained from selenium or tellurium dioxide and the calculated amount of hydrogen halide was added with strong stirring to a solution of 30 mmoles N,N-diallylarylsulfamide I or II in 150 ml diethyl ether at 0°C and stirred for 20 h. Then, the crystalline precipitate was filtered, crystallized (see Table 1) and dried in a vacuum dessicator to give IX-XIII. Azine XIV was isolated by crystallization of the residue from CCl_4, while XXII was obtained by recrystallization of the undissolved part from dichloroethane.

The organic layer was separated from the filtrate and dried with anhydrous sodium sulfate. The solvent was removed in vacuum to give XV-XVIII.

N,N-Diallylphenylsulfamide-tetrabromotelluride (XXI, $C_{12}H_{15}Br_4NO_2STe$) was obtained in 30% yield, dec. at 133-134°C (from $C_2H_4Cl_2$). IR spectrum: 1610 (C=C), 1165 (SO_2N), 582 cm^{-1} (C—Br). PMR spectrum: 3.70-3.86 (4H, d, J = 10 Hz, $2CH_2N$); 5.02-5.28 (4H, m, $2CH_2$=), 5.47-5.89 (2H, m, 2CH=), 7.67-7.84 (5H, m, C_6H_5).

N,N-Diallyl-p-tolylsulfamide-tetrabromotelluride (XXII) was obtained in 9% yield, dec. 128-129°C ($C_2H_4Cl_2$). IR spectrum: 1600 (C=C), 1162 (SO_2N), 575 cm^{-1} (C—Br). PMR spectrum: 2.61 (3H, s, CH_3), 3.89 (4H, d, J = 7.0 Hz, $2CH_2N$) 4.38 (4H, m, $2CH_2$=); 5.18-6.00 (2H, m, 2CH=); 7.65 (2H, d, 2CH), 7.93 (2H, d, 2CH).

2,6-Dihalomethyl-4-arylsulfonylperhydro-1,4-selenazines (XV-XVIII). A solution of 5.0 mmoles IX-XII in 50 ml acetone was heated at reflux in a round-bottomed flask equipped with a reflux condenser until the reaction was complete as indicated by thin-layer chromatography. Then, 70 ml water was added. The crystalline precipitate was filtered and dried in a vacuum dessicator.

1-p-Tolylsulfonyl-4-phenyl-3,5-dihaloperhydro-1,4-azaselenonium Halides (XIX and XX). A sample of 14 mmoles phenylselenium trihalide in 50 ml diethyl ether was added with strong stirring to a solution of 14 mmoles sulfamide II in 150 ml diethyl ether cooled to −30°C. At the completion of the reaction, the crystalline precipitate was filtered off and dried in a vacuum dessicator.

1-p-Tolylsulfonyl-4-phenyl-3,5-dibromomethylperhydro-1,4-azaselenonium bromide (XIX, $C_{19}H_{22}Br_3NO_2SSe$) was obtained in 63% yield, mp 86°C (CCl_4). IR spectrum: 1105 (SO_2N), 760 (C—Se), 560 cm^{-1} (C—Br). PMR spectrum ($CDCl_3$): 2.85 (3H, s, CH_3), 3.40-3.98 (8H, m, $2CH_2N$, $2CH_2Br$), 3.98-4.78 (2H, m, 2CHSe), 7.78 (2H, d, C H), 7.88-8.46 ppm (7H, m, C_6H_4, C_6H_5).

1-p-Tolylsulfonyl-4-phenyl-3,5-dichloromethylperhydro-1,4-azaselenonium chloride (XX, $C_{19}H_{22}Cl_3NO_2SSe$) was obtained in 78% yield, mp 101-102°C ($CHCl_3$). IR spectrum: 1100 (SO_2N), 745 (C—Se), 575 cm^{-1} (C—Cl). PMR spectrum in $CCl_3)_2C{=}O$: 2.84 (3H, s, CH_3), 3.55-4.00 (8H, m, 2CHSe), 7.13-8.03 ppm (9H, m, C_6H_5, C_6H_4).

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