1692, 1718 cm^{-1} ($\Delta\nu$C=C). Mass spectrum: 462 (M$^+$, $C_{10}F_{18}^+$, 30.2), 443 ($C_{10}F_{17}^+$, 35.4), 355 ($C_9F_{13}^+$, 17.7), 243 ($C_6F_9^+$, 36.2), 181 ($C_4F_7^+$, 21.5), 69 (CF_3^+, 100).

(XVI), ^{19}F NMR spectrum: −11.6 (a), −13.8 (b), −2.2 (c), 33.4 (d), 101.1 (e), J: b-d = 10 Hz. Raman spectrum: 760 cm^{-1} (v.s, $\Delta\nu_s$C=C=C). Mass spectrum 462 (M$^+$, $C_{10}F_{18}^+$, 16.2), 443 ($C_{10}F_{17}^+$, 72.7), 393 ($C_9F_{15}^+$, 12.5), 355 ($C_9F_{13}^+$, 14.5), 293 ($C_7F_{11}^+$, 26.9), 243 ($C_6F_9^+$, 1.4), 181 ($C_4F_7^+$, 12.3), 69 (CF_3^+, 100). Mixture of isomers. Found: C, 25.93; F, 74.13%. Calculated for $C_{10}F_{18}$: C, 25.97; F, 74.03%.

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SYNTHESIS AND TRANSFORMATIONS OF METALLOCYCLES.

5. REGIOSELECTIVE SYNTHESIS OF β-SUBSTITUTED ALUMOCYCLOPENTANES BY THE CYCLOMETALLATION OF α-OLEFINS USING Et₃Al IN THE PRESENCE OF Cp₂ZrCl₂

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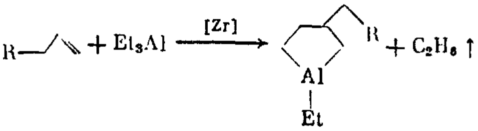
A. P. Zolotarev, R. R. Muslukhov,
and G. A. Tolstikov

UDC 542.97:547.256.2:547.514

A new method has been proposed for the synthesis of N-, O-, and S-containing alumocyclopentanes by the reaction of Et_3Al with functional α-olefins in the presence of catalytic amounts of Cp_2ZrCl_2. The alumocyclopentanes obtained may react with S_8 to give β-substituted tetrahydrothiophenes.

We recently were the first to report the synthesis of alumocyclopentanes, which are five-membered metallocycles, by the reaction of simple α-olefins with Et_3Al catalyzed by Cp_2ZrCl_2 [1-4]

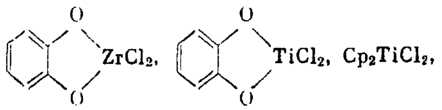


$R = C_3H_7, C_5H_{11}, C_8H_{17}$.

This reaction has been termed catalytic olefin cyclometallation [1]. In order to expand the scope of this unusual reaction, elucidate the possibility of using this method for the synthesis of functionally substituted alumocyclopentanes, and study the reactivity of these compounds, we investigated the reaction of Et_3Al with more complex olefins, including functionally substituted olefins.

We were unable to carry out this reaction using the following complexes and salts as catalysts:

$TiCl_4$, $ZrCl_4$, $Zr(OBu)_4$,

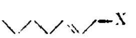
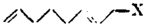
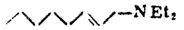
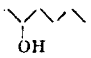
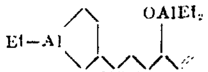
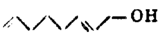
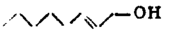
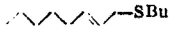


Cp_2TiCl_2,

Institute of Chemistry, Bashkir Science Center, Urals Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2831-2841, December, 1990. Original article submitted October 12, 1989.

0568-5230/90/3912-2570$12.50

TABLE 1. Cyclometallation of Functionally Substituted 2,7-Octadienes by Triethylaluminum in the Presence of Cp_2ZrCl_2*

	[Zr], mole % relative to 	Reaction time, h	Solvent	Reaction products	Yield of OAS (XXI), %
	2	16	hexane	(XXIa)	87
	3	6	cyclohexane	(XXIb)	81
	3	6	hexane	 (XXVIII)	88
	3	6	hexane	(XXIc)	92
	3% [Zr]+ +3% i-Bu_2AlH	1	hexane	(XXIc)	96
	5% [Zr]+ +5% i-Bu_3Al	4	benzene	(XXIc)	83
	5% [Zr]+ +5% $EtAlCl_2$	6	hexane	(XXId)	1
	5	20	hexane	(XXId)	80

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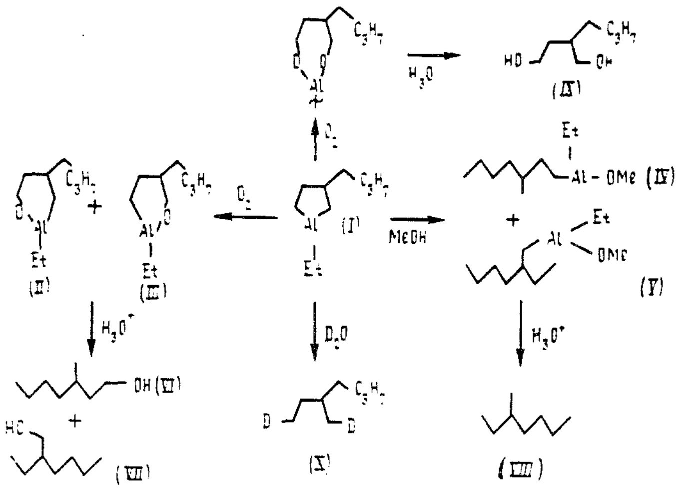
*Reaction conditions: 25°C, Et_3Al/ = 2.5:1 for X = NEt_2, OCH_3 and 3:1 for X = OH, SBu.

as well as various complexes and salts of Cu, Fe, Co, Ni, Pd, Rh, Ru, and Ir. Of the transition metal compounds tested, alumocyclopentanes could be obtained from Et_3Al and α-olefins only in the presence of Cp_2ZrCl_2. Furthermore, the cyclometallation of α-olefins proceeds under mild conditions in aliphatic or aromatic solvents and also without solvent. In this regard, all the following experiments on the preparation of alumocyclopentanes were carried out using Cp_2ZrCl_2 under the optimal conditions found.

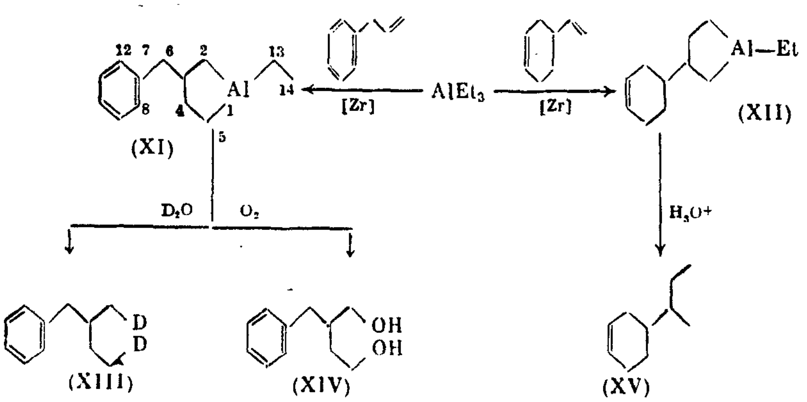
In order to obtain more reliable proof for the structure of the alumocyclopentane (I) obtained from Et_3Al and 1-hexene, we studied some of the chemical transformations of this product. Thus, a ~1:1 mixture of isomeric alkoxides (II) and (III) was formed upon the incomplete oxidation of (I) by O_2 in hexane at 10-25°C for 2 h. The reaction of (I) with methanol gave (IV) and (V), which, upon hydrolysis, were converted to alcohols (VI) and (VII), and hydrocarbon (VIII). The complete oxidation or deuterolysis of (I) leads to 2-butyl-1,4-butanediol (IX) or 2-butyl-1,4-dideuterobutane (X).



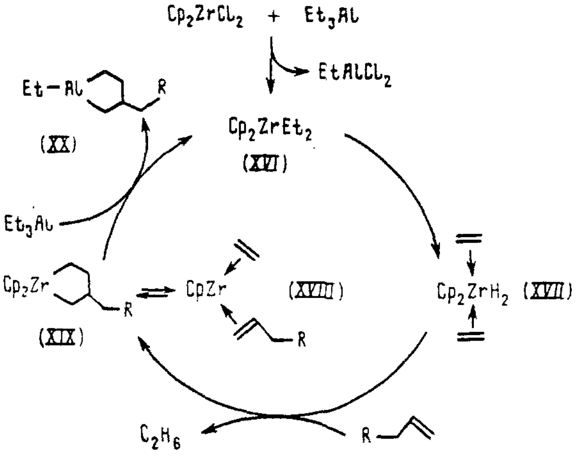
These results indicate that the metal—carbon bonds in the five-membered ring have higher reactivity than the Al—Et bond.

We then attempted to carry out the cyclometallation of linear and cyclic olefins in order to obtain more complex alumocyclopentanes. 3-Vinylcyclohexene and allylbenzene react with Et_3Al with catalysis by Cp_2ZrCl_2. The existence of an additional bond or aromatic substituent in the starting α-olefin has virtually no effect on the direction and selectivity of the reaction. Alumocyclopentanes (XI) and (XII) were obtained in 82 and 90% yield at room temperature in the presence of catalytic amounts of Cp_2ZrCl_2 (Et_3Al:α-olefin:[Zr] = 120:100:2). These products were identified by ^{13}C NMR spectroscopy. Thus, the ^{13}C NMR spectrum of

(XI) shows three broad upfield signals corresponding to the carbon atoms bonded to the central aluminum atom: 14.5 t (C^2), 5.9 t (C^5), 1.4 t (C^{13}). Such signals are also found for (XII). Oxidation, hydrolysis, or deuterolysis of alumocyclopentanes (XI) and (XII) lead to diol (XIV) or hydrocarbons (XIII) and (XV).



Literature data and our experimental results indicate that the catalytic cycle of the cyclometallation of α-olefins involves the alkylation of Cp_2ZrCl_2 by triethylaluminum with the formation of zirconium alkyl complexes. Subsequent β-cleavage of the hydrogen atom in zirconium alkyl complex (XVI) leads to (XVII), which is stabilized by ethylene molecules. The intramolecular hydrozirconation of ethylene in the coordination sphere of the metal proceeds with the formation of ethane. The entry of the starting α-olefin into the coordination sphere of the central atom gives mixed complex (XVIII). Then, activated ethylene and starting α-olefin molecules undergo intramolecular cyclometallation with the formation of zirconocyclopentane (XIX). Subsequent transmetallation of (XIX) by excess Et_3Al leads to alumocyclopentane (XX) and catalytically active complex (XVI).



The release of ethane during the reaction is indirect evidence for the proposed mechanism. The addition to Cp_2ZrCl_2 of catalytic amounts of i-Bu_2AlH, which facilitates the formation of zirconium hydride complexes [5, 6], accelerates the reaction. On the other hand, the reaction is strongly suppressed upon the introduction of $EtAlCl_2$ to the catalyst.

Unsaturated compounds containing functional substituents and capable of complexation with organoaluminum compound were used in the cyclometallation reaction. 1-Methoxy-2,7-octadiene, diethyl-2,7-octadienylamine, 2,7-octadien-1-ol, butyl 2,7-octadienyl sulfide,and 1,7-octadien-3-ol were selected as the functionally-substituted α-olefins. Depending on the nature of the starting olefin, the amount of Cp_2ZrCl_2, and reaction time, the yields of the alumocyclopentanes range from 80 to 96% (Table 1). Hexane, cyclohexane, and benzene were selected as the solvents. A sharp decrease in the reaction rate is noted in ethereal (Et_2O, THF, and amyl ether) or halogenated solvents such as CH_2Cl_2 or $(CH_2Cl)_2$ and the yields of alumocyclopentanes do not exceed 2-8% over 15 h. More complete conversion of the starting 2,7-octadienes is achieved when a 2.5-fold excess of Et_3Al is used in the reaction for 1-methoxy-2,7-octadiene, diethyl-2,7-octadienylamine and when a three-fold excess is used for 2,7-octadien-1-ol, 1,7-octadien-3-ol, and butyl 2,7-octadienyl sulfide.

TABLE 2. ^{13}C NMR Spectra of (IV)-(VII), (XI), (XIII), (XIV), (XXI)-(XXIII), (XXV), (XXVI), (XXIX), and (XXX) (δ, ppm, J, Hz)

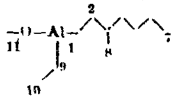
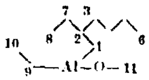
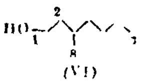
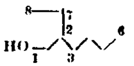
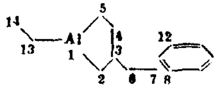
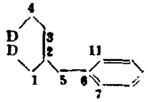
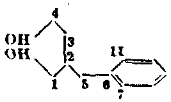
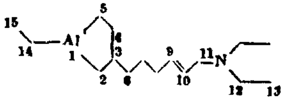
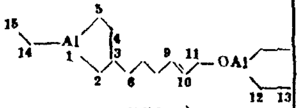
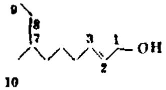
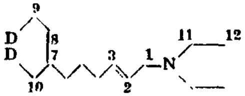
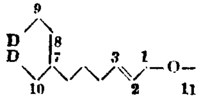
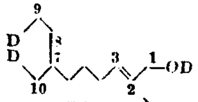
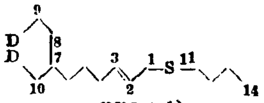
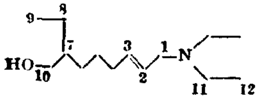
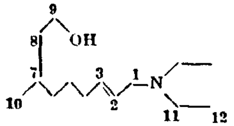
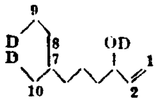
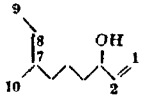
Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}
 (IV)*	6,9 t	34,8 t	38,8 d	36.6 t	30,0 t	23,7 t	14,5 q	19,5 q	2,0 t	9,5 q	50,6 q				
 (V)*	15,6 t	37,2 d	38,2 d	30,0 t	23,7 t	14.5 q	31.8 t	11,6 q	2,0 t	9,5 q	50,6 q				
 (VI)	61,0 t	40,3 t	30,0 d	37,3 t	29,6 t	23,4 t	14,3 q	19,8 q							
 (VII)	65,1 t	42,4 d	30,6 t	29,6 t	23,5 t	14,3 q	43,8 q	11,2 q							
 (XI)	–	14.5 t	44,5 d	35,4 t	5,9 t	48.3 t	141,6 s	129.2 d	128.2 d	125.8 d	128,2 d	129,2 d	1,4 t	8,7 q	
 (XIII)	18.7 t	36,7 d	29,2 t	11.2 t	43.5 t	141,6 s	128,1 d	129,2 d	125,6 d	129,2 d	128,1 d				
 (XIV)	65,0 t	40,9 d	34,9 t	60.5 t	38,0 t	140,3 s	128.2 d	129.0 d	125,9 d	129.0 d	128,2 d				
 (XXIa)	–	14,2 t	42.5 d	33,8 t	5,9 t	40,1	27.5 t	33,2 t	121,7 d	139,4 d	56,4 t	48,2 t	10,7 q	2,2 t	9,1 q
 (XXI c)	–	13,3 t	42,5 d	36,2 t	6,3 t	41.4 t	28,0 t	33,3 t	126,5 d	138,4 d	64.8 t	1,0 t	8.8 q	1,7 t	9,3 q
 (XXII c)	63,0 t	131.4 d	130,8 d	33.1 t	27,5 t	36,7 t	34,9 d	30,0 t	11.6 q	19.4 q					

TABLE 2 (continued)

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}
 (XXIIIa)	55,8 t	132,9 d	128,7 d	33,2 t	27,5 t	36,6 t	34,7 d	29,9 t	11,3 q $^1J_{^{13}C-D}$= =19,0	19,1 q $^1J_{^{13}C-D}$= =18,9	47.0 t	12,4 q			
 (XXIIIb)	73,5 t	134,3 d	127,6 d	33,2 t	27,4 t	36,8 t	34,9 d	30,0 t	11,3 $^1J_{^{13}C-D}$= =19,0	19,2 $^1J_{^{13}C-D}$= =18,6	57,4 q				
 (XXIII c)	63,1 t	131,2 d	131.0 d	33,2 t	27,5 t	36,7 t	34,9 d	29,9 t	11,3 $^1J_{^{13}C-D}$= =19,5	19,2 $^1J_{^{13}C-D}$= =19,1					
 (XXIII d)	32,6 t	133,5 d	126,1 d	34,0 t	27,0 t	36,2 t	32.2 d	29,4 t	11,1 $^1J_{^{13}C-D}$= =18.6	19,0 $^1J_{^{13}C-D}$= =18,5	30,3 t	31,6 t	22,1 t	13.7 q	
 (XXVa)	54,9 t	134,3 d	126,2 d	32,6 t	26,6 t	29,4 t	41,9 d	23,4 t	11,4 q	64,4 t	46,2 t	11,2 q			
 (XXVIa)	54,9 t	134,3 d	126,2 d	32,8 t	26,6 t	36,6 t	30,0 d	40,0 t	60,1 t	19,7 q	46,2 t	11,2 q			
 (XXIX)	113,2 t	143,3 d	72,7 d	38,4 t	23,5 t	37,2 t	34,9 d	29,9 t	11,3 $^1J_{^{13}C-D}$= =19,5	19,1 $^1J_{^{13}C-D}$= =18,6					
 (XXX)	114,2 t	141,5 d	73,0 d	37,5 t	23,0 t	36,7 t	34,5 d	29,5 t	11,4 q	19,2 q					

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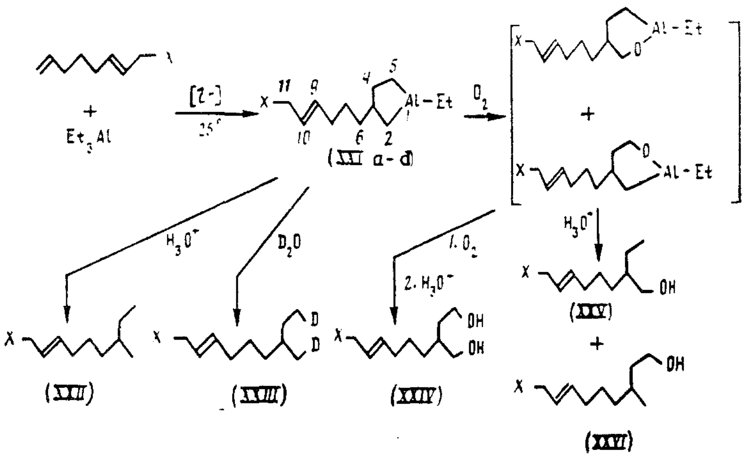
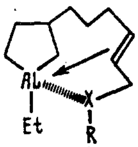
*In THF.



X = NEt_2 (a), OCH_3 (b), OH (c), SBu (d).

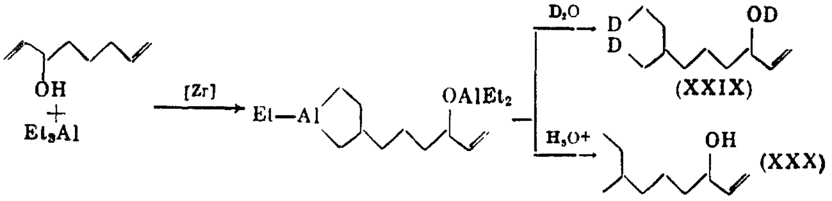
Analysis of the ^{13}C NMR spectra of alumocyclopentanes (XXI) showed that the functional substituents in the starting olefins form a donor–acceptor bond with the aluminum atom due to the unshared electron pair on the oxygen, nitrogen, and sulfur atoms to give complexes (XXVII).



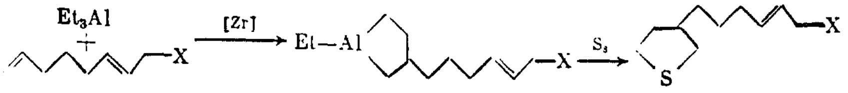
(XXVII)

It is not excluded that the allylic double bond also participates in the formation of the coordination sphere of the aluminum atom. The downfield displacement of the signal for C^{10} in (XXIa) at 6.5 ppm in comparison with the signal of the analogous atom (C^2) in (XXIIIa) and of the upfield displacement of the signal of C^9 by 7 ppm in relation to C^3 in (XXIIIa) indicates π-p interaction of the aluminum atom with the π-electrons of the double bond. The downfield displacement of the signal for C^{11} in (XXIa) by 0.6 ppm relative to C^1 in (XXIIIa) and of the signal for C^{12} at the nitrogen atom in (XXIa) by 1.2 ppm relative to C^{11} in (XXIIIa) indicates the formation of a donor–acceptor bond between the aluminum and nitrogen atoms.

The cyclometallation of functionally substituted 2,7-octadienes using Et_3Al in the presence of Cp_2ZrCl_2 proceeds exclusively at the terminal double bond. Attempts to carry out this reaction using compounds with an internal disubstituted double bond in the allylic position to the nitrogen, oxygen, or sulfur atom were unsuccessful. In the case of the cyclometallation of 1,7-octadien-3-ol, the reaction proceeds at the double bond farthest from the hydroxyl group.



We have established that the alkyl-substituted nitrogen-, oxygen-, and sulfur-containing alumocyclopentanes (XXI) rather readily undergo a reaction with S_8, leading to β-substituted N-, O-, and S-containing tetrahydrothiophenes, which is nontrivial for organoaluminum compounds [7]. The reaction proceeds upon heating the corresponding alumocyclopentanes (XXIa)-(XXIc) with S_8 in benzene at 60-80°C over 6-8 h with a 3:1 S_8:Et_3Al ratio. The yields of the thiacyclanes range from 31 to 68%.



(XXIa — c) (XXXIa —c)

X=OCH$_3$ (a), OH (b), SBu (c).

EXPERIMENTAL

The N-, O-, and S-containing octadienes were synthesized by reported procedures [8-11]. The reactions were carried out in a dry argon atmosphere. The gas-liquid chromatographic analysis was carried out on a Chrom-41 chromatograph using helium as a carrier gas on a 1.2 m × 3 mm column packed with 5% SE-30 or 15% PEG-6000 on Chromaton N-AW. The IR spectra were taken neat on a UR-20 spectrometer. The mass spectra were taken on an MKh-1306 spectrometer at 70 eV and 130°C. The PMR spectra were taken in CCl_4 on a Tesla BS-567 spectrometer at 100 MHz and a Tesla BS-467 spectrometer at 60 MHz with TMS as the internal standard. The ^{13}C NMR spectra were taken on a Jeol FX90Q spectrometer at 22.5 MHz with broad-band and off-resonance proton suppression with external field stabilization. The yield of the alumocyclopentanes was determined by gas-liquid chromatography of the hydrolysis or deuterolysis products.

Synthesis of β-Substituted Alumocyclopentanes. a. A mixture of 0.0524 g (0.2 mmole) Cp_2ZrCl_2 and 1.368 g (12 mmoles) Et_3Al was prepared in a 50-ml glass reactor equipped with a magnetic stirrer in an inert gas atmosphere and, then, 1.18 g (10 mmoles) allylbenzene was added. The reaction mixture was stirred for 10 h at 23-25°C. Hydrolysis of the organoaluminum compounds gave 1.20 g (82%) 2-benzylbutane.

b. A mixture of 0.0876 g (0.3 mmole) Cp_2ZrCl_2 and 3.534 g (31 mmoles) Et_3Al in 3 ml hexane was added to a reactor under the conditions of procedure (a) and cooled to 0°C. A sample of 1.26 g (10 mmoles) 2,7-octadien-1-ol in 2 ml hexane was added dropwise, warmed to -20°C, and stirred for 6 h. Deuterolysis of the organoaluminum compound (OAC) obtained gave 1.46 g (92%) 2-(4-hexen-6-ol)-1,4-dideuterobutane.

c. A mixture of 0.0524 g (0.2 mmole) Cp_2ZrCl_2 and 2.51 g (22 mmoles) Et_3Al in 3 ml hexane was introduced into a reaction under conditions of procedure (a) and, then, 1.81 g (10 mmoles) diethyl-2,7-octadienylamine in 2 ml hexane was added dropwise. The reaction mixture was stirred for 16 h. A sample of 20 ml hexane was added and cooled to 0°C. The organoaluminum compound obtained was oxidized by dry air with vigorous stirring for 30 min at 0°C and for 1 h at 20-30°C. Finally, the oxidation was carried out by introducing oxygen for 3 h at 30-40°C. The reaction mixture was treated with 5% aq. NaOH and extracted with ether to give 1.29 g (53%) 2-(6-diethylamino-4-hexenyl)-1,4-butanediol.

d. A solution of 0.131 g (0.5 mmole) Cp_2ZrCl_2 and 2.51 g (22 mmoles) Et_3Al in 3 ml benzene was added to a reactor under the conditions of procedure (a) and a sample of 1.98 g (10 mmoles) butyl 2,7-octadienyl sulfide in 2 ml benzene was added dropwise. The reaction mixture was stirred for 7 h and 25 ml benzene was added. Then, 2.11 g (66 mg-atom, 8.25 mmoles) sulfur powder was added in small amounts and heated for 6 h at 80°C. The reaction mixture was cooled to -20°C and treated with water and 2 N hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether to give 1.74 g (68%) 3-(7-thio-4-undecenyl)tetrahydrothiophene. The purity of the products isolated by distillation or column chromatography on silica gel L40/100 manufactured in Czechoslovakia was ≥95%. The ^{13}C NMR spectra of the products are given in Table 2.

~1:1 3-Methyl-1-heptanol (VI):2-ethyl-1-hexanol (VIII), bp 72-75°C (8 mm), n_D^{20} 1.4319. IR spectrum (ν, cm^{-1}): 3360, 2950, 2880, 1470, 1070. PMR spectrum (δ, ppm): 0.85 m (6H, CH_3), 1.03-1.83 m (9H, CH, CH_2), 3.27-3.67 m (2H, OCH_2), 3.92 br.s (1H, OH), m/z 112 $(M - H_2O)^+$.

2-Benzyl-1,4-dideuterobutane (XIII), bp 78-79°C (5 mm), n_D^{22} 1.4629. IR spectrum (ν, cm^{-1}): 3060, 3030, 2920, 2850, 2170, 1600, 1490, 1440, 1270, 730, 690. PMR spectrum (δ, ppm): 0.80 m (4H, CH_2D), 1.03-1.60 m (3H, CH, CH_2), 2.42 m (2H, CH_2), 7.03 s (5H, Ph), M^+ 150.

2-Benzyl-1,4-butanediol (XIV), bp 139-140°C (1 mm), n_D^{25} 1.5327. IR spectrum (ν, cm^{-1}): 3360, 3035, 1605, 1500, 1460, 750, 720. PMR spectrum (δ, ppm): 1.23-2.00 m (3H, CH, CH_2), 2.31-2.42 m (2H, CH_2Ph), 3.22-3.60 (4H, CH_2O), 4.52 s (2H, OH), 7.05 s (5H, Ph).

4-(2-Butyl)-1-cyclohexene (XV), bp 57-58°C (5 mm), n_D^{17} 1.4609. IR spectrum (ν, cm^{-1}): 3010, 2840, 1640, 1450, 750. PMR spectrum (δ, ppm): 0.83 m (6H, CH_3), 1.00-1.50 m (6H, CH, CH_2), 1.60-2.17 m (4H, CH_2), 5.38-5.60 m (2H, CH=CH). M^+ 138.

1-Methoxy-7-methyl-2-nonene (XXIIb), bp 50-51°C (1 mm), n_D^{26} 1.4321. IR spectrum (ν, cm^{-1}): 3030, 2920, 1650, 1460, 1380, 1200, 1120, 975. PMR spectrum (δ, ppm): 0.85 m (6H, CH_3), 1.02-1.58 m (7H, CH, CH_2), 1.77-2.28 m (2H, CH_2), 3.13 s (3H, CH_3), 3.70 d (2H, OCH_2), 5.30-5.60 m (2H, CH=CH). M$^+$ 170.

7-Ethyl-2-octen-1-ol (XXIIc), bp 80-81°C (1 mm), n_D^{23} 1.4517. IR spectrum (ν, cm^{-1}): 3340, 3030, 1670, 1460, 1380, 975. PMR spectrum (δ, ppm): 0.83 m (6H, CH_3), 1.00-1.50 m (7H, CH, CH_2), 1.73-2.17 m (2H, CH_2), 2.55 s (1H, OH), 3.88 d (2H, CH_2O, J = 4 Hz), 5.33-5.63 m (2H, CH=CH), m/z 138 $[M - H_2O]^+$.

2-(6-N,N-Diethylamino-4-hexenyl)-1,4-dideuterobutane (XXIIIa), R_f 0.49 (4:1 benzene–methanol), n_D^{22} 1.4471. IR spectrum (ν, cm^{-1}): 3030, 2980, 2940, 2870, 2810, 1650, 1465, 980. PMR spectrum (δ, ppm): 0.90 t (6H, CH_3, J = 7 Hz), 0.65-0.92 m (4H, CH_2D), 1.05-1.52 m (7H, CH, CH_2), 1.70-2.12 m (2H, CH_2), 2.37 q (4H, N-CH_2), 2.88 d (2H, CH_2N, J = 5 Hz), 5.25-5.53 m (2H, CH=CH). Mass spectrum (m/z): 213 $[M]^+$, 198 $[M - CH_3]^+$, 183 $[M - C_2H_4D]^+$, 154 $[M - C_4H_5D_2]^+$, 126 $[M - C_6H_9D_2]^+$.

2-(6-Methoxy-4-hexenyl)-1,4-dideuterobutane (XXIIIb), R_f 0.64 (5:1 hexane–ether), n_D^{23} 1.4378. IR spectrum (ν, cm^{-1}): 3030, 2190, 1670, 1130, 985, 930. PMR spectrum (δ, ppm): 0.78 m (4H, CH_2D), 1.03-1.42 m (7H, CH, CH_2), 1.72-2.17 m (2H, CH_2), 3.10 m (3H, CH_3), 3.70 d (2H, CH_2O, J = 4 Hz), 5.25-5.77 m (2H, CH=CH). M$^+$ 172.

2-(6-Deuteroxy-4-hexenyl)-1,4-dideuterobutane (XXIIIc), bp 82-84°C (2 mm), n_D^{23} 1.4499. IR spectrum (ν, cm^{-1}): 3350, 2940, 2870, 1100, 1030, 980. PMR spectrum (δ, ppm): 0.80 m (4H, CH_2D), 1.00-1.50 m (7H, CH, CH_2), 1.72-2.12 m (2H, CH_2), 3.87 m (2H, CH_2O), 5.53 m (2H, CH=CH), m/z 140 $[M - DHO]^+$.

2-(6-N,N-Diethylamino-4-hexenyl)-1,4-butanediol (XXIVa), R_f 0.19 (methanol), n_D^{26} 1.4830. IR spectrum (ν, cm^{-1}): 3360, 2940, 1670, 1470, 1380, 1070, 980. PMR spectrum (δ, ppm): 0.95 t (6H, CH_3, J = 7 Hz), 1.12-1.67 m (7H, CH, CH_2), 1.75-2.13 m (2H, CH_2), 2.42 q (4H, CH_2N, J = 7 Hz), 2.88 d (2H, CH_2N, J = 4 Hz), 3.20-3.67 m (4H, OCH_2), 4.75 s (3H, OH), 5.17-5.55 m (2H, CH=CH).

~1:1 N,N-Diethyl-N-(7-ethyl-8-hydroxy-2-octenyl)amine (XXVa):N,N-diethyl-N-(7-methyl-9-hydroxy-2-nonenyl)amine (XXVIa), R_f 0.32 (methanol), n_D^{22} 1.4716. IR spectrum (ν, cm^{-1}): 2930, 1440, 1370, 1050, 970. PMR spectrum (δ, ppm): 0.98 m (9H, CH_3), 1.17-1.67 m (7H, CH, CH_2), 1.75-2.17 m (2H, CH_2), 2.45 q (4H, NCH_2, J = 7 Hz), 2.93 d (2H, CH_2N, J = 4 Hz), 3.25-3.72 m (2H, OCH_2), 5.27-5.58 m (2H, CH=CH).

~1:1 1-Methoxy-7-ethyl-2-octen-8-ol (XXVb):1-methoxy-7-methyl-2-nonen-9-ol (XXVIb), R_f 0.54 (4:1 benzene–methanol), n_D^{23} 1.4634. IR spectrum (ν, cm^{-1}): 3390, 2390, 2860, 1650, 1450, 1370, 970. PMR spectrum (δ, ppm): 0.86 (3H, CH_3), 1.03-1.75 m (7H, CH, CH_2), 1.83-2.25 m (2H, CH_2), 2.88 s (1H, OH), 3.20 s (3H, CH_3), 3.25-3.67 m (2H, CH_2O), 3.72 d (2H, CH_2O, J = 4 Hz), 5.33-5.67 m (2H, CH=CH).

2-(4-Deuteroxy-5-hexenyl)-1,4-dideuterobutane (XXIX), bp 62-63°C (1 mm), n_D^{23} 1.4451. IR spectrum (ν, cm^{-1}): 3350, 3085, 2940, 2870, 1650, 915, 935. PMR spectrum (δ, ppm): 0.82 m (4H, CH_2D), 1.00-1.67 m (9H, CH, CH_2), 3.70-4.12 m (1H, CHO), 4.72-6.10 m (3H, CH=CH_2), m/z 140 $[M - DHO]^+$.

3-Hydroxy-7-methyl-1-nonene (XXX), bp 63-66°C (1 mm), n_D^{23} 1.4437. IR spectrum (ν, cm^{-1}): 3350, 2980, 2940, 2870, 1640, 1460, 990, 920. PMR spectrum (δ, ppm): 0.86 m (6H, CH_3), 1.02-1.67 m (9H, CH, CH_2), 2.83 s (1H, OH), 3.72-4.15 m (1H, OCH), 4.78-6.00 m (3H, CH=CH_2), m/z 138 $[M - H_2O]^+$.

3-(6-Methoxy-4-hexenyl)tetrahydrothiophene (XXXIa), R_f 0.39 (4:1 hexane–ether), n_D^{27} 1.5249. IR spectrum (ν, cm^{-1}): 3030, 2940, 2860, 1635, 1450, 1390, 1265, 1130, 985. PMR spectrum (δ, ppm): 1.17-1.58 m (4H, CH_2), 1.83-2.32 m (5H, CH, CH_2), 2.58-3.00 m (4H, CH_2S), 4.83 s (3H, CH_3O), 3.72 d (2H, CH_2O, J = 4.5 Hz), 5.33-5.60 m (2H, CH=CH). M$^+$ 200.

3-(6-Hydroxy-4-hexenyl)tetrahydrothiophene (XXXIb), R_f 0.50 (1:4 hexane-ether), n_D^{30} 1.5238. IR spectrum (ν, cm^{-1}): 3400, 2940, 2860, 1670, 1450, 1380, 1260, 1220, 1105, 975. PMR spectrum (δ, ppm): 1.20-1.50 m (4H, CH_2), 1.83-2.38 m (5H, CH, CH_2), 2.58-3.08 m (4H, CH_2S), 2.70 s (1H, OH), 3.83-4.00 m (2H, CH_2O), 5.40-5.62 m (2H, CH=CH). M$^+$ 1.86.

3-(7-Thio-4-undecenyl)tetrahydrothiophene (XXXIc), R_f 0.71 (9:1 hexane–ether), n_D^{25} 1.5248. IR spectrum (ν, cm^{-1}): 3025, 2935, 2860, 1650, 1430, 1380, 1260, 1215, 970. PMR spectrum (δ, ppm): 0.91 t (3H, CH_3), 1.25-1.70 m (8H, CH_2), 2.04-2.22 m (5H, CH, CH_2), 2.45 t (2H, CH_2S), 2.78-2.93 m (4H, CH_2S), 3.09 d (2H, CH_2S), 5.40-5.52 m (2H, CH=CH).

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