INVESTIGATIONS IN THE FIELD OF OXYGEN-CONTAINING HETEROCYCLES

VIII. The Addition of 2,3-Dichlorotetrahydrofuran to Dienes*

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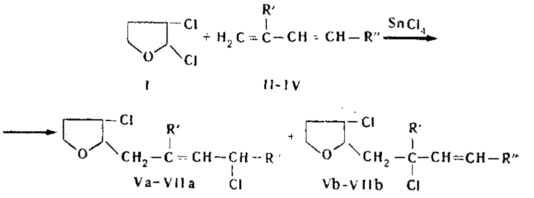
In the presence of stannic chloride, 2,3-dichlorotetrahydrofuran adds to isoprene with the formation of 3-chloro-2-(4'-chloro-2'-methylbut-2'-enyl)tetrahydrofuran and to piperylene and bivinyl with the formation, predominantly, of 3-chloro-2-(4'-chloropent-2'-enyl)- and 3-chloro-2'-(4'-chlorobut-2'-enyl)tetrahydrofuran, respectively, with their allyl isomers. The amount of the latter was estimated from the NMR spectra at 20–30%.

The addition of 2,3-dichlorotetrahydrofuran (I) to dienes in the presence of zinc chloride was first described by Vartanyan [2,3,7]. In the present paper we give the results of an independently undertaken investigation of this reaction in the cases of isoprene (II), piperylene (III), and bivinyl (IV). We were interested primarily in the isomeric composition of the addition products in accordance with the following scheme:



II, V $R' = CH_3$, $R'' = H$; III, VI $R' = H$, $R'' = CH_3$; IV-VII $R' = H$, $R'' = H$

the structure of the products, which boiled within narrow temperature limits, was established from their IR and NMR spectra. In the IR spectra (Fig. 1) the presence of the isomer of type **b** was detected in product IV (stretching vibrations of the C=C and C—H bonds of the terminal vinyl group at 1645 and 3100 cm^{-1}, respectively) but was absent from product V. In the olefin region, the NMR spectrum of product V (Fig. 2) had only a triplet with δ 5.6 ppm corresponding to the structure **Va**; the isomer **Vb** was practically absent. In the same region the product VII gave an unsymmetrical group of signals of which the signal with δ 5.7 ppm corresponded to the olefinic protons of the isomer **VIIa** and the 3' proton of the terminal vinyl group of the isomer **VIIb** and the signal in the δ 5.3–4.9 ppm region corresponded to the 4' protons of the terminal vinyl group of the isomer **VIIb**. A comparison of the areas of the peaks permitted an approximate evaluation of the content of the isomer **VIIb** as 20–30%. In the NMR spectrum of product VI, the signals of the methyl group represented the superposition of two doublets: δ 1.5 ppm, J 8 Hz (isomer **VIa**), and δ 1.65 ppm, J 4 Hz (isomer **VIb**). In this case analysis by peak areas was difficult. For strong signals, quantitative conclusions can be based on the amplitudes of the resonance peaks [4]. On this basis, we estimated the content of isomer **VIb** as 20% from the ratio of the amplitudes of the methyl doublets.

For the assigment of the signals, we made use of a published compilation [5]. The purities of the products were checked by thin-layer chromatography on alumina in benzene. In this process no differences were found between the isomers. The chlorides obtained were characterized by the picrates of the corresponding S-substituted thiouronium salts.

The authors are deeply obliged to B. I. Ionin for help in recording and interpreting the NMR spectra.

Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %			Calculated, %			Yield*, %	Picrate of thiouronium salt			
				found	calculated		C	H	Cl	C	H	Cl		mp, °C	empirical formula	N, % found	N, % calculated
V	91.5—92 (1)	1.1768	1.5013	52.41	52.58	$C_9H_{14}Cl_2O$	51.59	6.63	34.08	51.69	6.75	33.43	44	161—162	$C_{10}H_{17}ClN_2OS \cdot C_6H_3N_3O_7$	14.56	14.66
VI	93—93.5 (1)	1.1536	1.4925	52.65	52.58	$C_8H_{12}ClO_2$	52.36	6.73	33.82	51.69	6.75	33.43	83	163—164	$C_{10}H_{17}ClN_2OS \cdot C_6H_3N_3O_7$	14.70	14.66
VII	90.5—91 (1)	1.1952	1.4968	47.74	47.97	$C_8H_{12}Cl_2O$	49.61	6.51	36.12	49.25	6.20	36.35	77	162	$C_9H_{15}ClN_2OS \cdot C_6H_3N_3O_7$	14.96	15.10

*Without taking the unchanged chloride I into account the yield of V was 48% and of VI 60%.

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*For part VII, see [1].

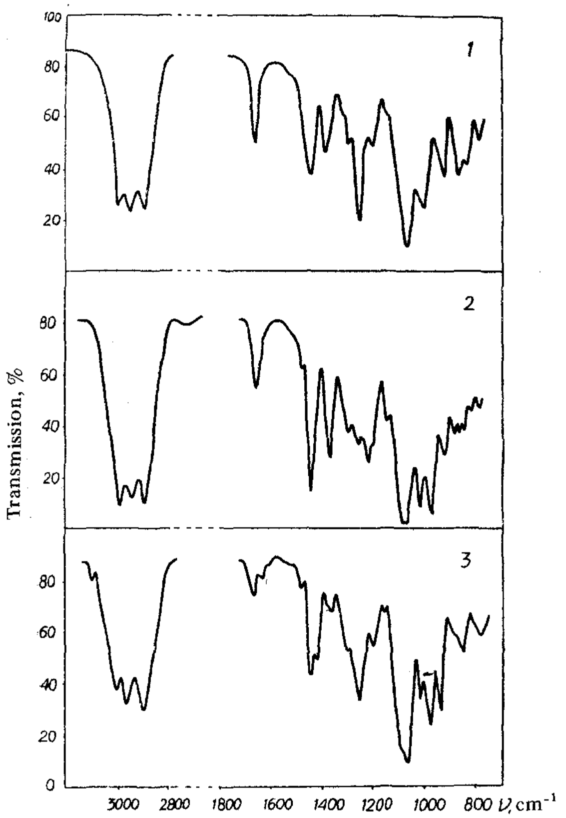

Fig. 1. IR spectra: 1) 3-chloro-2-(4'-chloro-2'-methylbut-2'-enyl)tetrahdrofuran (V); 2) 3-chloro-2-(4'-chloro-2'-methylpent-2'-enyl)tetrahydrofuran (VI); 3) 3-chloro-2-(4'-chlorobut-2'-enyl)-tetrahydrofuran (VII).

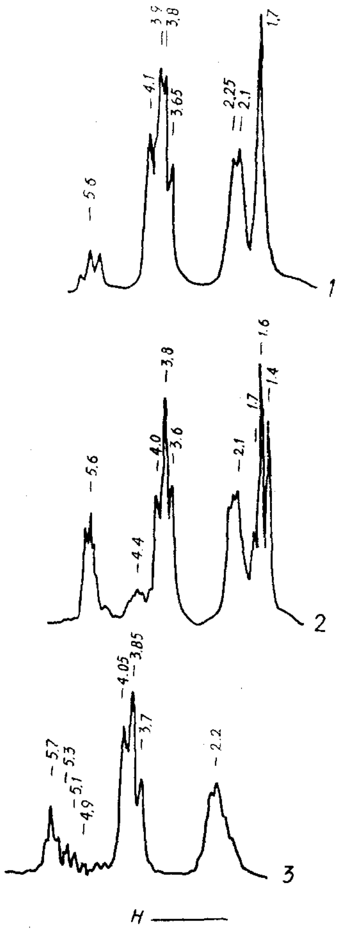

Fig. 2. NMR spectra: 1) 3-chloro-2-(4'-chloro-2'-methylbut-2'-enyl)tetrahydrofuran (V); 2) 3-chloro-2-(4'-chloro-2'-methylpent-2'-enyl)tetrahydrofuran (VI); 3) 3-chloro-2-(4'-chlorobut-2'-enyl)tetrahydrofuran (VII). (Shifts in ppm shown on the δ scale.)

EXPERIMENTAL

Addition of 2,3-dichlorotetrahydrofuran (I) to dienes. In drops, 0.1 mole of the appropriate diene in 5 ml of carbon tetrachloride was added with stirring and cooling to a mixture of 0.1 mole of the chloride I [6] in 30 ml of dry carbon tetrachloride and 2 ml of a 10% solution of stannic chloride in carbon tetrachloride. Stirring was continued at 15–20° C for 4 hr. The reaction was stopped by the addition of 0.4 ml of pyridine in 20 ml of petroleum ether. The precipitate was filtered off and the filtrate was distilled in vacuum (see table). The picrates of the S-substituted thiouronium salts were recrystallized from ethanol.

The IR spectra were taken on a UR-10 instrument in a thin layer. The NMR spectra were taken on a JNM-3 (40 MHz) instrument for the pure substances with hexamethyldisiloxane as internal standard.

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