# INVESTIGATIONS IN THE FIELD OF OXYGEN-CONTAINING HETEROCYCLES

## VII. Reaction of 2-Chlorotetrahydrofuran with Dienes*

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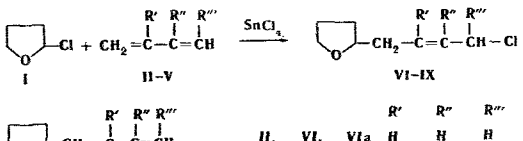
In the presence of $SNCl_4$, 2-chlorotetrahydrofuran adds to isoprene, dimethylbutadiene, piperylene, and bivinyl in the 1,4 position with the formation of the corresponding allyl chlorides. In the case of bivinyl, appreciable amounts of the product of 1,2-addition are also formed. The structure of the compounds obtained has been established by means of IR and NMR spectra.

We have previously shown [2] that 2-chlorotetrahydropyran adds to dienes in a similar manner to aliphatic α-halo ethers [3]. In the present work we have studied the analogous reactions of 2-chlorotetrahydrofuran (I) with bivinyl (II), isoprene (III), dimethylbutadiene (IV), and piperylene (V) in the presence of $SnCl_4$.

The products of the reaction of the chloride I with the dienes III–V distilled within narrow temperature ranges and were homogeneous on chromatography in a thin layer of alumina (eluant benzene). The product of the interaction of the chloride I with bivinyl gave two spots on the chromatogram under the same conditions ($R_f$ 0.76, 0.78) and distilled over a wide range. The higher-boiling compound ($R_f$ 0.76) was isolated in the pure form by careful fractionation; the second component could not be isolated. In all cases, the reaction was accompanied by considerable resinification.

It might have been expected that the reaction would lead both to the products of 1,4-addition (VI–IX) and to their allyl isomers (VIa–IXa) by the following scheme:



| | R′ | R″ | R‴ |
|---|---|---|---|
| II, VI, VIa | H | H | H |
| III, VII, VIIa | $CH_3$ | H | H |
| IV, VIII, VIIIa | $CH_3$ | $CH_3$ | H |
| V, IX, IXa | H | H | $CH_3$ |

A study of the IR and NMR spectra of the products obtained led to the conclusion that the formation of compounds of type VI–IX is predominating in the case of bivinyl and piperylene and exclusive in the case of isoprene and dimethylbutadiene. It must, however, be borne in mind that the allyl rearrangement may take place during distillation.

In the IR spectra (Fig. 1) of the chromatographically homogeneous compounds VI–VIII, the comparatively high values of the frequencies of the stretching vibrations of the —C=C— bond (1660–1670 $cm^{-1}$) and the absence of absorption in the 3100 $cm^{-1}$ region (stretching vibrations of the =C—H bond) correspond to a nonterminal position of the double bond [4]. In the spectrum of the low-boiling fraction with bp 60° C (1 mm) obtained in the isolation of compound VI, the absorption at 1645 and 3100 $cm^{-1}$ shows the presence of appreciable amounts of compound **VIa**. In the spectrum of compound IX there is an inflection at 1645 $cm^{-1}$ which can be assigned to the presence of a compound with a terminal double bond. A similar impurity was detected in the products of the additional of 1-chloro-3-methyl-2-butene to piperylene [5]. It is not excluded that electrophilic addition to piperylene may take place in the 3,4 position. An analysis of the IR spectra in the region of the deformation vibrations of the =C—H bond is complicated by the absorption of the tetrahydrofuran ring.

In the NMR spectra of compounds VI–III, the region of the olefinic protons is of the greatest interest (Fig. 2). The group of signals of the olefinic protons of compound VI has a symmetrical shape, agreeing with the 2,3 position of the double bond in the side chain. The single olefinic proton of compound VII gives a triplet, δ = 5.5 ppm, J = 8.6 Hz. In the spectrum of compound VIII, the signals of the terminal olefinic protons are practically absent. No differences between structures IX and **IXa** appear in the weak-field region. The weak signals with δ = 5.25 ppm in the spectrum of IX may be ascribed to a content of a compound with a terminal vinyl group (cf. the IR spectrum).

A choice can be made between structures IX and **IXa** in the region of the methyl protons. In the spectra of compounds VII and VIII, the signals of the allylic-methyl protons and the β protons of the ring overlap (δ = 1.7–1.8 ppm). In the spectrum of compound IX, a doublet with a smaller shift (δ = 1.5 ppm) than was to be expected for the allyl protons in compound **IXa** corresponds to the methyl group. The other protons of compounds VI–IX appear in the following regions of the spectrum [6]: the α protons of the ring, δ = = 3.6–3.7; the protons of the chloromethyl group, δ = 3.9–4.1; the methylene group adjacent to the ring, δ = 2.1–2.3; and the proton of the chloromethyl group in compound IX gives a quartet with δ = 4.5 ppm.

Compounds VI–VIII were characterized by the picrates of the corresponding S-substituted thiouronium salts.

## EXPERIMENTAL

**2-Chlorotetrahydrofuran (I)** was obtained by the photochemical chlorination of tetrahydrofuran at –50° C [7].

**2-(4-Chloro-2-butenyl)tetrahydrofuran (VI).** To 32 g (0.3 mole) of the chloride I in 20 ml of $CH_2Cl_2$ were added first 6 ml of a 10%

*For part VI, see [1].

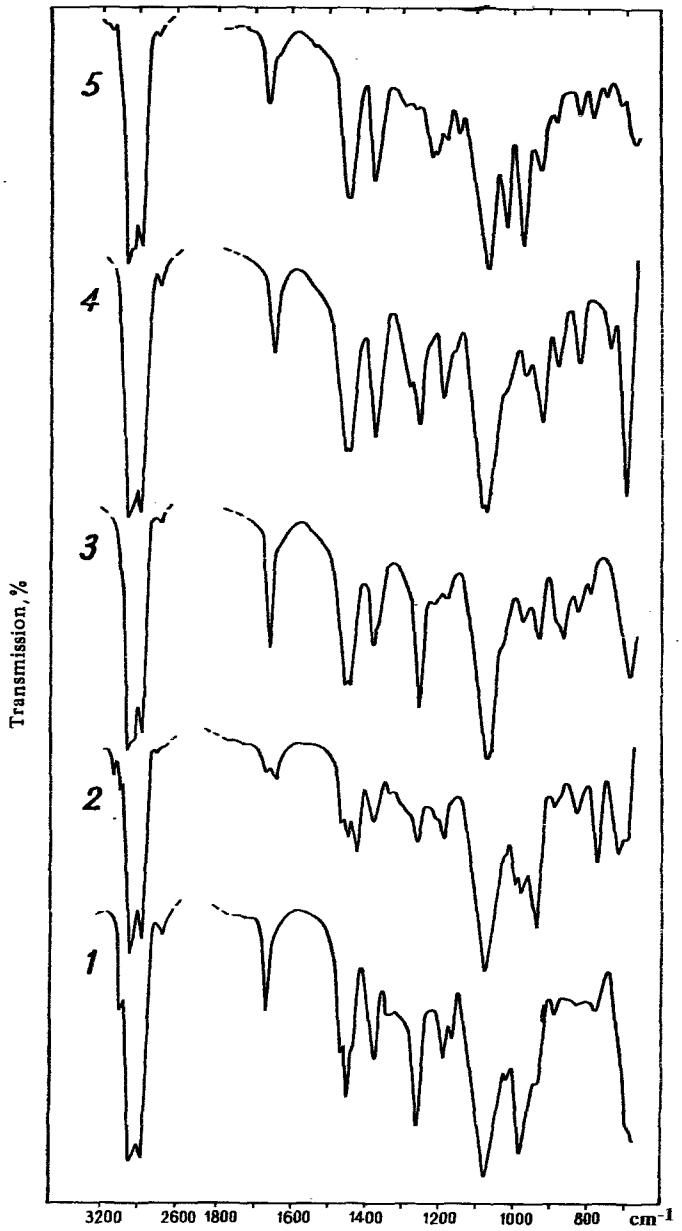



Fig. 1. IR spectra: 1) 2-(4-chloro-2-butenyl)tetrahydrofuran (VI); 2) compound VI containing some 2-(2-chloro-3-butenyl)tetrahydrofuran (VIa) [fraction with bp 60° C (1 mm)]; 3) 2-(4-chloro-2-methyl-2-butenyl)tetrahydrofuran (VII); 4) 2-(4-chloro-2, 3-dimethyl-2-butenyl)tetrahydrofuran (VIII); 5) 2-(4-chloro-2-pentenyl)tetrahydrofuran (IX).

Products of the Addition of 2-Chlorotetrahydrofuran to Dienes

| Compound | Name | Bp, °C (pressure, mm) | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ found | $MR_D$ calculated | Empirical formula | Found, % C | Found, % H | Found, % Cl | Calculated, % C | Calculated, % H | Calculated, % Cl | Yield, % | Picrate of the S-substituted thioronium salt** mp, °C | Picrate empirical formula | N, % found | N, % calculated |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| VI | 2-(4-Chloro-2-butenyl)tetrahydrofuran | 71.5* (1.2) | 1.0927 | 1.4870 | 41.70 | 42.28 | $C_8H_{13}ClO$ | 60.12 | 8.46 | 21.85 | 59.81 | 8.15 | 22.07 | — | 158 | $C_{15}H_{19}N_5O_8S$ | 16.65 | 16.38 |
| VII | 2-(4-Chloro-2-methyl-2-butenyl)tetrahydrofuran | 73 (1) | 1.0605 | 1.4879 | 47.44 | 47.92 | $C_9H_{15}ClO$ | 62.20 | 8.74 | 20.14 | 61.88 | 8.65 | 20.29 | 53 | 125 | $C_{16}H_{21}N_5O_8S$ | 15.66 | 15.83 |
| VIII | 2-(4-Chloro-2,3-dimethyl-2-butenyl)tetrahydrofuran | 79 (1.5) | 1.0437 | 1.4935 | 52.48 | 52.54 | $C_{10}H_{17}ClO$ | 64.44 | 8.93 | 18.64 | 64.17 | 9.08 | 18.78 | 43 | 181 | $C_{17}H_{24}N_5O_8S$ | 15.18 | 15.31 |
| IX | 2-(4-Chloropent-2-enyl)tetrahydrofuran | 75 (1.3) | 1.0322 | 1.4757 | 47.65 | 47.92 | $C_9H_{15}ClO$ | 61.71 | 8.88 | 19.88 | 61.88 | 8.65 | 20.29 | 58 | — | — | — | — |

* 69° C (1 mm)
** Recrystallized from ethanol.

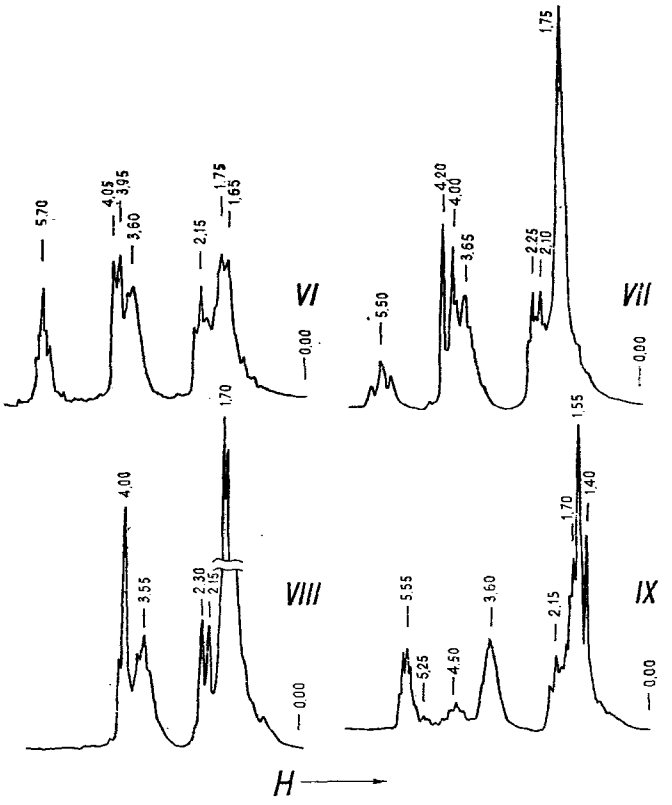



Fig. 2. NMR spectra (the numbers correspond to the numbers of the compounds in the table).

solution of $SnCl_4$ in $CCl_4$ and then, in drops with stirring, 100 ml of a solution of bivinyl in $CCl_4$ containing 18 g (0.3 mole) of the diene, and stirring was continued for 4 hr at 18–20° C. The reaction was stopped by the addition of 1.2 ml of pyridine, the product was filtered, the solvent was driven off, and the residue was distilled in vacuum. This gave 7 g of the unchanged chloride I, bp 30° C (13 mm), and 17 g (46%) of compound VI contaminated with compound VIa, bp 60–69° C (1 mm). Vacuum fractionation gave compound VI (see table). The initial fraction with bp 60° C (1 mm), $d_4^{20}$ 1.0584, $n_D^{20}$ 1.4761, was used for recording the IR spectrum.

**Addition of the chloride I to the dienes III-V.** To 0.2 mole of the chloride I in 25 ml of $CH_2Cl_2$ was added 4 ml of a 10% solution of $SnCl_4$ in $CCl_4$ and then, at 0° C, 0.2 mole of the diene, and the mixture was stirred at 0° C for 1.5 hr and at 20° C for 1 hr. The reaction was stopped by the addition of 0.8 ml of pyridine, the product was filtered, the solvent was driven off, and the residue was distilled in vacuum (see table).

**The IR spectra** were recorded on a UR-10 instrument in a thin layer. Prisms: NaCl in the 700–1800 $cm^{-1}$ region, LiF in the 2700–3200 $cm^{-1}$ region.

**The NMR spectra** were taken on a JNM-3 instrument (40 MHz) with hexamethyldisiloxane as internal standard.

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