INVESTIGATIONS IN THE FIELD OF OXYGEN-CONTAINING HETEROCYCLES

VI. Synthesis of 2-Alkenyltetrahydropyrans*

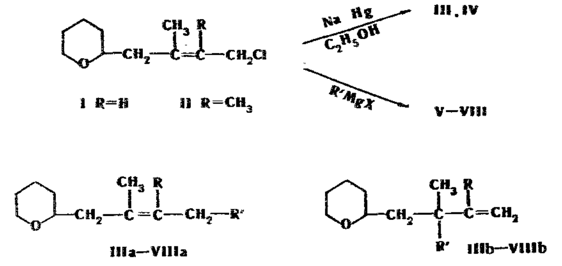
M. M. Tarnopol'skaya, Yu. I. Tarnopol'skii, B. I. Ionin, and V. N. Belov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 3, pp. 387–390, 1968

UDC 547.811

2-(4'-Chloro-2'-methyl-2'-butenyl)tetrahydropyran and 2-(4'-chloro-2',3'-dimethyl-2'-butenyl)tetrahydropyran react with organomagnesium compounds and also with sodium amalgam with the formation of mixtures of the 2-(2'-alkenyl)tetrahydropyrans corresponding to the initial chlorides and the 2-(3'-alkenyl)tetrahydropyrans corresponding to the allyl isomers of the initial chlorides. The structure and composition of the products have been established by IR and NMR spectroscopy and by gas-liquid chromatography.

We have previously [2] described allyl chlorides of the tetrahydropyran series (I, II) obtained by the addition of 2-chlorotetrahydropyran to dienes. In the present work, these compounds were used for the synthesis of unsaturated homologs of tetrahydropyran of interest as odoriferous materials. The reaction of the chlorides I and II with organomagnesium compounds and sodium amalgam takes place generally by the following scheme:



III R=H, R'=H
IV R=CH$_3$, R'=H
V R=CH$_3$, R'=CH$_3$

VI R=H, R'=C$_2$H$_5$
VII R=H, R'=C$_3$H$_7$
VIII R=H, R'=i-C$_5$H$_{11}$

The products obtained distilled within relatively narrow ranges and were homogeneous on chromatography in a thin layer of alumina (with benzene as the eluant). The formation of isomers of types a and b (with a predominance of the former) was established from the data of gas-liquid chromatography, from the IR spectra, and, for compounds V and VI, also from the NMR spectra. On gas-liquid chromatograms, all the products gave two peaks of which the larger (with the greater resonance time) we assigned to the isomer of type a and the smaller to the isomer of type b. Two typical chromatograms are given in Fig. 1. In the IR spectra of the same products V and VI (Fig. 2), the band of the stretching vibrations of the =C—H of the terminal C=CH$_2$ group (3090–3100 cm^{-1}) is practically absent. In the region of the stretching vibrations of the C=C bond, in addition to a band at 1670 cm^{-1} corresponding to a central position of a double bond, absorption is found at 1645 cm^{-1} due to a terminal double bond [3]. Its low intensity, approximating to the intensity of the absorption at 1670 cm^{-1}, shows that the amount of the isomer of type b is small, since absorption in this region rises sharply with a decrease in the degree of symmetry of the molecule about the double bond [4]. The IR spectra of the other products have a similar form and are described in the Experimental part. A further confirmation of the assumed assignment of the peaks on the gas chromatograms can be obtained from the NMR spectra (Fig. 3). The weak-field region is of the greatest interest for the distinction of structures of types a and b. The group of signals in the range δ = 3.0–4.0 ppm relates to the α protons of the ring [5]. In the spectrum of product V, in the region of olefinic protons, which should be free from signals in the case of compound Va, there is a singlet with δ = 4.7 ppm belonging to the terminal olefinic protons of compound Vb. The content of compound Vb, calculated from the ratio of the areas of the peaks of the three α protons of the ring and the two olefinic protons is 20%, which agrees well with the chromatographic data (19.5%). In the NMR spectrum of product VI, the presence of compound VIb is shown in a small distortion of the symmetry of the triplet of the olefinic proton (δ = 5.6 ppm). A comparison of areas analogous to that described above enables us, although very unreliably, to estimate the content of compound VIb as 5% (6% according to the chromatogram). The compositions of the other products calculated from the chromatograms are given in the table.

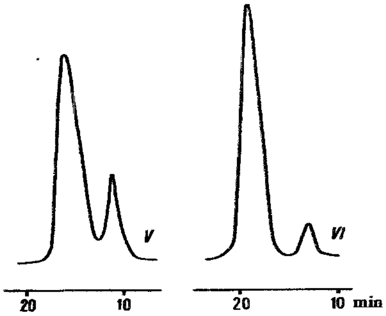


Fig. 1. Gas-liquid chromatograms of mixtures of the 2-(2'-alkenyl)-tetrahydropyrans V and VI.

Product IV possesses an indole odor and the others floral odors.

EXPERIMENTAL

Reaction of the chlorides I and II with organomagnesium compounds. Over 30 min, in drops, with stirring, 0.04 mole of the

---

*For part V, see [1].

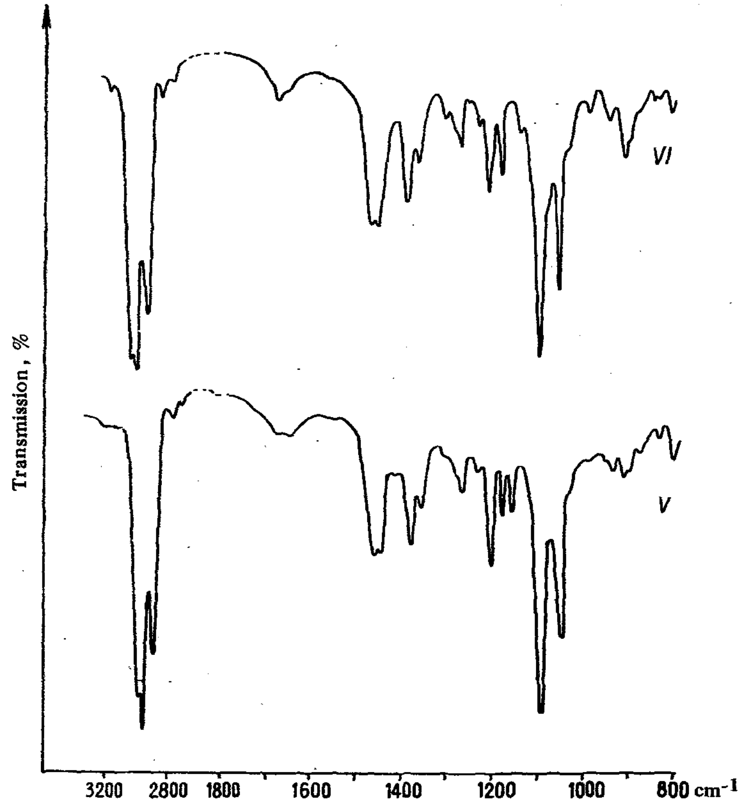


Fig. 2. IR spectra of mixtures of the 2-(2'-alkenyl)-tetrahydropyrans V and VI.

Characteristics of the Mixtures of Isomeric 2-Alkenyltetraphydropyrans*

Compound	Composition		Conditions for chromatographic analysis		Bp °C (mm)	d_{20}^4	n_D^{20}	MR_D		Empirical formula	Found, %		Calculated %		Yield %
	isomers	content, %	flow of nitrogen, ml/min	column temperature, °C.				found	calculated		C	H	C	H	
III	2-(2'-Methyl-2'-butenyl)tetrahydropyran	94	90	133	93—94 (24)	0.8915	1.4679	47.2	47.6	$C_{10}H_{18}O$	77.80	12.05	77.93	11.76	63
	2-(2'-Methyl-3'-butenyl)tetrahydropyran	6													
IV	2-(2'-3'-Dimethyl-2'-butenyl)tetrahydropyran	99	90	133	102—103 (27)	0.9147	1.4710	51.4	52.3	$C_{11}H_{20}O$	78.47	12.03	78.51	11.98	65
	2-(2',3'-Dimethyl-3'-butenyl)tetrahydropyan	1													
V	2-(2',3'-Dimethyl-2'-pentenyl)tetrahydropyran	80.5	60	133	68 (1)	0.9028	1.4689	56.2	56.9	$C_{12}H_{22}O$	78.95	12.28	79.05	12.21	60
	2-(2',2',3'-Trimethyl-3'-butenyl)tetrahydropyran	19.5													
VI	2-(2'-Methyl-2'-hexenyl)tetrahydropyran	94	125	154	76—78 (4)	0.8854	1.4620	56.6	56.9	$C_{12}H_{22}O$	78.75	12.64	79.05	12.21	54
	2-(2'-Methyl-2'-ethyl-3'-butenyl)tetrahydropyran	6													
VII	2-(2'-Methyl-2'-heptenyl)tetrahydropyran	95	118	175	68—70 (0.5)	0.8819	1.4628	61.2	61.6	$C_{13}H_{24}O$	79.36	12.30	79.54	12.31	65
	2-(2'-Methyl-2'-propyl-3'-butenyl)tetrahydropyan	5													
VIII	2-(2',7'-Dimethyl-2'-octenyl)tetrahydropyran	87	125	180	102—105 (1)	0.8814	1.4633	70.3	70.9	$C_{15}H_{28}O$	80.38	12.99	80.24	12.53	64
	2-(2'-Methyl-2'-isopentyl-3'-butenyl)tetrahydropyran	13													

---

*For the synthesis of compounds **V**, **VI**, **VII**, and **VIII** we used, respectively, CH_3MgI, C_2H_5MgBr, C_3H_7MgBr, and i-$C_5H_{11}MgCl$.

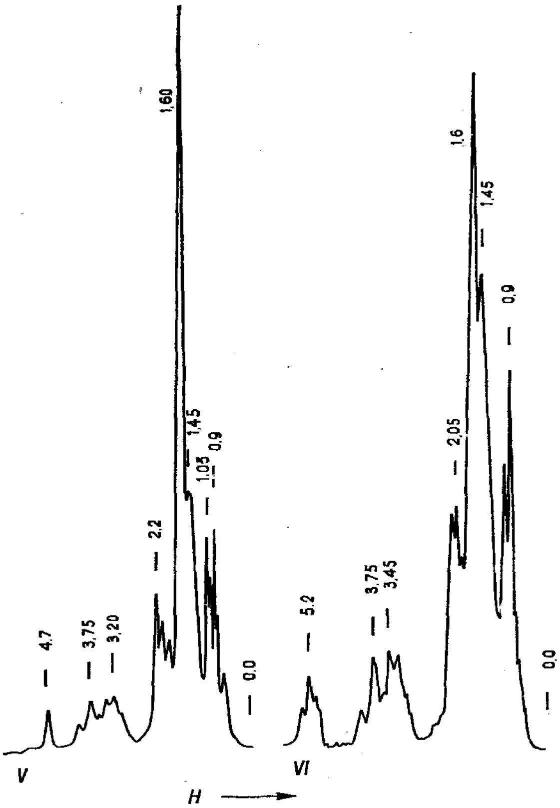


Fig. 3. NMR spectra of mixtures of the 2-(2'-alkenyl)tetrahydropyrans V and VI.

chloride was added to a solution of the alkylmagnesium halide obtained from 0.06 g-atom of magnesium in 30 ml of ether. The mixture was then boiled for 2 hours and treated with an excess of a saturated solution of NH_4Cl, and the ethereal layer was separated off, combined with an ethereal extract of the aqueous layer, and dried with $MgSO_4$, after which the solvent was distilled off, and the residue was distilled in vacuum (see table).

Reduction of the chlorides I and II with sodium amalgam. A mixture of 0.027 mole of the chloride and 120 g of 2% sodium amalgam was stirred for 5 hr, after which 200 ml of water was added, the mixture was extracted with ether, the extract was dried with $MgSO_4$, the solvent was driven off, and the residue was distilled in vacuum (see table).

Gas-chromatographic analysis was carried out on a UKh-1 instrument, carrier gas N_2, column containing 20% of silicone oil on diatomite brick.

The IR spectra were recorded in a thin layer on a UR-10 instrument with a NaCl prism in the 700–1800 cm^{-1} region and a LiF prism in the 2600–3200 cm^{-1} region. The following weak bands were observed: III 1645, 1670 (3100 absent); IV 1645, 1670 (inflection), 3090 (v.w.); VIII 1645, 1670 (3100 absent); VII 1640 (inflection), 1670, 3090 cm^{-1}.

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

REFERENCES

1. Yu. I. Tarnopol'skii, I. S. Shraiber, and V. N. Belov, KhGS [Chemistry of Heterocyclic Compounds], 3, 10, 1967.
2. Yu. I. Tarnopol'skii, M. M. Tarnopol'skaya, and V. N. Belov, ZhOrKh, 1, 938, 1965.
3. N. Sheppard and D. Simpson, Quart. rev., 6, 1, 1952.
4. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, 59, 1963.
5. D. McLaughlin, M. Tamres and S. Searls, J. Am. Chem. Soc., 82, 5621, 1960.

18 May 1966

Siberian Technological
Institute, Krasnoyarsk