Distillation yielded 53.2 g (61%) of hydrazino alcohol Ic with bp 98-102°C (16 mm), d_4^{20} 0.9265, and n_D^{20} 1.4497. Found: N 20.7; 21.3%; equivalent weight 134; MR_D 38.32. $C_6H_{16}N_2O$. Calculated: N 21.2%; equivalent weight 132; MR_D 38.82.

2-Alkylperhydro-1,3,4-oxadiazines (IIa, b, d-f). These compounds were obtained by condensation of hydrazino alcohols Ia-c with aliphatic aldehydes by the method in [5]. The characteristics of the new compounds are presented in Tables 1 and 2.

4-Isopropylperhydro-1,3,4-oxadiazine (IIc, Tables 1 and 2). A mixture of 31.7 g (0.27 mole) of 2-(N-isopropylhydrazino)ethanol (Ib) [5], 8.1 g (0.09 mole) of paraformaldehyde, and 30 ml of benzene was refluxed with a Dean–Stark trap until the water was removed completely. The residual mixture was then distilled with a column.

5,6-Dihydro-4H-1,3,4-oxadiazines (IIIa-f, Tables 3 and 4). Perhydrooxadiazines IIa-f were added cautiously to a 10% molar excess of yellow mercuric oxide. The reaction usually began spontaneously when the mixture was stirred; when the reaction was too vigorous, the mixture was cooled with ice water. The mixture was heated on a boiling-water bath for 30-60 min to complete the reaction. The organic layer was separated, dried with potassium carbonate, and distilled.

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REACTIONS OF TELLURIUM TETRAHALIDES WITH 1,5- AND 1,6-DIOLEFINS AND THEIR DERIVATIVES*

Yu. V. Migalina, I. M. Balog,
V. G. Lendel, A. S. Koz'min,
and N. S. Zefirov

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1,4-Dihalo-substituted tellurolanes were obtained by reaction of tellurium tetrabromide and tetrachloride with 1,5-hexadiene, and the corresponding six-membered heterocyclic compounds with a tellurium atom in the ring were obtained with 1,6-diolefins.

A few examples of heterocyclic systems that contain a tellurium heteroatom have been described [2]. Considering the ability of tellurium tetrahalides to add to double bonds (for example, propylene [3]), we decided to extend this reaction to diolefins in order to obtain heterocyclic compounds.

We selected 1,5-hexadiene (I), diallyl ether (IIa), diallyl sulfide (IIb), diallylamine (IIc), and N-methyldiallylamine (IId) as the diolefins. By varying the order of addition, the reagent ratio, the temperature, and the solvent we found conditions under which crystalline substances that do not contain multiple bonds are formed in good yields from tellurium tetrahalides and diolefins. After reaction of 1,5-hexadiene with tellurium tetrabromide and tetrachloride, we were able to isolate 1,1-dibromo-2,5-dibromomethyl- (IIIa) and 1,1-dichloro-2,5-dichloromethyltellurolane (IIIb), respectively, from the reaction mixtures.

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Uzhgorod State University, Uzhgorod 294000. M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1212-1214, September, 1978. Original article submitted December 9, 1977.

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TABLE 1. Constants, Spectral Characteristics, and Yields of the Products of the Reaction of Tellurium Tetrahalides with 1,5- and 1,6-Diolefins

Compound	Name	mp, °C	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm	Found, %				Empirical formula	Calc., %				Yield, %
					C	H	Hal	N		C	H	Hal	N	
IIIa	1,1-Dibromo-2,5-dibromomethyltellurolane[a]	118–119 (from CH_3CN)	1465, 1380, 1330, 1295, 1258, 1220, 1208, 1108, 1005, 985, 895, 842, 718	m, 3,98–4,33 (2H, 2CH) m, 3,07–3,29 (4H, $2CH_2Br$) m, 2,03–2,66 (4H, $2CH_2$)[b]	13,2	1,7	60,8	—	$C_6H_{10}Br_4Te$	13,6	1,8	60,4	—	34
IIIb	1,1-Dichloro-2,5-dichloromethyltellurolane	135(dec., from ether)	—	m, 4,70–5,20 (2H, 2CH) m, 3,33–4,46 (4H, $2CH_2Cl$) m, 2,03–2,93 (4H, $2CH_2$)[b]	20,4	2,5	40,2	—	$C_6H_{10}Cl_4Te$	20,5	2,6	40,3	—	6
IVa	1,1-Dibromo-2,6-dibromomethyl-1,4-telluroxane	128 cis 108 trans (from benzene)	1470, 1385, 1255, 1210, 1140, 1040, 1000, 952, 905	m, 5,28–6,25 (4H, $2CH_2O$) m, 3,80–5,13 (6H, 2CH, $2CH_2Br$)[b]	13,1 13,1	1,8 1,7	58,8 58,6	— —	$C_6H_{10}Br_4OTe$ $C_6H_{10}Br_4OTe$	13,2 13,2	1,8 1,8	58,7 58,7	— —	69
IVb	1,1-Dibromo-2,6-dibromomethyl-1,4-tellurathiane	136–137 (from benzene)	1470, 1387, 1230, 1153, 1100, 990, 880, 800, 740, 723, 680	—	12,7	1,7	56,7	—	$C_6H_{10}Br_4STe$	12,8	1,7	56,9	—	41
IVc	1,1-Dibromo-2,6-dibromomethyl-1,4-tellurazan	175 (dec., from CH_3OH)	1460, 1385, 1225, 1165, 1090, 1040, 995, 950, 900, 780	—			59,8	2,5	$C_6H_{11}Br_4NTe$			59,9	2,5	35
IVd	1,1-Dibromo-2,6-dibromomethyl-4-methylperhydro-1,4-tellurazan	170 (dec., from CH_3OH)	1650, 1458, 1400, 1325, 1275, 947, 870, 795, 720	—			56,6	2,5	$C_7H_{13}Br_4NTe$			57,0	2,5	79
IVe	1,1-Dichloro-2,6-dichloromethyl-1,4-telluroxane	142–143 (from benzene)	—	m, 3,86–4,30 (2H, 2CH) m, 3,16–3,80 (4H, $2CH_2Cl$) m, 2,70–3,16 (4H, $2CH_2O$)[c]	19,4	2,8	38,8	—	$C_6H_{10}Cl_4OTe$	19,6	2,7	38,6	—	55
IVf	1,1-Dichloro-2,6-dichloromethyl-1,4-tellurathiane	109(dec., from CCl_4)	—	m, 3,93–4,27 (2H, 2CH) m, 3,07–3,44 (4H, $2CH_2Cl$) m, 2,26–2,69 (4H, $2CH_2S$)[c]	18,8	2,8	36,9	—	$C_6H_{10}Cl_4STe$	18,8	2,6	37,0	—	50
IVg	1,1-Dichloro-2,6-dichloromethyl-4-methylperhydro-1,4-tellurazan	90–91 (from CH_3OH)	1650, 1535, 1510, 1440, 1410, 990, 957, 948, 790, 710	—			37,0	3,7	$C_7H_{13}Cl_4NTe$			37,3	3,7	39

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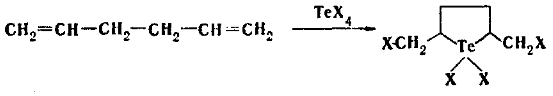
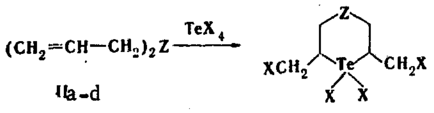
[a] Found: Te 23.9%. Calculated: Te 24.0%. [b] The PMR spectrum was obtained from a solution in $CDCl_3$. [c] The PMR spectrum was obtained from a solution in C_6H_6.

Under the same conditions 1,6-diolefins IIa-d are converted to six-membered heterocyclic compounds (IVa-g).



IIIa, b



IIa-d

IVa-g

IIa Z=O; b Z=S; c Z=NH; d Z=NCH$_3$; IIIa X=Br; b X=Cl; IVa X=Br, Z=O; b X=Br, Z=S; c X=Br, Z=NH; d X=Br, Z=NCH$_3$; e X=Cl, Z=O; f X=Cl, Z=S; g X=Cl, Z=NCH$_3$

Despite the fact that all of the substances obtained may consist of mixtures of isomers, we were able to separate them into the cis and trans isomers by fractional crystallization only in the case of IVa. The use of the PMR spectra for the rigorous assignment of the isomers to the cis or trans series was hindered by the poor resolution of the signals of the ring protons and the closeness of the multiplets.

The structure of cis-IVa was also confirmed by alternative synthesis from allyl formate (V) and tellurium tetrabromide via the scheme

$$2HCOOCH{=}CH_2 + TeBr_4 \rightarrow \text{cis-IVa}.$$

The mass spectrum of IVa does not contain a molecular ion; however, it does contain a set of isotopic peaks with m/e 459-471 (the $C_6H_{10}OTeBr_3^+$ ion), 282-292 ($TeBr_2^+$), 203-211 ($TeBr^+$), and 124, 125, 126, 128, and 130 (Te^+).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of the compounds were obtained with a Tesla BS-487-A spectrometer with tetramethylsilane as the internal standard. The mass spectrum was obtained with an MKh-1303 spectrometer. The substances obtained were purified by repeated recrystallization. It was not possible to use adsorption chromatography on aluminum oxide or silica gel to establish the individuality of the compounds and to purify them because of their decomposition during chromatography.

Reaction of Tellurium Tetrahalides with 1,5- and 1,6-Diolefins. An equimolar amount of tellurium tetrabromide, obtained from tellurium dioxide and the corresponding hydrohalic acid, was added dropwise with vigorous stirring to a solution of 0.02 mole of the diolefin in 200 ml of ether, and the mixture was stirred for 6 h. It was then allowed to stand for 12 h, after which the organic layer was dried with anhydrous sodium sulfate, the solvent was removed in vacuo, and the crystalline residue was removed by filtration and recrystallized. The constants, spectral characteristics, and the yields of IIIa, b and IVa-g are presented in Table 1.

1,1-Dibromo-2,6-dibromomethyl-1,4-telluroxane (IVa). A solution of 17.2 g (0.2 mole) of allyl formate in 600 ml of ether was added with cooling and vigorous stirring to a solution of 16 g (0.1 mole) of tellurium dioxide in 120 ml of hydrobromic acid, and the mixture was stirred at room temperature for 2 h. It was then refluxed for 80 h, after which the organic layer was dried with anhydrous calcium chloride and filtered. The solvent was removed by distillation to give 4.8 g (8.7%) of IVa with mp 128-130°C (from benzene). No melting-point depression was observed for a mixture of this product with a sample of IV synthesized by the preceding method.

1,1-Dichloro-2,6-dichloromethyl-1,4-telluroxane (IVe). This compound, with mp 141-142°C (from benzene), was similarly obtained in 50% yield from allyl formate and tellurium tetrachloride.

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