Proc. Estonian Acad. Sci. Chem., 1992, 41, 4, 175-184

https://doi.org/10.3176/chem.1992.4.04

UDC 632.936

Heino RANG*, Tõnis PEHK**, Sirje VIITMAA*, Lilja LAHE*, Ants ERM*, Ilme LÕIVEKE*, and Koit LÄÄTS*

SYNTHESIS OF JUVENILE HORMONE ANALOGUES. 15. SYNTHESIS OF NOVEL 1-AROXY-3-METHYL-5-(MONO-, DI-, AND TRIOXA-ALKYL)-2-PENTENES

The first to synthesize herbicidally and insecticidally active oxa compounds from chloromethyl ether were Mamedov and coworkers [1, 2]. In 1972—1986 a number of oxa compounds, derivatives of benzene and benzodioxolan [3], oxa-alkenyl carboxylic acids [4], oxa-alkenylbenzene [5], and ethers of hydroquinone [6-13] were patented as insecticides, acaricides, and juvenoids. One of the authors with coworkers has earlier worked out a number of oxa compounds [14-18] with juvenoidal activity, of which ephoxene was registered in 1991 [19].

Based on the scheme presented in $[1^{18}]$ we have synthesized some novel 1-aroxy-3-methyl-5- (mono-, di-, and trioxa-alkyl)-2-pentenes with juvenoidal activity which have been tested on leaf louse $[2^{20}]$. These compounds have been synthesized from cyclohexylchloromethyl ether $[2^{14}]$ and novel chloromethyl ethers (see Table 1). From the adduct of chloromethyl ether and isoprene a quaternary salt has been obtained with dimethylaniline $[1^{15, 22}]$ and alkylated in water solution to the corresponding phenolate $[1^{5}]$. The aroxy compound was separated, vacuumdistilled, and identified by IR and 13 C NMR spectra.

Experimental

1. Synthesis of chloromethyl ethers

1-Chloro-3,5-dimethyl-2-oxahexane. 1380 g (13.5 moles) of 4-methyl-2pentanol and 480 g (16.0 moles) of paraform were stirred and cooled to -5 °C. Hydrogen chloride was directed into the mixture. The temperature of the mixture was -5 to 0 °C. The reaction was finished when the paraform was dissolved. The organic layer was separated and distilled in vacuum. The yield of 1-chloro-3,5-dimethyl-2-oxahexane was 1899 g (93.2%). The new chloromethyl ethers synthesized are presented in Table 1.

2. Addition of chloromethyl ether to isoprene

Synthesis of the adduct of 1-chloro-3,5-dimethyl-2-oxahexane and isoprene. To 152.6 g (1 mole) of chloromethyl ether (Table 1, No. 1) and 81.6 g (1.2 mole) of isoprene, 1.3 ml of 5.9% solution of tin tetrachloride in dichloroethane was added while stirring in an atmosphere of argon. The reaction temperature was 20-27 °C. The density of the mixture increased from 0.835 to 0.913 ($\Delta d = 0.078$). Then 5 g of carbamide was added, the mixture was stirred, settled, and carbamide with the catalyst complex was filtered off. The unreacted substances were evaporated and the mono adduct was distilled from the residue at 93-96 °C/1 mm torr, yield 161.9 g (70.4%). Mono adducts are characterized in Table 2.

^{*} Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences). Akadeemia tee 15, EE0026 Tallinn. Estonia.

^{**} Eesti Teaduste Akadeemia Keemilise ja Bioloogilise Füüsika Instituut (Institute of Chemical Physics and Biophysics, Estonian Academy of Sciences). Rävala pst. 10, EE0001 Tallinn. Estonia.

Kon LANTS, Heine P. O.	100	18 P.C.N	Siri				
le	%	- p	175-1	41, 4,	, 1992,		
ab	CI,	ete	3.5	9.8	5.6	9.4	
L	f	DE	61	-	5	1	
	H	1001-2	tsüklel				
	ter	-no	3	4	00	0	
Sanday 5-meijiligoranojikio	Con	lat	3.5	9.8	5.5	9.4	selle kondensatsioonik
etsetoonige stablishe BM/tb.	-	0	5	1	5	16	
	100	Nation.	19879				
speeter ja lõne orndokti 10		ter	5	œ.	7	3	
HYL-S-(MONO- DI-	ass	De	149	177	138	83	SYNIHESIS
110 ,01011,011	E		6177		YOU		i cicaninie .ci
	ol.	- 7	10	0	0	-	34
	W	alcuate	0.6	3.7(8.6(5.5	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
and cownders [1.2]	191	C	150	170	13	182	
	-	0200					
		, °			~		
		LC	38.7	38.1	38.2	7.3	
	6	20	0,	0,	0,	6	
	7	121-217		hain			
	7	, o d	3.2	8.0	7.1	6.7	
lave synthesized some	U:D	6	6	6	6	6	
ecvi) 2-pentenes with	27	t trio				-2-170	
et louse [20]. These	1	to be	ET D	40	53	40	viivitae lebiogevui
Soromethyl ether [21]	VX	4 50	937	94	062	60	
is he adduct of chloro-	TOI	a	0.	0	-ind	- Tin	
Shas been obtained	100						methyl ether and
essolution to the cor-	tev.	ni l	58	372	85	32	
a separated, vacuum-	17 - 13	n20	.42	.45	.42	.44	
			termined.				
0	rio	R spe	C NM				
ion o	cir	R spe	C RM				
zation o	ectr	R spe	C NM	0		fied by	
erization o	etr	R spe	C NM	1/10	SI V	8/5	
acterization o	to to	torr	1/5	-101/10	2/10	-108/5	
hardes) of t-methyl-5-	B to	°C/torr	71/5	00-101/10	62/10	17-108/5	
Charles) of turcthyl-3-	B to	°C/torr	71/5	100-101/10	62/10	107-108/5	
Charles) of 4-methyl-2- charles) of 4-methyl-2- charles) of 4-methyl-2- charles of 4-methyl	B to	°C/torr	71/5	100-101/10	62/10	107-108/5	
Characterization of temper-		°C/torr	21/5	100-101/10	62/10	107-108/5	
Characterization of the methyl-2- characterization of the temper- misture. The temper- misture and distilled	etr B to 1 B 1 D 1 D	°C/torr	1-11/5	100-101/10	62/10	107-108/5	
o characterization e mixture. The temper- eparated and distilled was finished when the eparated and distilled xahexane was 1899 g	B to	r o C/torr	thyl71/5	100-101/10	a-1-1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	107-108/5	
o tracterization of 4-methyl-2- charates) of 4-methyl-2- charates) of 4-methyl-2- charates) of 4-methyl-2- charates) of 4-methyl-2- was insided when the eparated and distilled scales are presented in ted are presented in	B to	ther as of contract of the second sec	methyl	yl-2- 100—101/10	oxa 5 0 62/10	tri- 107-108/5	
o definition current and cooled current and cooled was inished when the eparated and distilled examption was 1899 g examption of the second of the cod are presented in	ectr B B C C C C C C C C C C C C C C C C C	roether °C/torr	-dimethyl- 71/5 71/5	thyl-2- 100-101/10	-dioxa	,8-tri-	
Characterization Charac	ectr B ¢ B B B B B B B B B B B B B B B B B B	aloroether °C/torr	3,5-dimethyl- 71/5 71/5	4-ethyl-2- 100—101/10 e	2,5-dioxa 62/10	2,5,8-tri- 107-108/5 e	
CP stirred and cooled e mixture. The temper- e mixture. The temper- was inished when the esparated and distilled exahexane was 1899 g ced are presented in cashexane and iso-	ectr B B B B B B B B B B B B B B B B B B B	Chloroether °C/torr	ro-3,5-dimethyl-71/5 71/5 1	ro-4-ethyl-2- 100—101/10 tane	ro-2,5-dioxa	ro-2,5,8-tri- ane	
CP stirred and cooled e mixture. The temper- e mixture. The temper- was inished when the esparated and distilled exahexane was 1899 g ead are presented in cahexane and iso- ced are presented in (Table 1, No. 1) and (Table 1, No. 1) and	etr Buy Buy Buy Buy Buy Buy Buy Buy Buy Buy	Chloroether °C/torr	hloro-3,5-dimethyl-71/5 xahexane	hloro-4-ethyl-2- 100—101/10 oktane	hloro-2,5-dioxa- 62/10 62/10 tane	hloro-2,5,8-tri- decane 107108/5	 distilled, and tdentil 1. Synthesis of chile 1-Chloro-3,5-dimethy pentanol and 480 i pentanol and 480 i ature of the mixture paraform was dissedired (93.2%) The new Table 1. 2. Addition of chilo Synthesis of the a prene. To 152.6 g
CP stirred and cooled e mixture. The temper- e mixture. The temper- was inished when the esparated and distilled exahexane was 1899 g ead are presented in cal are presented in (Table 1, No. 1) and (Table 1, No. 1) and atmosphere of areon.	ectr B B B B B B B B B B B B B B B B B B B	Chloroether °C/torr	-Chloro-3,5-dimethyl-71/5 2-oxahexane	I-Chloro-4-ethyl-2- 00-101/10 0xaoktane	-Chloro-2,5-dioxa- 62/10 heptane	-Chloro-2,5,8-tri- 0xadecane	 distilled, and tdentil 1. Synthesis of chile 1-Chloro-3,5-dimethy pentanol and 480 i pentanol and 480 i atme of the mixture paraform was dissedired (93.2%). The new (93.2%). The new Table 1. 2. Addition of chilo Synthesis of the a prene. To 152.6 g prene of the prisedire
CP stirred and cooled e mixture. The temper- e mixture. The temper- was inished when the esparated and distilled exahexane was 1899 g east are presented in cad are presented in (Table 1, No. 1) and (Table 1, No. 1) and in letrachloride in atmosphere of argon.	ectr B B B B B B B B B B B B B B B B B B B	Chloroether °C/torr	1-Chloro-3,5-dimethyl-71/5 2-oxahexane	1-Chloro-4-ethyl-2- oxaoktane 100—101/10	1-Chloro-2,5-dioxa- heptane	1-Chloro-2,5,8-tri- 0xadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 pentanol to -5°C. Hydroger paraform was disso paraform was disso (93.2%) The mixture (93.2%) The new Table 1. Synthesis of the a prene. To 152.6 g 81.6 g (I.2 mole) o in dichlorochane w
• • • • • • • • • • • • • • • • • • •	etr B B B B B B B B B B B B B B B B B B B	101 Chloroether °C/torr	ol 1-Chloro-3,5-dimethyl- 71/5 1 2-oxahexane	l-Chloro-4-ethyl-2- oxaoktane	1-Chloro-2,5-dioxa- heptane	ol 1-Chloro-2,5,8-tri- 107—108/5 oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 pentanol to -5°C. Hydroger paraforn was disso in vacuum. The win (93.2%) The new 1 Table 1. Synthesis of the a Synthesis of the a Bi.6 g (1.2 mole) o in dichlorocthane w Streaged from 0.835
• • • • • • • • • • • • • • • • • • •	ectr ⁹ ⁹ ¹⁰ ¹	cohol Chloroether °C/torr	tanol 1-Chloro-3,5-dimethyl- 71/5 2-oxahexane	iol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	ol 1-Chloro-2,5-dioxa- 62/10 heptane	anol 1-Chloro-2,5,8-tri- 107108/5 oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 pentanol to -5°C. Hydroger atme of the mixture paraform was disso (93.2%). The new (93.2%). The new Table 1. Synthesis of the a Synthesis of the a Bi.6 g (L2 mole) o in dichlorochane w Staded from 0.835 Creased from 0.835
• • • • • • • • • • • • • • • • • • •	ectr ⁹ ⁹ ¹ ¹ ¹ ¹ ¹ ¹ ¹ ¹	alcohol Chloroether °C/torr	entanol 1-Chloro-3,5-dimethyl- 71/5 2.0xahexane	xanol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	anol 1-Chloro-2,5-dioxa- 62/10 62/10 heptane	oktanol 1-Chloro-2,5,8-tri- oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 (to -5°C. Hydroger atme of the mixture paraform was disse (93.2%). The new (93.2%). The new Table 1. Synthesis of the a Synthesis of the a B1.6 g (L2 mole) o in dichlorochane w the reaction tempe added, the mixture complex was filter
 o e harder 	ectr B B B B B B B B B B B B B B B B B B B	ing alcohol Chloroether °C/torr	2-pentanol 1-Chloro-3,5-dimethyl- 71/5 2. 2-oxahexane	hexanol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	entanol 1-Chloro-2,5-dioxa- 62/10 heptane	-1-oktanol 1-Chloro-2,5,8-tri- oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 (to -5°C. Hydroger atme of the mixture paraform was disse (93.2%). The new (93.2%). The new (93.2%). The new Table 1. Synthesis of the a Synthesis of the a B1.6 g (L2 mole) o added, the mixture added, the mixture complex was filtere
 o acterization classinger of the temper- emisture. The temper- emisture. The temper- emisture. The temper- emparated and distilled was finished when the exahexane was 1899 g ced are presented in ced are presented in the thrachloride (Table I, No. 1) and atmosphere of argon. atmosphere of argon. atmosphere of argon. g of carbamide was a were evaporated and the catalyst every with the catalyst of 93-96 °C/1 mm torr. 	ectr 2 2 2 2 2 2 2 2 2 2 2 2 2	arting alcohol Chloroether °C/torr	yl-2-pentanol 1-Chloro-3,5-dimethyl- 71/5 2. 2-oxahexane	(-1-hexanol 1-Chloro-4-ethyl-2- 100-101/10 oxaoktane	I-pentanol I-Chloro-2,5-dioxa- 62/10 heptane	xa-1-oktanol 1-Chloro-2,5,8-tri- 0xadecane	 distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 (pentanol and 480 (atme of the mixture of the section temperated from 0.835 The reaction temperated from 0.835 added, the mixture of t
• o erization • charles) of 4-methyl-2- • charles) of 4-methyl-2- • charles) of 4-methyl-2- • charles) of 4-methyl-2- • charles and distilled • matherane was 1899 g • cad are presented in • cade are presented in -2-oxaherane and iso- • (Table I, No. I) and -2-oxaherane of argon. • (Table I, No. I) and •	ectr 2 2 2 2 2 2 2 2 2 2 2 2 2	Starting alcohol Chloroether °C/torr	ethyl-2-pentanol 1-Chloro-3,5-dimethyl- 71/5 2 2-oxahexane	hyl-1-hexanol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	ca-1-pentanol 1-Chloro-2,5-dioxa- 62/10 62/10 heptane	Dioxa-1-oktanol 1-Chloro-2,5,8-tri- 107-108/5 oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 i to -5°C. Hydroger to -5°C. Hydroger paraform was distor (93.2%). The mixture (93.2%). The new (93.2%). The new 2. Addition of chilo 2. Addition of the a Synthesis of the a Synthesis of the a bit of g (1.2 mole) o in dichlorochhane w the reaction tempe complex was filtere yield 161.9 g (70.4
• • • • • • • • • • • • • • • • • • •	ectr	Starting alcohol Chloroether °C/torr	-Methyl-2-pentanol 1-Chloro-3,5-dimethyl- 71/5 1	-Ethyl-1-hexanol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	-Oxa-1-pentanol 1-Chloro-2,5-dioxa- 62/10 heptane	.6-Dioxa-1-oktanol 1-Chloro-2,5,8-tri- 107-108/5 oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 i to -5°C. Hydroger ature of the mixture paraform was disso ature of the mixture (93.2%) The new (93.2%) The new (93.
 o 4-methyl-2- nacterization c barries) of 4-methyl-2- c barries) of 4-methyl-2- c barries and cooled c barries and cooled c barries and distilled c barries and distilled c barries and a stilled c barries and second in c barries and second in the catalyst c barries and in Table 2. c barries and in Table 2. 	ectr P P P P P P P P P P P P P	Starting alcohol Chloroether °C/torr	4-Methyl-2-pentanol I-Chloro-3,5-dimethyl- 71/5 2-oxahexane	2-Ethyl-1-hexanol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	3-Oxa-1-pentanol 1-Chloro-2,5-dioxa- 62/10 62/10 heptane	3,6-Dioxa-1-oktanol 1-Chloro-2,5,8-tri- 107-108/5 oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 i to -5°C. Hydroger ature of the mixture paraforn was disse (93.2%) The new (93.2%) The new (93.2%) The new Synthesis of the a Synthesis of the a creased from 0.835 The reaction tempe added, the mixture complex was filtere yield 161.9 g (70.4 * Eesti Teadeste Aka
 Participant 	ectr P P P P P P P P P P P P P	No. Starting alcohol Chloroether °C/torr	1 4-Methyl-2-pentanol 1-Chloro-3,5-dimethyl- 71/5 2-0xahexane	2 2-Ethyl-1-hexanol 1-Chloro-4-ethyl-2- 100—101/10 oxaoktane	3 3-Oxa-1-pentanol 1-Chloro-2,5-dioxa- 62/10 62/10	4 3,6-Dioxa-1-oktanol 1-Chloro-2,5,8-tri- 107-108/5 oxadecane	distilled, and tdentil 1. Synthesis of chill 1-Chloro-3,5-dimethy pentanol and 480 i to -5°C. Hydroger ature of the mixture paraforn was disse (93.2%) The new (93.2%) The new (93.2%) The new Synthesis of the a Synthesis of the a Synthesis of the a fine treaction tempe in dichloroethane w added, the mixture complex was filtere widd 161.9 g (70.4 * Eesti Teaduste Akac (Chemical Physics a

		00	Table 2		Yield, %	66.0	62.1 62.1	52.8	60.6	64.5	
				%	Sapo- nified	16.2	13.9	16.7	13.0	15.9	
551.0° 2040 ¹ 1230 ² 1834				ntent of CI,	Primary	14.8	12.4	14.03	0.6	14.0	
				Co	* Calcu- lated	16.21	14.36	17.15	14.14	16.36	
				nass	Deter- mined	277.2	239.2	203.9	248.1	212.4	_
			- 0	Mol. I	Calcu- lated	288.77	246.82	206.71	250.77	216.75	unity, GLC
			o adduct		0	85		683		140	a l
			of mone		$\sim n_D^{20}$	565—1.45	700	578-1.45	660	840	888111
			erization	-	550 42	1.4	310.81	1.4	1.4	1.4	IoM
			Charact		B. t°, °C/torr	93—96/1	110-115/0.1	95—99/1	113-114/0.1	110-115/1	-
			H ² 134-130/01E		Mono adduct	C ₁₂ H ₂₃ CIO	C ₁₄ H ₂ TCIO	C10H19CIO2	C ₁₂ H ₂₃ CIO ₃	C ₁₂ H ₂₁ CIO	
	origeli Suguesi (SN) 2,52		CH3)3CHCH3CH(CH4). C ³ H	Starting	(CdP) chloromethyl- (CdP) cdP ether	1-Chloro-3,5-dimethyl-2- C oxahexane	1-Chloro-4-ethyl-2-oxa- C oktane	1-Chloro-2,5-dioxaheptane C	1-Chloro-2,5,8- C trioxadecane	Cyclohexyl C	chloromethyl ether
			-		No.	-	5	3	4	S	

Cistingistication of bpsnoxy combounds.

Table 3

Relative re- tention time (Z-isomere 1,0)	12	1.23	1.22	1.20	1.23
IR spectrum, cm ⁻¹	. pore II opport of	650; 660; 690; 840; 1020; 1100; 1250; 1370; 1400; 1410; 1490; 1510;	1600; 1620; 2880; 2940; 2980; 3060; 3100 820; 1020; 1090; 1240; 1380; 1470; 1510; 1590; 1620; 2880; 2930; 2960;	3040; 3070; 3100 830; 1020; 1100; 1240; 1380; 1390; 1470; 1510; 1580; 1610; 2870; 2940; 2970; 3040; 3060; 3100	830; 1010; 1100; 1240; 1380; 1390; 1480; 1520; 1590; 1620; 2870; 2940; 2970; 3040; 3070
Yield, %	10	53.9	67.2	65.4	70.5
from this E isomer, %	6	71.5	76.7	70.3	81.6
Purity E+Z isomers, %	80	95.4	93.2	90.1	91.2
mass Determin- ed	7	308.6	289.1	303.2	317.6
Mol. Calculat- ed	9	310.87	290.45	304.48	318.51
n_D^{20}	5	1.5058	1.4990	1.4980	1.4945
B. t°, °C/torr	4	122—126/0.1	123—126/0.1	124—130/0.15	127—130/0.1
R ²	3	CI	CH3	C ₂ H ₅	i-C ₃ H ₇
cheoperation appart. Cheoperation Cheoperation R ¹	optane 2	(CH ₃) ₂ CHCH ₂ CH(CH ₃)	(CH ₃) ₂ CHCH ₂ CH (CH ₃)	(CH ₃) ₂ CHCH ₂ CH(CH ₃)	(CH ₃) ₂ CHCH ₂ CH (CH ₃)
No.		1	5	3	4

Characterization of phenoxy compounds

OR

P.2

continue	12	1.21		1.23	1.34	1.21	1.24	1.24	1.20	2
Table 3	caon popol apont acon	830; 1020; 1120; 1240;	1380; 1470; 1520; 1590; 1620; 2870; 2940; 2970; 3040	640; 650; 680; 830; 1020; 1110; 1240; 1390; 1470; 1500; 1590; 1600; 2000, 0050, 0070, 0050	2000; 2330; 2370; 3000; 3100	830; 1020; 1120; 1250; 1360; 1380; 1400; 1460; 1520; 1600; 1620; 2870; 2950; 3040; 3070; 3100	830; 1020; 1110; 1240; 1360; 1370; 1390; 1460; 1520; 1590; 1620; 2870; 3040; 3070; 3100	640; 650; 680; 840; 1020; 1110; 1250; 1360; 1380; 1400; 1460; 1500; 1590; 1610; 2870; 2950; 3040; 3080; 3100	820; 1020; 1120; 1250;	1300; 1390; 1460; 1520; 1590; 1620; 2880; 2940; 3040: 3070
a volume	10	63.2		58.2		65.2	64.8	53.9	40.8	10
1.0	6	76.5		67.4		66.4	72.5	6.17	54.0	10
	8	93.2		96.7		92.1	93.3	97.1	0.96	-
	2	330.1		336.7		280.5	300.9	307.6	272.1	-
-	9	332.54	MA. 5525	338.92		288.43	302.46	308.85	278.39	8
-	5	1.4958	1.001	1.5054		1.5182	1.5200	1.5320	1.5040	~
-	4	138-140/0.04		137/0.03		135—136/0.2	146—147/0.1	148—149/0.1	126-130/0.3	4
	3	2 C2H5		2 CI		CH3	C ₂ H ₅	Ū	CH3	8
	2	CH ₃ (CH ₂) ₃ CH(C ₃ H ₅)CH	CHPOICHPPOCH CH	CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)CH		Cyclohexyl	Cyclohexyl	Cyclohexyl	C2H3OCH2CH2	20
	-1	S		9	ż	2	8	0	10	-

2	3	4	5	9	2	8	6	10	1280	II	5040: 10000	12
CH2CH2	CI H.	138—139/0.2	1.5032	298.81	295.3	93.8	58.4	39.2	630; 1010; 1390;	640; 670; 1120; 1240; 1470; 1500;	830; 1360; 1590;	1.21
									1600; 3040;	2870; 2930; 3080; 3100	2980;	
CH ₂ CH ₂	C ₂ H ₅	120—126/0.07	1.5021	292.42	291.5	95.2	61.0	47.1	830; 1 1360; 1 1590; 1 2970; 3	(020; 1120; (380; 1460; (610; 2880; 030; 3060	1240; 1520; 2940;	1.20
(CH ₂) ₂ OCH ₂ CH ₂	H	132-135/0.06	1.5022	308.42	305.9	93.0	76.0	32.5	700.	760- 1000-	1010-	1 93
									1040; 1 1390; 1 1600; 2	120; 1240; 460; 1500; 880; 2950;	1370; 1590; 2980;	
	CH3			288.43					3030; 3	070; 3470	152010	131
(CH ₂) ₂ OCH ₂ CH ₂	CI	135—139/0.03	1.5114	342.87	336.9	91.2	80.0	29.8	640; 1010; 1 1240; 1	650; 680; 050; 1100; 360; 1400;	840; 1140; 1480;	1.24
Haller (Chiller)	0	124,0102	1001	Ser.820		- 198 2007	ent.		1500; 1 2880; 2 3080; 3	530; 1590; 950; 2980; 100; 3470	1600; 3050;	
(CH ₂) ₂ OCH ₂ CH ₂	CH ₃	130133/0.03	1.5016	322.44	320.1	93.4	81.8	38.2	820; 1 1350; 1 1580- 1	020; 1120; 380; 1460; 610- 2880-	1240; 1510; 9990.	1.23
2	8			8	T	. 8	6	10	2980; 3	030; 3060;	3480;	12

ile 3 contin

				24	E.
_		A F.		1	
ed		~	un segundaru	P. States	a market by the standard in the set
nu	12	5	24	Part	
tin	1000	- al guiller	- Calina had	S. marshaw	
uo	-	100			hue and mahine of the nume of
Ö	1034	mondes	1. 00.4 g (4.04		of dimetuyianthine, and 50 ml of
3	eth	0000	0000		ensternary salt was chialand
le	-	242324	24252949494		an and 100 ml of it is man
ab		0001	1-00		
T	Se.	0000	0000		a of the quaternary sail was
	0.34	12 12 88 88 88 88 88 88 88 88 88 88 88 88 88	12474		
	1		1120		a of 956 mathem budenets
	-	0000	:0000		The of the potential material
		61 61 04	02 35 05 05 05 05 05 05 05 05 05 05 05 05 05	10. 146 31	
	1.21	3	3111		
		00000	00000		h The mixtere and endad and
		36 36 36	844 98 98		
	1.00	32-1	30-1		
ST	110	m hydroxide			it waten Toluena and dimethyl-
37		e was a si			
		0	0		
	10	22.	10		
134		0 - 2 - 1 -	N		
00	-	bunde Haff A			
-		Lin 82 82			
~	1	4	A. 8 8 2 9		and the second se
	6	33.	6	Carly and -	
17.1	201	00	1		
1-					
100			22 19 28		and a man a star a special fills
14	100	6			
31	00	4.	0	A CONTRACTOR	
	p	0	0		
-	_	2 2 2 2 2			
1	1.03				postov (ka) on gass capillary
00	U.D.	6	0		with PISEAS (plenvidiethanol-
art	2	34.	.6	- anterna	
		3	34		and the set of the set of the set
111	_		32 2 2 2 2 2 2 B		r tess ay auriture
	-11		No.	1 200	bord 70 qR spectremeter (Zeiss,
Je	hall	4.	47	In Pusit	or the Billy window
	9	36	000		
		3	ŝ		bende (Colleman Subcers andre
111			LANCIA 2801 (210)		aruge A.M. and Spectrometer,
21	10.1	6	and and and		Malions ^o were used
		02	00		A A A A A A A A A A A A A A A A A A A
	2	ŝ.	.5(
		-			a contraction of the second
	-				
				~	
		03			
		.0,			
		13 HN 111	MIN MIN MIN		
	4	-1-	0		
			0/		
1		40	34		
11	M	Medae III. A.	OFinos O. 5., 30		
	3.0		H		and the second second second second second second
	0	H	131		
		C	i-0		
			The Real Provent		the second s
	-	I2	H 3	1844	
		C	D O		
	1	T	12	1037 31	and the second
		G	C	6939	
	3.	0	0		
	2	(2)	(1)		
		H	H		
		0)	0 0		and a set of the set o
10.	111	0	0	a block and a second second	
		H	H,		
		S.	() [7]		
	-	T 24. (2100.02)	1000		and the second of the second second
12.		9	N 1 1		
	-1	I L C	TEE		
		H H	A H O		
					181

	able						×	23.79			15.38	15.54		
	T						-	32.82	19.66	L	27.52	27.71		
						1		2				3.78		
						100	111	22.73 22.67				2.83 13		
						100	332	22.13 222.14		14.24		9.89 2		
						10	1993	4.16		65.47		0.42 2		
						16	Y	5.98 24		9-67-(5.46	.80 3		
						1000		4	65.77 65.79	68.91 69 68.89 69	23.57 23.46 2	23:70 10 10		
						10		(19.43)	69.13 69.17	59.59 59.65	31.74 31.70	39.46 (39.51		
								73.05	69.46 69.60	59.22 (69.36 (76.78	73.33		
-						-	9	66.32 66.09	69.04 68.81	68.63 (68.41	65.90 65.58	69.31 69.06	-	
		s of					2J	39.54 32.94	38.69 32.12	38.44 31.92	39.50	39.24 32.64		6
		somer		7		9	4	16.39 23.40	16.08 23.11	15.84 22.78	16.43 23.44	16.50 23.52		
		Z is		9-0-	0		ŝ	137.06	136.73 136.81	137.15	137.34	137.42		
		and	7		2		2	21.20	21.00	20.13	21.00	21.31 22.18		
		of E		-~>	2	8	1	14.14 1 14.05 1	63.93 1 63.82 1	4.01 1 33.96 1	64.17 1	54.34 1 54.23 1		
		shifts			0	08.42	р	140.06 6 140.02 6	128.71 (128.68 (124.25 6 124.20 6	135.50 6 135.46 6	135.66 6 135.64 6		
		mical		C	E		m	126.56	129.06	128.24	128.03	128.21		
		³ C che		×		1.502	0	114.02	113.80	115.08	114.01	114.21	1.905	
						80	s	156.63	156.10	156.59	156.51	156.72		
						135/0	Isomer	NE	2 Z	ЧN	ZE	SE		
						133	ElZ	3.5	1.5	5.8	3.2	3.6		
									Hs	I2CH3		H ₂ CH		
						*		H3)2	[2-C]	20CF		CH2CI	C ⁸ H ⁹	
						in the	Y	CH(C	-CH	H ₂ CH		CH ₂ C	aH	
						CH		CH ₂ (I2-0	I20CI		C2H5)	CHFC	
						Raya		(CH ₃)	2-CF	2-CF	141 .0	CH(10
						210		CH	CH	CH	CeH	CH		
						Call		H		CHL	P	H2-		
						2 .	X	I3) 2C	L	F	3CH2	-CF	2	

3. Synthesis of aroxy compounds

1-(4-Chlorophenyl)-1.7-dioxa-4.8.10-trimethyl-3-undecene. 100 g of the adduct of 1-chloro-3,5-dimethyl-2-oxahexene and isoprene (0.43 mole of primary chlorides), 65.4 g (0.54 mole) of dimethylaniline, and 55 ml of methanol were stirred at 50 °C for 5 h; quaternary salt was obtained. The mixture was cooled, 200 ml of water and 100 ml of toluene were added, and stirred. The water solution of the guaternary salt was separated and alkalified to pH=9, then extracted with toluene, 55.3 g (0.43 mole) of 4-chlorophenol and 86 g of 20% sodium hydroxide solution (0.43 mole) were stirred. At 70°C the extracted water solution of the quaternary salt was added to the phenolate solution obtained and stirred at the same temperature for 4 h. The mixture was cooled and extracted with toluene. The toluene solution was washed with 10% sodium hydroxide solution and then with water. Toluene and dimethylaniline were distilled from the toluene solution in vacuum. From the residue 1-(4-chlorophenyl)-1.7-dioxa-4.8.10-trimethyl-3-undecene was distilled at 122-126°C/0.1 torr. The yield was 75.5 g (53.9%). The phenoxy compounds obtained are presented in Table 3 and the 13C NMR spectra in Table 4.

Chloride compounds were analysed by means of a gas chromatograph Chrom 5 (Laboratorne Pristroje, Chechoslovakia) on glass capillary column 1-24 m, i.d. -0.27 mm coated with TCEP -1.2.3-tris-(2-cyanoethoxy) propane. Temperature of column oven 70-100 °C, temperature of injection port 150-180 °C, carrier gas N₂, flow rate 1.2 cm³/min.

Phenoxy compounds were analysed by means of a gas chromatograph Chrom 5 (Laboratorne Pristroje, Chechoslovakia) on glass capillary column 1-47 m, i.d. - 0.3 mm coated with PDEAS (phenyldiethanol-aminesuccinate), temperature of column oven 200 °C, temperature of injection port 270 °C, carrier gas N₂, flow rate 2.0 cm³/min.

Infrared spectra were taken on a Specord 75 IR spectrometer (Zeiss. Jena) in the region 400-4000 cm⁻¹ using the KBr window.

Mol. mass is determined ebullioscopically, ¹³C NMR spectra were measured from CDCl₃ solutions with Bruker AM-500 spectrometer. Standard pulse programmes for 2D correlations were used.

REFERENCES

1. Мамедов Ш. А., Осипов О. Б., Зейналова В. М. Ядохимикаты. Авт. свид. СССР

- № 128683. Б. И., 1960, 10, 55. 2. Мамедов Ш. А., Низкер И. Л., Гришина Е. Н. Способ получения 1'-алкоксиметил-2-хлорциклогексанов. Авт. свид. СССР № 136602. — Б. И., 1961, 5, 64.
- 3. FRG Pat. 2161159; 1972, C. A. 77, 101563.
- 4. FRG Pat. 2226523; 1973, C.A. 78, 71483.
- 5. FRG Pat. 2339671; 1974, C. A. 81, 10487.
- 6. Europat. 169169; 1986, C. A. 104, 206939.
- 7. Jap. Pat. 6172733; 1986, C. A. 105, 208592.
- Swiss Pat. 643223, 1984.
 Fr. Pat. 2522650, 1983.
- 10. US Pat. 4334104, 1982.
- 11. FRG Pat. 3326180, 1984.
- 12. US Pat. 4616082, 1986.
- 13. US Pat. 4482728, 1984.

- Лээтс К., Когерман А., Аммон К. Синтез некоторых аналогов ювенильного гормона. — Изв. АН ЭССР. Хим., 1978, 27, 1, 36—38.
- Когерман А., Аммон К., Ранг Х., Лээтс К. Синтез аналогов ювенильного гормона. 2. Алкилирование замещенных фенолов хлористым геранилдиметилфениламмонием. — Изв. АН ЭССР. Хим., 1979, 28, 4, 257—260.
- 16. Лээтс К., Шмидт М., Каал Т., Куузик А., Вялимяэ Т. Синтез аналогов ювенильного гормона. 7. Получение и ювенильная активность некоторых простых эфиров 3-метил-5-алкокси-2-пентен-1-олов. Изв. АН ЭССР. Хим., 1986, 35, 1, 76—78.
- Лээтс К., Шмидт М., Каал Т., Куузик А., Вялимяэ Т. Синтез аналогов ювенильного гормона.
 8. Получение и ювенильная активность некоторых бензиловых и фенилэтиловых эфиров 3-метил-5-алкокси-2-пентен-1-олов. Изв. АН ЭССР. Хим., 1986, 35, 3, 223—225.
- Лээтс К., Каал Т., Шмидт М., Куузик А., Когерман А., Метспалу Л., Хийесаар К. Синтез аналогов ювенильного гормона. 5. Получение и ювенильная активность некоторых алкоксиалкенилфениловых эфиров. — Изв. АН ЭССР. Хим., 1984, 33, 2, 133—134.

19. Защита растений, 1991, 1, 52.

 Зильберминц И., Лээтс К., Кудрявцев И., Когерман А., Журавлева Л. Новые гормональные инсектициды и их действие на тлей. — Изв. АН Эстонии. Хим., 1991, 40, 1, 46—55; 3, 142—148.

21. Поконова Ю. В. Галоидэфиры. Москва-Ленинград, Химия, 1966.

 Шмидт М., Крумм Л., Лээтс К. Изучение кинетики реакции 1-хлор-3-метил-5-изопропокси-2-пентена с N,N-диметилфениламином. — Изв. АН ЭССР. Хим., 1989, 38, 1, 21—24.

Received Received In 1992 Received Will PLAS (phenyldicthanol 1992 Received 1992 Recei

Heino RANG, Tõnis PEHK, Sirje VIITMAA, Lilja LAHE, Ants ERM, Ilme LÕIVEKE, Koit LÄÄTS

JUVENIILHORMOONI ANALOOGIDE SÜNTEES. 15. UUTE 1-AROKSÜ-3-METÜÜL-5-(MONO-, DI- ja TRIÖKSAALKÜÜL)-2-PENTEENIDE SÜNTEES

Saadi rida 1-aroksü-3-metüül-5-(mono-, di- ja trioksaalküül)-2-penteene, mida iseloomustati infrapunaste ja ¹³C TMR-spektritega. Süntees teostati isopreeni haloalküleerimisel vastavate klorometüüleetritega ja järgneval asendatud fenoolide *o*-alküleerimisel saadud aduktidega.

Хейно РАНГ, Тынис ПЕХК, Сирье ВИЙТМАА, Лилья ЛАХЕ, Антс ЭРМ, Ильме ЛЫЙВЕКЕ, Койт ЛЭЭТС

СИНТЕЗ АНАЛОГОВ ЮВЕНИЛЬНОГО ГОРМОНА. 15. СИНТЕЗ НОВЫХ 1-АРОКСИ-3-МЕТИЛ-5-(МОНО-, ДИ- И ТРИОКСА-АЛКИЛ)-2-ПЕНТЕНОВ

Получен ряд 1-арокси-3-метил-5- (моно-, ди- и триоксаалкил)-2-пентенов, которые охарактеризованы ИК- и ¹³С ЯМР-спектрами. Синтез осуществлен галоалкилированием изопрена соответствующими хлорметиловыми эфирами и последующим *о*-алкилированием замещенных фенола получаемыми галоаддуктами.