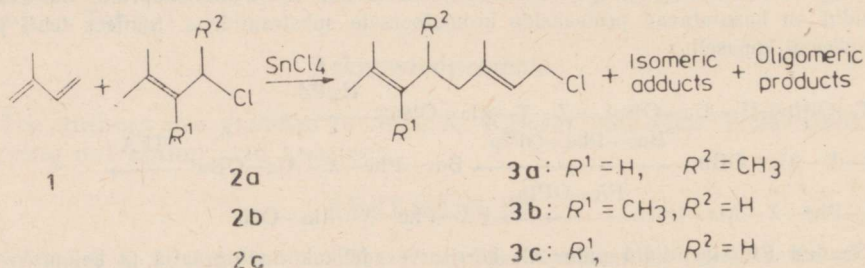


UDC 547.315.2+547.322

Elvi MUKS,* Ants ERM,* Tõnis PEHK,** Mati MÜURISEPP,*
Milana LIIV,* and Koit LÄÄTS*LEWIS ACID CATALYZED ADDITION OF ALLYLIC CHLORIDES
TO ISOPRENE

The 1,4-adducts of isoprene with some allylic and alkoxyalkyl chlorides are involved as synthons in the synthesis of various biologically active compounds and fragrances. As in the respective works [1–5] emphasis has been on obtaining the 1,4-adducts, we undertook a study of some of the reactions which have been insufficiently characterized so far. In this paper, we present data on the isomeric composition of adducts and its dependence on the reaction conditions for the addition of 2-chloro-4-methyl-3-pentene (2a) and 1-chloro-2,3-dimethyl-2-butene (2b) to isoprene (1):



Experimental

NMR spectra were registered in CDCl₃ solution (δ_{TMC} = 77.0 and 7.27 ppm) on a Bruker AMX-500 instrument. ¹³C and ¹H (in parentheses) chemical shifts from C-1 to C-11 for 3a: 40.5 (4.04), 121.81 (5.39), 141.04, 47.48 (1.97), 30.77 (2.57), 130.61 (4.88), 129.69, 25.45 (1.67), 15.93 (1.70), 20.61 (0.91), 17.66 (1.62). *E* configuration of C-2—C-3 double bond follows from the carbon chemical shifts of C-4 and C-9 on the basis of model olefins [6]. For 4a: 132.30, 119.60 (5.35), 25.89 (2.07 and 2.24), 50.01 (1.73), 30.21 (2.10), 37.20 (1.70 and 2.07), 23.24 (1.64), 74.87, 30.55 (1.60), 31.51 (1.59), 22.50 (1.09). *Trans* orientation of substituents is indicated from the carbon chemical shifts of C-3 and methyl group at C-5 on the basis of model mono- and dialkylcyclohexenes [7].

Chromatomass-spectrometric investigations were carried out using a Hitachi M-80B gas Chromatograph Double Focusing Mass Spectrometer. Quartz capillary column (15 m × 0.52 mm) with liquid phase SUPEROX

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was used. The temperature was programmed from 60 to 150°C (5°C/min). 70 eV electron impact mass spectra were recorded for the adducts of **1** with **2b**. The data m/z (%) for the five most intensive peaks for the adducts of **1** with **2b** are as follows. **3b**: 83 (100), 55 (72), 41 (45), 93 (30), 43 (27); **4b**: 107 (100), 67 (59), 28 (50), 41 (37), 83 (37); **5b**: 83 (100), 55 (90), 41 (54), 68 (52), 67 (31); **6b**: 55 (100), 96 (70), 83 (64), 69 (60), 41 (59); **8b**: 83 (100), 55 (49), 41 (20), 171 (3), 186 (2).

GC analyses (Fig. 1) were performed on a glass capillary column (37 m \times 0.3 mm i.d.) with 1,2,3-tris(2-cyanoethyl)propane (TCEP) liquid phase at 80°C using a Chrom 5 Gas Chromatograph (Czecho-

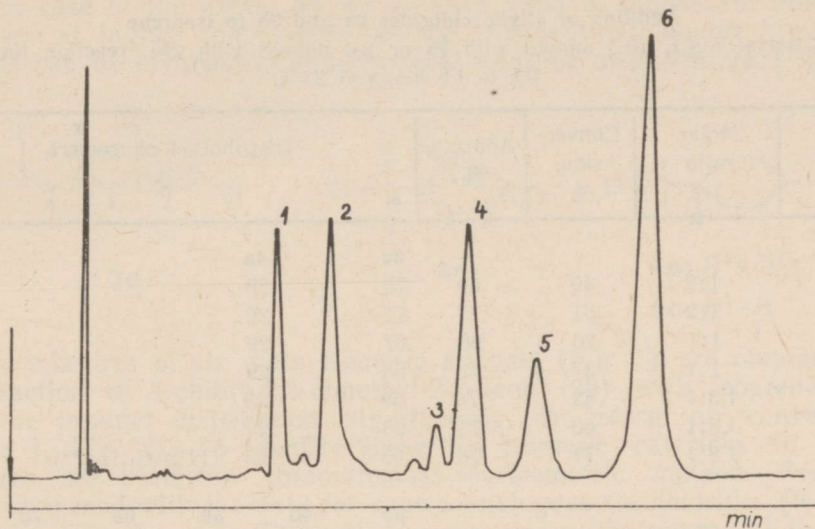


Fig. 1. A chromatogram of C_{11} adducts in the reaction of 1-chloro-2,3-dimethyl-2-butene (**2b**) with isoprene (**1**).

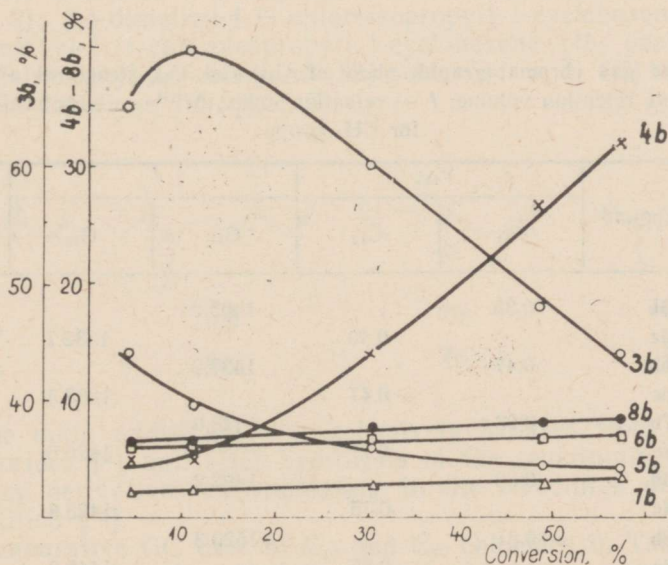


Fig. 2. The relative yields of the isomeric adducts **3b**–**8b** depending on conversion.

slovakia) with FID. The retention indexes of the adducts studied were calculated via the retention times of *n*-alkanes [8, 9].

The starting materials were prepared and the procedure of isoprene alkenylchlorination with **2a** or **2b** (at 23°C using 3% SnCl₄ in 1,2-dichloroethane as a catalyst) was performed as described earlier [10]. After the evaporation of the unreacted starting compounds, the C₁₁ adducts were distilled: a mixture of **3a** and **4a** at 60–70°C (2 mm Hg) and a mixture of **3b**–**8b** at 60–90°C (2 mm Hg). The remaining higher products were not investigated. The isomeric composition of the adducts was established using GC, NMR, and CMS methods. The experimental data are given in Tables 1 and 2, and in Figs. 1 and 2.

Table 1

Addition of allylic chlorides **2a and **2b** to isoprene**
Catalyst SnCl₄ (0.3 mmol/l with **2a** or 2.0 mmol/l with **2b**), reaction time 0.5 to 1.5 hours at 23°C

RCl	Molar ratio 1:2	Conversion, %	Adducts, %	Distribution of isomers, %						
				3a	4a	3b	4b	5b	6b	7b
2a	1:2	40	80	70	28					
2a	1:2	61	71	71	26					
2a	1:1	20	80	67	29					
2a	1:1	37	79	68	29					
2a	1.8:1	42	76	69	28					
2a	1.8:1	68	73	68	29					
2a*	1.8:1	71	76	65	23	(11% C ₁₁ H ₁₈ **)				
2b	1:1	20	61	58	11	9	9	1	9	
2b	1:1	49	41	52	22	4	8	2	9	

* Catalyst anhydrous ZnCl₂;

** Dehydrochlorinated products.

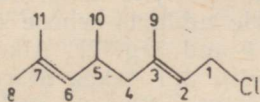
Table 2

Comparative gas chromatographic data of C₁₁ and C₁₀ structural analogues
*V*_{rel} — relative retention volume; *I* — retention index; Δ*I*^{CH₃} — structural increment for CH₃ group

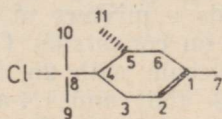
Peak No. in Fig. 1	Compound	<i>V</i> _{rel}		<i>I</i>		Δ <i>I</i> ^{CH₃}
		C ₁₁	C ₁₀	C ₁₁	C ₁₀	
1	5b	0.38		1405.2		72.5
	5c		0.40		1332.7	
2	6b	0.47		1437.2		78.9
	6c		0.47		1358.3	
3	7b	0.63		1478.6		58.6
	7c		0.71		1420.0	
4	4b	0.68		1492.2		63.4
	4c		0.75		1428.8	
5	8b	0.81		1520.3		74.1
	8c		0.85		1446.2	
6	3b	1.00		1549.5		78.1
	3c		1.00		1471.4	

Results

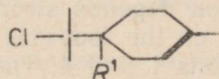
The reaction of the allylic chloride **2a** with isoprene gives in good yield the (*E*)-1,4-adduct **3a** [1-3] and an isomeric adduct at an approximate ratio of 2.5:1 as established by GC (Table 1). On the basis of ¹³C and ¹H spectra, it was ascertained that the ordinary adduct (*E*)-1-chloro-3,5,7-trimethyl-2,6-octadiene (**3a**) is accompanied by a cyclic adduct 1,5-dimethyl-4-(1-chloroisopropyl)-1-cyclohexene (**4a**). GC data showed that there could be some other isomeric adducts present, but not more than 1% if at all. The product distribution in the reaction of **2a** with **1** (Table 1) is only slightly affected by the initial ratio of the reactants, the nature of the Lewis acid, and the degree of conversion. Only in case of the excess **2a** the relative yield of oligomeric products increases at higher conversions, as the trisubstituted double bonds of adducts can be involved in a subsequent addition step with **2a** [11].



3a



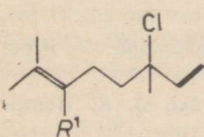
4a



4b: $R^1 = \text{CH}_3$

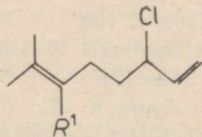
4c: $R^1 = \text{H}$

The mixtures of six main isomeric adducts (Fig. 1) are obtained in the reaction of 1-chloro-2,3-dimethyl-2-butene (**2b**) with isoprene (**1**) with the product distribution significantly depending on conversion (Table 1, Fig. 2). To identify these C₁₁ isomeric chlorides in their mixtures, we used the chromatomass-spectrometric method. Besides, when compared with the data for known analogous C₁₀ chlorides [10, 12-14] (c series with $R^1 = \text{H}$ in Table 2), the conversion dependence of the isomeric composition (Fig. 2) and the GC characteristics were in good agreement with the proposed structures. So, the following C₁₁ chlorides as **2b** adducts with isoprene have been identified: 3-chloro-3,6,7-trimethyl-1,6-octadiene (**5b**, peak 1 in Fig. 1); 3-chloro-2,6,7-trimethyl-1,6-octadiene (**6b**, peak 2); 2,4-dimethyl-4-(1-chloroisopropyl)-1-cyclohexene (**7b**, peak 3); 1,4-dimethyl-4-(1-chloroisopropyl)-1-cyclohexene (**4b**, peak 4); (*E*)-1-chloro-2,6,7-trimethyl-2,6-octadiene (**8b**, peak 5); and (*E*)-1-chloro-3,6,7-trimethyl-2,6-octadiene (**3b**, peak 6).



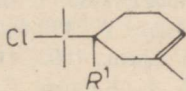
5b

5c



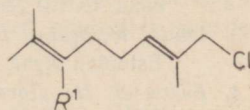
6b

6c



7b

7c



8b: $R^1 = \text{CH}_3$

8c: $R^1 = \text{H}$

Earlier the main adduct **3b** was selectively isolated from the mixture of C₁₁ chlorides [4] and after hydrolysis of the remaining C₁₁ chlorides the hydroxy derivatives corresponding to the structures of **4b** and **5b** were identified [15].

The comparative GC data of C₁₁ and C₁₀ chlorides in Table 2 (b and c series respectively) show that the values of relative retention volumes (V_{rel}) for analogous isomers are nearly the same. The structural increment values for the CH₃ group, i.e. the difference in retention indexes

for the corresponding C_{11} and C_{10} isomers [$\Delta I^{CH_3} = I(C_{11}) - I(C_{10})$], vary from 72.5 to 78.9 index units (i.u.) for linear isomers, but for cyclic isomers these values are lower (58.6 and 63.4 i.u.). That may be explained by higher temperature increments of cyclic compounds [8].

Conclusions

By means of comparing the GC data (relative retention volumes and structural increment values) for a series of known compounds with those for their structural analogues under study (differing in a certain structural unit at a certain position, e.g., the 6-methyl group in our case in Table 2), the structures of the latter may be predicted. So, the use of GC and chromatomass-spectroscopy enabled us to identify the isomeric adducts of isoprene with **2b** without separation of components with adequate reliability.

Isoprene alkenylchlorination with the primary allylic chloride **2b** (like with **2c** [10, 12]) yields a mixture of isomeric adducts whose composition depends strongly on conversion (Table 1 and Fig. 2). Alkenylation of the isoprene molecule with **2b** (like with **2c**) takes place in positions 1 and 4. The 1,2- (**5b**) and 1,4-adducts (**3b**) (like **5c** and **3c**) readily ionize with $SnCl_4$ and give subsequent addition with a double bond intra- or intermolecularly yielding a cyclic isomer **4b** and higher addition products in the course of the reaction. The content of 4,3- (**6b**) and 4,1-adduct (**8b**) (like **6c** and **8c**) is nearly constant.

In contrast, isoprene and the secondary allylic chloride **2a** afforded a nearly invariable mixture of the 1,4-adduct (**3a**), cyclic adduct (**4a**), and oligomeric products (Table 1) up to rather high conversion (kinetic control). Besides, the electrophilic attack of a secondary carbenium ion (from **2a** and (*E*)-2-chloro-3-pentene [16]) takes place regioselectively in position 1 to the isoprene molecule. Thus, there are different reaction schemes for the adducts formation in the reaction of isoprene with various types of carbenium ions. These problems will be discussed in a following paper.

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LEWIS HAPPE-KATALUUTILINE ALLÜULSETE KLORIIDIDE LIITUMINE ISOPREENIGA

SnCl₄ manulusel toimub primaarsete ja sekundaarsete allüülsete kloriidide liitumine isopreeniga erinevate reaktsiooni skeemide kohaselt.

2-kloro-4-metüül-3-buteeni liitumisel isopreeniga saadakse 1,4-adukt, tsükliline adukt ja kõrgemad produktid ligilähedases suhtes 2,5:1:1. Viimane sõltub vähe konversioonist ja teistest reaktsiooni tingimustest. 1-kloro-2,3-dimetüül-2-buteen annab isopreeniga koos identifitseeritud C₁₁-adukti ja kõrgemaidprodukte, kusjuures produktide koostis sõltub oluliselt konversiooni astmest.

Эльви МУКС, Антс ЭРМ, Тынис ПЕХК, Мати МЮЮРИСЕПП, Милана ЛИИВ, Койт ЛЭЭТС

ПРИСОЕДИНЕНИЕ АЛЛИЛЬНЫХ ХЛОРИДОВ К ИЗОПРЕНУ, КАТАЛИЗИРУЕМОЕ КИСЛОТАМИ ЛЬЮИСА

Установлено, что в присутствии SnCl₄ присоединение первичных и вторичных аллильных хлоридов к изопрену протекает по различным реакционным схемам. Присоединение 2-хлор-4-метил-3-бутена к изопрену приводит к 1,4-аддукту, циклическому аддукту и высшим продуктам в соотношении примерно 2,5:1:1 почти независимо от конверсии и других условий. 1-Хлор-2,3-диметил-2-бутен дает с изопреном шесть идентифицированных C₁₁-аддуктов и высших продуктов, причем состав продуктов значительно зависит от степени конверсии.