REACTIONS OF N-SUBSTITUTED ALLYLACETIC ACID AMIDES WITH SELENIUM AND TELLURIUM TETRAHALIDES*

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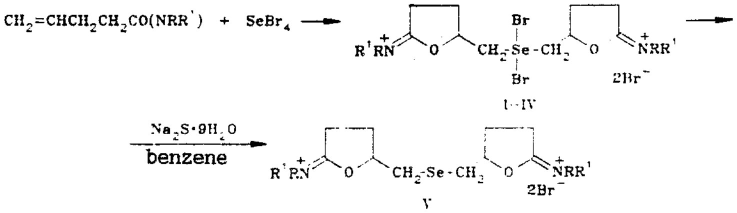
The addition of selenium tetrabromide to the olefinic bond of N-substituted allylacetic acid amides (reagent molar ratio 2:1) proceeds counter to Markownikoff's rule with the formation of tetrahydrofuran derivatives. The addition of tellurium tetrahalides under the same conditions (reagent molar ratio 1:1) proceeds in accordance with Markownikoff's rule with the formation of tetrahydropyran derivatives.

It is known that the addition of electrophilic agents to carbon—carbon multiple bonds is facilitated significantly when the molecule contains an electron-donor group, due to which ring formation is possible, and is hindered by electron-acceptor substituents.

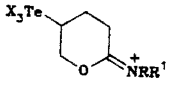
We studied the addition of selenium and tellurium tetrahalides to N-substituted allylacetic acid amides. Tetrahydrofuran derivatives I-IV are formed in the reaction of selenium tetrabromide with N-substituted allylacetic acid amides under the conditions of two-phase selenohalogenation [2], i.e., the reagents react in a ratio of 2:1 with the addition of selenium tetrabromide counter to Markownikoff's rule.



I $R=CH_3$, $R^1=H$; II R, $R^1=CH_3$; III, V R, $R^1=(CH_2)_5$; IV R, $R^1=(CH_2)_2O(CH_2)_2$

Compound III reacts with sodium sulfide nonahydrate to give dehalogenation product V. The results of elementary analysis confirm the formation of compounds with the compositions presented.

Under the same conditions tellurium tetrahalides react with N-substituted allylacetic acid amides to give tetrahydropyran derivatives VI-IX:



VI–IX

VI $R=R^1=CH_3$, X=Br; VII $R=R^1=CH_3$, X=Cl; VIII R, $R^1=(CH_2)_5$, X=Br; IX R, $R^1=(CH_2)_5$, X=Cl

In this case the reagents react in a ratio of 1:1, and the addition of tellurium tetrahalides to the carbon-carbon multiple bond proceeds in accordance with Markownikoff's rule.

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C (dec.)	IR spectrum, νCN, ν_1COC, cm^{-1}
I	$C_{12}H_{22}Br_4N_2O_2Se$	123	1690, 1228, 1140
II	$C_{14}H_{26}Br_4N_2O_2Se$	93	1708, 1224, 1208
III	$C_{20}H_{34}Br_4N_2O_2Se$	117...118	1690, 1220, 1190
IV	$C_{18}H_{30}Br_4N_2O_2Se$	127...129	1690, 1225, 1185
VI	$C_7H_{13}Br_4NOTe$	216...218	1702, 1230, 1195
VII	$C_7H_{13}Cl_4NOTe$	228...230	1705, 1235, 1200
VIII	$C_{10}H_{17}Br_4NOTe$	185...186	1695, 1205, 1195
IX	$C_{10}H_{17}Cl_4NOTe$	187	1695, 1210, 1180

According to the available literature data [3, 4], the addition of tellurium tetrahalides to olefinic bonds proceeds in accordance with Markownikoff's rule in most cases.

Data from the IR and PMR spectra of I-IV and VI-IX are presented in Table 1.

The signal of the $CHTeX_3$ methylidyne proton of VI-IX appears at weak field at 6.10 ppm (the signal of the CHO group of I-V shows up at 5.54-6.00 ppm); this is associated with the higher (than in the case of oxygen) electronegativity of the TeX_3 group. The $CHTeX_3$ group forms an ABX system with the protons of the CH_2O group and the tetrahydropyran ring.

From the data presented above it is apparent, first of all, that the addition of selenium and tellurium tetrahalides to the olefinic bond of N-substituted allylacetic acid amides proceeds differently, although a constant tendency for regioselective addition is observed in all cases. Second, the addition of selenium tetrabromide proceeds mainly counter to Markownikoff's rule; this constitutes evidence in favor of kinetic rather than thermodynamic control in this reaction. Furthermore, the addition of selenium and tellurium tetrahalides to the olefinic bond of allylacetic acid amides is accompanied by nucleophilic participation of the carboxamido group with attack on the intermediately formed carbonium ion center by the carbonyl oxygen atom.

EXPERIMENTAL

The IR spectra of KBr pellets or CCl4 solutions of the compounds were recorded with UR-10 and Specord spectrometers. The PMR spectra of solutions in DMSO were obtained with Tesla BS-487A (80 MHz) and Tesla BS-497 (100 MHz) spectrometers; the PMR spectra of I and II were obtained with an RYa-2310 spectrometer (60 MHz). The constants were calculated by the method in [5]. The yields and constants of the synthesized compounds are presented in Table 1; the results of elementary analysis for C, H, N, and Hal were in agreement with the calculated values.

Bis[(5-immonia-2-tetrahydrofuryl)methyl]Dibromoselenide Dibromides (I-IV). A solution of 20 mmole of selenium oxide in 18 ml of hydrobromic acid (d 1.48) was added dropwise with cooling to 0°C and vigorous stirring to a solution of 20 mmole of the starting amide in 100 ml of chloroform. At the end of the reaction the organic layer was separated and dried with anhydrous calcium chloride. The chloroform was removed in vacuo, and the residual oily substance was crystallized from dichloroethane.

Bis-[(5-cyclopentamethyleneimmonia-2-tetrahydrofuryl)methyl/Selenide Dibromide (V $C_{20}H_{34}Br_2N_2O_2Se$). A 2.88-g (12 mmole) sample of sodium sulfide nonahydrate dissolved in 3 ml of water was added to a suspension of 1.47 g (2.4 mmole) of dibromide III in 35 ml of benzene with stirring. Partial decomposition of the compound with the liberation of selenium metal occurred during the reaction. At the end of the reaction the organic layer was separated and dried with calcium chloride, and the benzene was removed in vacuo. The residual oily substance was crystallized from dichloroethane to give 0.11 g (8%) of V with mp 230-232°C. IR spectrum: 1695 (CN), 1190-1220 cm^{-1} (COC).

TABLE 1 (continued)

PMR spectrum, δ, ppm				Yield,, %
$-CH_2-CH_2-$	R, R^1	CH_2SeX_2, $CHTeX_3$	CHO, CH_2O	
2,70 ... 3,10	3,40 (s, 2H); 3,66 (s, 6H)	4,36	5,72 ... 6,02	41
2,70 ... 3,10	3,66 (s, 6H); 3,68 (s, 6H)	4,26	5,54 ... 6,0	52
2,20 ... 2,80	1,69 (m, 12H); 3,68 (m, 8H)	3,88	5,22 ... 5,87	33
2,00 ... 2,75	3,11 (m, 8H); 3,79 (m, 8H)	3,94	5,26 ... 5,61	50
2,16 ... 2,64	2,75 (s, 3H); 2,80 (s, 3H)	6,10 (J_{AB} = 14 Hz; J_{AX} = 13,2 Hz; J_{BX} = 1,2 Hz)	4,40; 4,48	86
2,16 ... 2,64	2,73 (s, 3H); 2,76 (s, 3H)	6,08 (J_{AB} = 16,6 Hz, J_{AX} = 12,6 Hz; J_{BX} = 4,2 Hz)	4,16; 4,28	78
2,28 ... 2,84	3,18 (m, 4H); 1,26 (m, 6H)	6,11 (J_{AB} = 14 Hz; J_{AX} = 13,2 Hz; J_{BX} = 1,2 Hz)	4,38; 4,46	64
2,35 ... 3,08	3,15 (m, 4H); 1,32 (m, 6H)	6,10 (J_{AB} = 14,2 Hz; J_{AX} = 13,0 Hz; J_{BX} = 1,2 Hz)	4,24; 4,50	55

5-Trihalotelluro-2-immoniatetrahydropyranyl Bromides (VI-IX). A solution of 10.0 mmole of tellurium(IV) oxide in the calculated amount of concentrated hydrobromic(chloric) acid was added dropwise with stirring and cooling to 0°C to a solution of 10.0 mmole of the starting amide in 200 ml of ether, and the mixture was stirred for 6 h. The resulting precipitate was removed by filtration, crystallized from acetonitrile, and dried in a vacuum desiccator.

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