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ORGANOBORON COMPOUNDS. ALLYLBORATION OF CARBONYL COMPOUNDS WITH ALLYL(ALKYL)BORANES

B.M. MIKHAILOV *, Yu.N. BUBNOV, A.V. TSYBAN' and M.Sh. GRIGORYAN

N.D. Zelinsky Institute of Organic Chemistry, Academy of Sciences USSR, Moscow, B-334 (U.S.S.R.)

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Summary

A convenient procedure for the synthesis of homoallylic alcohols from carbonyl compounds and allylboranes is described. Allyl-, 2-methylallyl-, crotyl- and 3,3-dimethylallyl(dialkyl)boranes, as well as diallyl(alkyl)boranes and derivatives of 3-allyl- and 3-metallyl-3-borabicyclo[3.3.1]non-6-ene are effective reagents for allylation of carbonyl compounds (aldehydes, ketones, esters, carboxylic acids and others) offering, in a number of cases, considerable advantages over use of corresponding allylmagnesium halides. Allylboration of carbonyl compounds is attended by the allylic rearrangement; while reacting crotyl- and 3,3-dimethyl-allylboranes are changed to homoallylic alcohols with terminal double bonds.

Introduction

Having worked out preparative methods of synthesis of mixed allyl(dialkyl)-boranes and diallyl(alkyl)boranes [1—3], we proceeded to the systematic study both of the chemical properties of this interesting type compounds and the possiblity of an application in organic synthesis [4]. The permanent intramolecular allylic rearrangement and the rupture of the boron—allyl bonds under the action of water and alcohols have been discussed [3].

We now report allylboration of aldehydes, ketones and esters by means of allyl(dialkyl)boranes, diallyl(alkyl)boranes, 3-allyl-3-borabicyclo[3.3.1]non-6-ene and some derivatives of the latter as well as (partly) triallylborane.

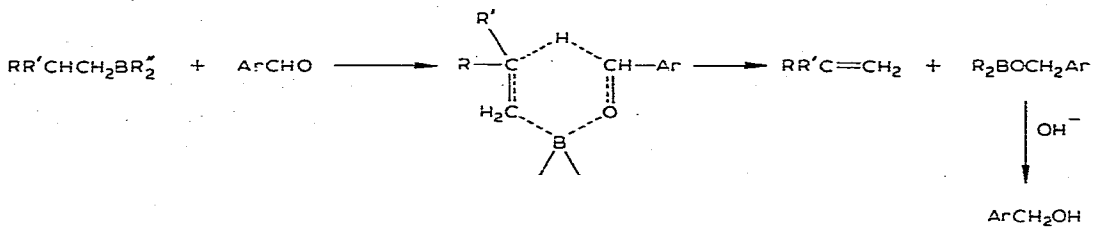
Results and discussion

The reactions of organoboron derivatives with aldehydes and ketones is affected by the nature of radicals attached to boron, structure of carbonyl compounds and process conditions [4].

Alkylboranes do not add to the double bond >C=O, the only exeption known being the reaction of trialkylboranes with monomeric formaldehyde, which in the presence of oxygen leads to higher esters of dialkylboronic acid R_2BOCH_2R. These esters hydrolyse to yield alcohols, RCH_2OH (an increase of the carbon chain by one carbon atom) [5].

Aromatic aldehydes are quantitatively reduced when heated above 100°C with trialkylboranes to give the corresponding alcohols [6—8] (Scheme 1).

SCHEME 1



The reaction proceeds with elimination of the olefin and was used for synthesis of pure α-olefins [6,7] and for contr-thermodynamic isomerization of methylcyclenes into methylencyclanes [6].

Aliphatic aldehydes and ketones react with triphenyl- and tribenzyl-borane on heating to form mainly enolic esters of the type RCH=CR'—OBR"$_2$ [9]. The latter compounds are easily obtained from trialkylboranes and carbonyl compounds in the presence of catalytic amounts of pivalic acid [10]. Most of cycloalkanones and aliphatic ketones are changed into dimeric or trimeric products of crotonic condensation on reacting with triethylborane and pivalic acid [11].

Both triallylborane [4,12,13] and other allylboranes [4,13—15] react with aldehydes and ketones, including steroids, in a similar manner to organomagnesium compounds, i.e. via an addition of boron—allyl fragment to the double bond C=O. Such peculiarity of allyl type boranes is conditioned, firstly, by the lowered bond energy of these compounds as compared with trialkylboranes and, secondly, by their ability to react via six-center mechanism and allylic rearrangement [4,13—15].

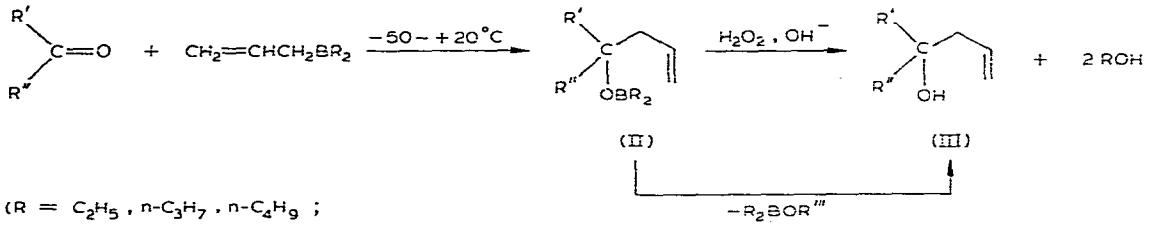
Depending on the ratio of reagents, triallylborane reacts with aldehydes to give 1-substituted butenylic esters of diallylboronic (1/1), allylboronic (1/2), or boronic (1/3) acids [12]. Reaction with ketones leads to esters of diallyl- (1/1) or allyl-boronic (1/2) acids. The third allyl fragment does not add to ketones which seems to be due to shielding of the boron atom. Alkaline hydrolysis of butenylic esters, just like re-esterification, affords 1-substituted butenylic alcohols [12].

We have studied the reactions of unsymmetrical allyl(dialkyl)boranes (I), diallyl(alkyl)boranes, and 3-allyl-3-borabicyclo[3.3.1]non-6-enes with various aldehydes, ketones, and esters. All these reactions were shown to occur via an organometallic synthesis (Scheme 2) to give primarily substituted butenylic esters, from which one can easily obtain the corresponding homoallylic alcohols. In a preliminary report [1] we described allylboration of propionaldehyde and acetone with allyl(diethyl)borane.

Allyl(dialkyl)boranes (I) react with aldehydes and ketones at —50 — +20°C

with large heat evolution to afford substituted esters of dialkylboronic acids (II).

SCHEME 2



(R = C_2H_5 , n-C_3H_7 , n-C_4H_9 ;

R', R'' = H , alkyl , aryl ;

R'''OH = n-hexanol , nonanol , ethanolamine , di- or tri-ethanolamine)

Allylboration of aldehydes and ketones, after this manner, can be effected both without solvent or in any inert solvent, e.g., isopentane, petroleum ether, hexane, benzene, ether, tetrahydrofuran, chloroform, carbon tetrachloride etc.

The reactions occur within several minutes and are not complicated by side-reactions. As mentioned above, trialkylboranes and dialkylborinates of type II do not react with carbonyl compounds either at 20°C or lower temperatures [4]. Butenylic esters of dialkylboronic acids (II) are isolated by distillation in 83—85% yield.

When heated with higher alcohols, esters II undergo re-esterification to afford 1-substituted homoallylic alcohols III, which are easily distilled from reaction mixtures under reduced pressure. Any alcohols with boiling points higher than that of the homoallylic alcohol III formed may be used (e.g. hexanol, nonanol, decanol, glycol, ethanolamine, diethanolamine, triethanolamine etc.) In this work triethanolamine (TEA) was usually used. To obtain homoallylic alcohols with higher molecular weight (over 200) from higher aldehydes and ketones, it is advisable to oxidize esters II with alkaline hydrogen peroxide, in the presence of sodium acetate or carbonate.

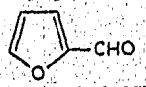
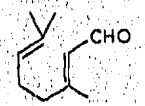
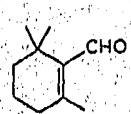
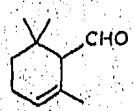
When using allylboration of aldehydes and ketones for synthesis of homoallylic alcohols there is no need to isolate esters II as individual compounds. Instead the reaction product (rough esters II) are oxidized (H_2O_2, OH^-) or treated with a higher alcohol (~1.1 mol) and subsequently the carbinol III is distilled from the mixture under reduced pressure.

Carbinols obtained by allylboration of some aldehydes (acetaldehyde, propionaldehyde, benzaldehyde, furfural, crotonaldehyde, cytral, α- and β-cyclocytral) and ketones (acetone, acetophenone, benzophenone, hexafluoroacetone, acrolein, β-chlorovinyl(methyl)ketone, mesityl oxide, benzalacetone, α- and β-ionone) with allyl(diethyl)-, allyl(di-n-propyl)- or allyl(di-n-butyl)-borane are listed in Tables 1 and 2, respectively. It will be noted that α,β-unsaturated aldehydes and ketones react with allylboranes via 1,2-addition only.

Allylborating reagents also used were 3-allyl-3-borabicyclo[3.3.1]non-6-ene (IV, R = H) and its 7-alkyl derivatives (IV, R = alkyl), obtained from triallylborane and acetylene or 1-alkynes [13] (Scheme 3). Homoallylic alcohols synthesized from 3-allyl-7-n-propyl-3-borabicyclo[3.3.1]non-6-ene and corresponding carbonyl compounds are listed in Table 3.

TABLE 1

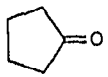
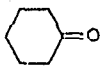
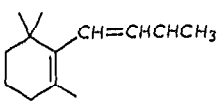
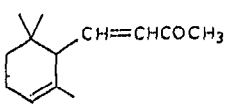
$$CH_2{=}CHCH_2BR_2 + R'CHO \xrightarrow[(2)\ \text{hydrolysis}]{(1)\ 0\text{–}10^{\circ}C} CH_2{=}CHCH_2\underset{\displaystyle R'}{\underset{|}{C}}HOH$$

R'CHO	R	Borate hydrolysis method [a]	Yield of carbinol (%)	B.p. (°C) (mmHg)	n_D^{20}	Lit. data		
						B.p.	n_D^{20}	Ref.
CH_3CHO	C_2H_5	TEA	88.3	114–116 (753)	1.4248	114.5–116 (760)	1.4245	17
C_2H_5CHO	C_4H_9	TEA	91.5	44–46 (22)	1.4319	33–35 (7)	1.4307	12
C_6H_5CHO	C_4H_9	TEA	94.7	114–116 (10)	1.5324	116–119 (13)	1.5322	18
	C_2H_5	TEA	92.4	62–63 (3)	1.4916	96–97 (31)	1.4919	19
$CH_3CH{=}CHCHO$	C_2H_5	TEA	89.2	59–61 (13)	1.4538	61–62.5 (15)	1.4540	20
$CH_3CH{=}CHCHO$	C_2H_5	H_2O_2, OH^-	81.2	100–102 (0.1)	1.5661	85–87 (0.025)	1.5650	20
	C_2H_5	H_2O_2, OH^-	72.8	106–108 (1)	1.4805	102–103 (0.4)	1.4800	20
	C_2H_5	H_2O_2, OH^-	79.6	108–110 (5)	1.4956	103–104 (0.4)	1.4950	20
	C_2H_5	H_2O_2, OH^-	84.3	60–62 (2)	1.4872	61–62 (2)	1.4880	20

[a] Re-esterification of an intermediate borate with triethanolamine (TEA) or oxidation with alkaline hydrogen peroxide (H_2O_2, OH^-) were used.

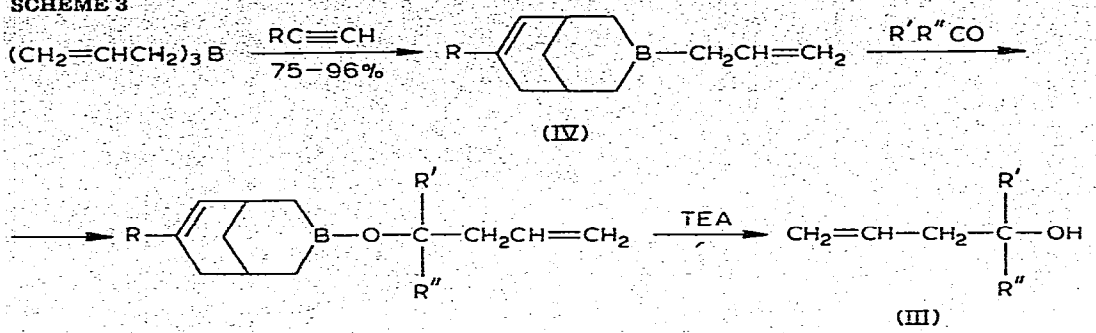
TABLE 2

$$CH_2{=}CHCH_2BR_2 + R'COR'' \xrightarrow[(2)\ \text{hydrolysis}]{(1)\ 0{-}10^\circ C} CH_2{=}CHCH_2\overset{\overset{R'}{|}}{\underset{\underset{R''}{|}}{C}}OH$$

R'COR''	Borate hydrolysis method [a]	Compound obtained			Lit. data		
		Yield (%)	B.p. (°C) (mmHg)	n_D^{20}	B.p. (°C) (mmHg)	n_D^{20}	Ref.
CH_3COCH_3	TEA	90.5	36–38(45)	1.4260	26(8)	1.4260	12
$C_6H_5COC_6H_5$	H_2O_2, OH^-	79.3	126–128(2)	1.5826	150–155(3)		21
	TEA	72.2	36–37(2)	1.4676	63(10)	1.4683	22
	TEA	75	34–36(2)	1.4768	95–97 (27.5)	1.4756	23
CF_3COCF_3	TEA	78	100–101(749)	1.3407	95–98	1.3400	24, 25
$CH_2{=}CHCOCH_3$	TEA	77.2	56–57(40)	1.4475	50–51(30)	1.4480	26
$ClCH{=}CHCOCH_3$	H_2O_2, OH^-	73.1	65–66(8)	1.4788	66–67(10)	1.4785	26
$(CH_3)_2C{=}CHCOCH_3$	H_2O_2, OH^-	92.2	64–66(15)	1.4612	53–54(10)	1.4600	26
$C_6H_5CH{=}CHCOCH_3$	H_2O_2, OH^-	92.4	121–123(2)	1.5521	89–90	1.5530	26
	TEA	97.4			(0.08)		
	H_2O_2, OH^-	90.3	96–98(1)	1.5018	85–87 (0.1)	1.5020	26
	H_2O_2, OH^-	86.6	114–115(3)	1.4956	110–112 (2.5)	1.4950	26

[a] See foot-note to Table 1.

SCHEME 3



(R = H, n-C_3H_7; TEA = triethanolamine)

SCHEME 4

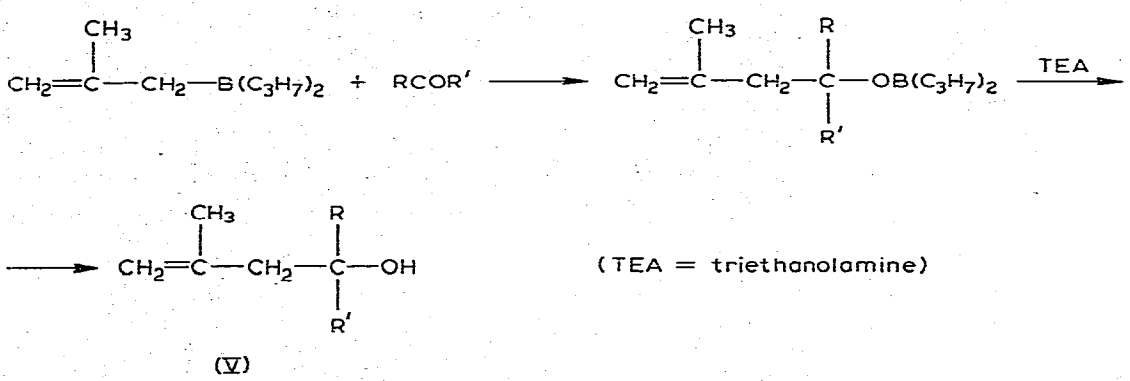
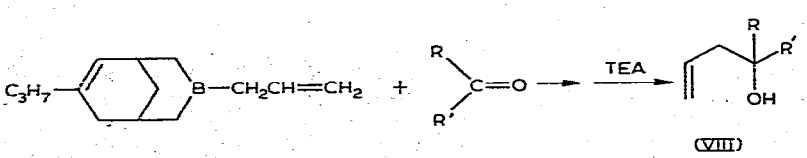
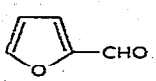
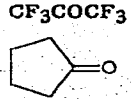
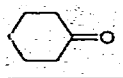


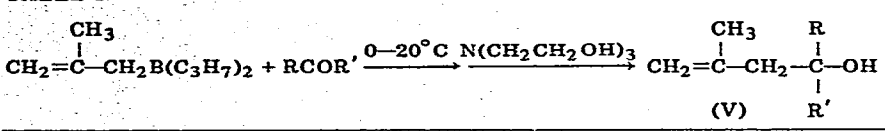
TABLE 3

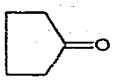


Carbonyl compound	Carbinol, yield (%) [a]
C_2H_5CHO	89.7
	71.1
CH_3COCH_3	92.3
CF_3COCF_3	82.6
	77.3
	88.1

[a] The constants of carbinols are in close agreement with those quoted in Tables 1 and 2.

TABLE 4



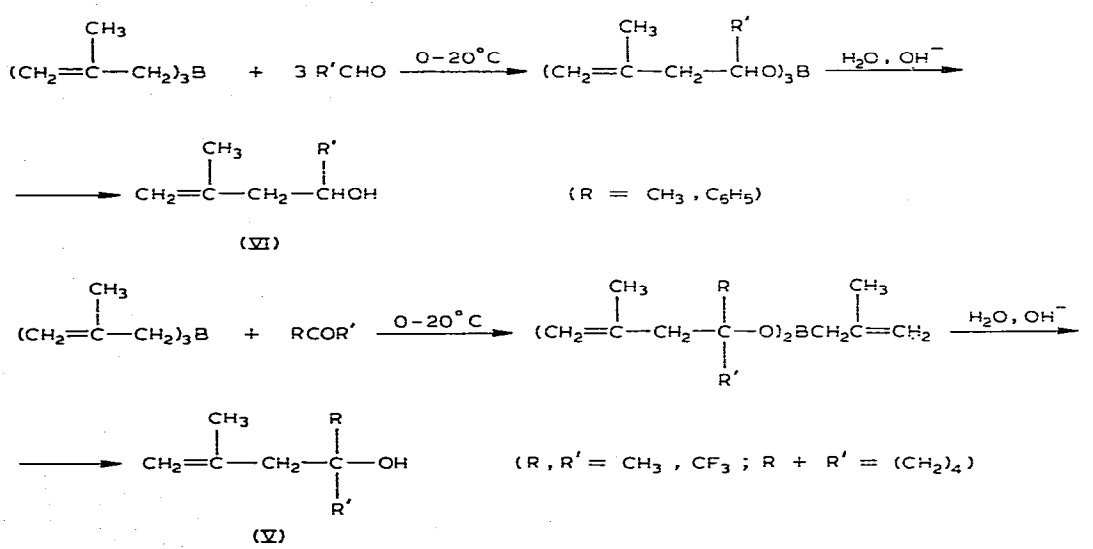
RCOR′	Compound V				Lit. data for V		
	Yield	B.p. (°C) (mm Hg)		n_D^{20}	B.p. (°C) (mm Hg)	n_D^{20}	Ref.
CH_3CHO	91.7	85–86	(157)	1.4337	129		27
CH_3CHO [a]	92.8	—		—			
CH_3COCH_3	94.4	73–73.5	(80)	1.4351	126		27
CH_3COCH_3 [a]	90.3	24–25	(9)	1.4359			
C_6H_5CHO	89.2	76–77	(2)	1.5273			
C_6H_5CHO [a]	78	78–79	(2)	1.5272 [b]			
	82.3	87–88	(30)	1.4716	98.5 (40)	1.4720	22
CF_3COCF_3	89.1	63–65	(120)	1.3499	113–115	1.3485	24

[a] Tri(2-methylallyl)borane was used as allylborating reagent. [b] d_4^{20} 0.9907.

2-Methylallyl(dialkyl)boranes react with aldehydes and ketones in a similar manner to their allyl analogs. 1-Substituted 3-methyl-1-butenols (V) synthesized from 2-methylallyl(di-n-propyl)borane and acetaldehyde, benzaldehyde, acetone, hexafluoroacetone or cyclohexanone are outlined in Table 4 (Scheme 4).

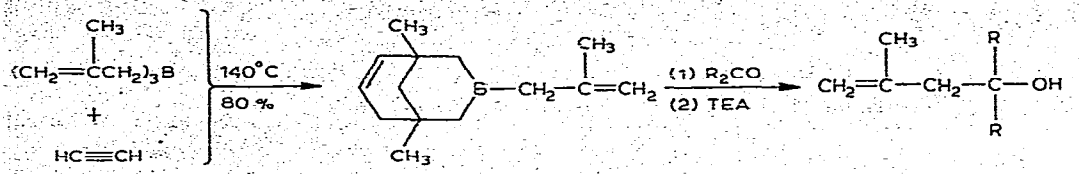
The same carbinols are obtained from trimetallylborane: aldehydes (1/3) or ketones (1/2) with consequent hydrolysis of the boron esters formed in alkaline solution (Scheme 5) (in Table 4, these carbinols are marked with asterisks).

SCHEME 5



methyl-3-borabicyclo[3.3.1]non-6-ene/acetone or hexafluoroacetone (1/1).

SCHEME 6



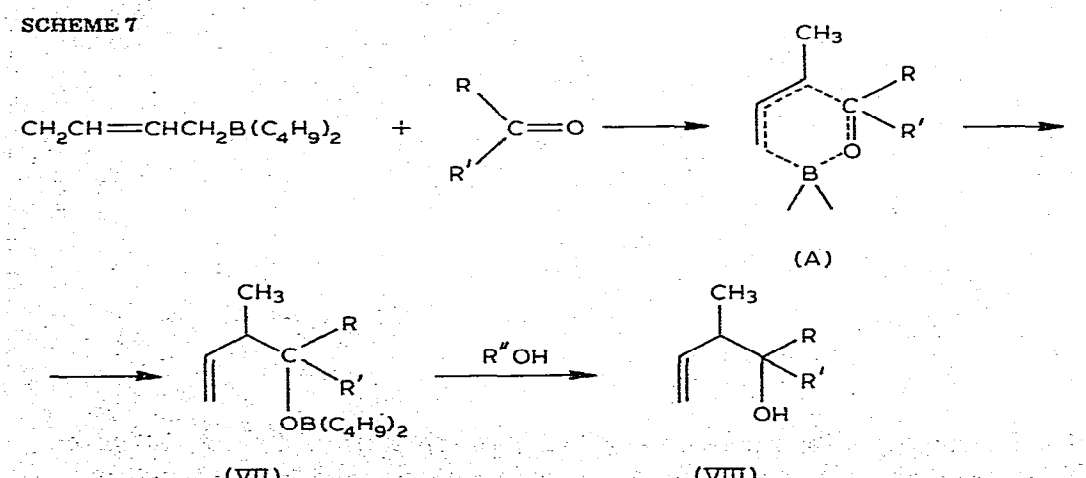
R = CH_3 (91%) ; R = CF_3 (86%)

The structures of alcohols III, V and VI are borne out by PMR spectroscopy data. For example, the spectrum of α-allylfurfuryl alcohol (III, R′ = H, R″ = α-C_4H_3O) shows the following signals (50% solution in CCl_4): 2.54 (t, J = 6.8 Hz, CH_2, 2H), 4.13 (s, OH, 1H), 4.63 (t, J 6.8 Hz, CHO, 1H), 4.82—5.22 (m, CH_2=C, 2H), 5.42—6.00 (m, C=CH, 1H), 6.18 and 7.28 ppm (2m, C_4H_3O, 2H and 1H). The PMR spectrum of some 2-methylbutenyl alcohols of type VI depend on the recording conditions which shows non-equivalence of the C=C—CH_2 group protons. In order to resolve, for example, the structure of carbinol (VI, R = CH_3) spectra of the latter were recorded under different conditions: pure compound, CCl_4 solution, in the presence of CF_3COOH, and by using double resonance procedure. PMR spectra both of neat sample and solution in CCl_4 exhibit a complex signal of CH_2-group protons in the region 2.1 ppm (a doublet of doublets or a multiplet). PMR spectrum of solution in CCl_4 (50%) in the presence of one drop of CF_3COOH shows following signals: 1.16 (d, J 6 Hz, CH_3, 3H), 1.73 (s, CH_3—C, 3H), 2.13 (d, J 6 Hz, CH_2, 2H), 3.92 (sextet, J 6 Hz, CHO, 1H), 4.72 (m, CH_2=C, 2H), 5.60 ppm (s, OH, 1H).

Addition of the boron—allyl fragment to carbonyl group proceeds with the allylic rearrangement [4,13,15].

We showed the reactions of crotyl(di-n-butyl)borane with acetaldehyde, acetone, hexafluoroacetone, mesityl oxide, and benzalacetone to afford only butenylic esters of type VII with the terminal double bond, i.e. again allylboration occurs with allylic rearrangement, apparently via a transition state with cyclic electron transfer (A) (Scheme 7).

SCHEME 7



(VII) (VIII)

TABLE 5

$$CH_3CH{=}CHCH_2B(C_4H_9)_2 + RCOR' \xrightarrow{0-5^\circ C} \xrightarrow{R''OH} CH_2{=}CH{-}\underset{H_3C}{\overset{|}{C}}H{-}\underset{R}{\overset{|}{C}}{-}\underset{R'}{\overset{|}{C}}{-}OH$$

(X)

RCOR'	R''OH	Compound X				Lit. data for X			
		Yield	B.p. (°C) (mm Hg)		n_D^{20}	B.p. (°C) (mm Hg)		n_D^{20}	Ref.
CH_3CHO	TEA	92.1	127–128.5		1.4319	127		1.4315	28
CH_3COCH_3	TEA	85	40–42	(14)	1.4362	62–63	(200)	1.4368	28
$(CH_3)_2C{=}CHCOCH_3$	TEA	81.4 [a]	65–66	(9)	1.4617	66–67	(10)	1.4620	29
$C_6H_5CH{=}CHCOCH_3$	H_2O_2, OH^-	76.6 [b]	99–100	(2)	1.5416	103.5–105.5	(3)	1.5409	29
CF_3COCF_3	$C_9H_{19}OH$	88.3 [c]	114–115	(750)	1.3552	113		—	24

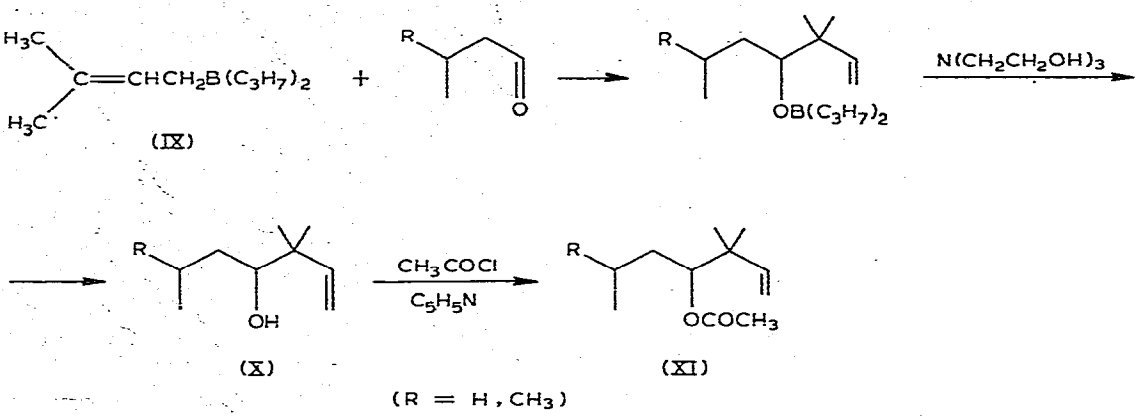
[a] The carbinol was first prepared by N.A. Nikolaeva [29] using: (a) tricrotylborane with subsequent hydrolysis of reaction mixture. [b] Idem using crotylboracyclopentane with subsequent re-esterification with diethanolamine. [c] The carbinol was synthesized from tricrotylborane and hexafluoroacetone, also in 87% yield.

Intermediate esters (VII) were not isolated, these were converted by means of re-esterification or oxidation into substituted 2-methyl-3-buten-1-ols (VIII) the constants of which are listed in Table 5. As was shown by GLC, carbinols VIII do not contain an admixture of crotyl isomers.

IR spectra of the carbinols VIII reveal absorption bands due to the terminal double bond (1640—1650, 1820, 3080 cm^{-1}) and hydroxyl group (3450 cm^{-1}). Structure of carbinols (VIII) is substantiated by PMR spectroscopy as well. Thus, the spectrum of 1,1,2-trimethyl-3-buten-1-ol (VIII, R = R′ = CH_3) shows the signals (neat): 0.82—1.25 (m, CH_3), 2.15 (q, CH, J 7 Hz), 3.55 (s, OH), 4.75—5.15 (m, CH_2=C), 5.45—6.15 ppm (m, =CH—). PMR spectrum of 1,1-di(trifluoromethyl)-2-methyl-3-buten-1-ol exhibits the signals: 1.26 (d, J 8.7 Hz, J 1.5 Hz, CH_3), 2.82 (q, CH), 3.62 (s, OH), and multiplets of CH_2=CH (4.96—5.41 and 5.45—6.23 ppm).

Reactions of 3,3-dimethylallyl(di-n-propyl)borane (IX) with butyric or isovaleric aldehydes, followed by treatment with triethanolamine led to 3,3-dimethyl-1-hepten-4-ols (X) (Scheme 8).

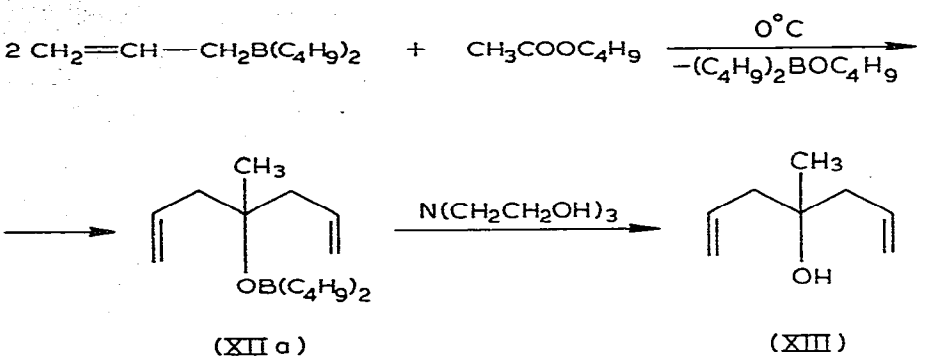
SCHEME 8



IR spectra of the carbinols X show intense absorption bands characteristic of the terminal double bond (1640, 3085 cm^{-1}). PMR spectra of these compounds exhibit a singlets of two *gem*-methyl group at 0.98 ppm and ABC-spectrum of the terminal double bond protons with δ = 4.60—5.09 (CH_2=C, 2H) and 5.50—6.20 ppm (=CH—, 1H). Acetylation of alcohols X with acetylchloride in pyridine gave corresponding acetates (XI).

Allylboration of esters with allyl(dialkyl)boranes or diallyl(alkyl)boranes proceeds with heat evolution at 0°C, and gives rise to esters of type XII which on re-esterification afford diallyl(alkyl)carbinols. Thus, as a result of distilling products of reaction of allyl(di-n-butyl)borane with butylacetate, the butyl ester of di-n-butylboronic acid was isolated together with 4-methyl-1,6-heptadiene-4-ylic ester of di-n-butylboronic acid (XIIa); re-esterification of the latter compound gave 4-methyl-1,6-heptadiene-4-ol-1 (XIII) in 85% yield (Scheme 9). First stage of the reaction involves addition of the boron—allyl fragment to the carbonyl group to afford a boron containing ketal XIV that is however unstable and undergoes β-elimination to give boron ester and allylmethylketone. This

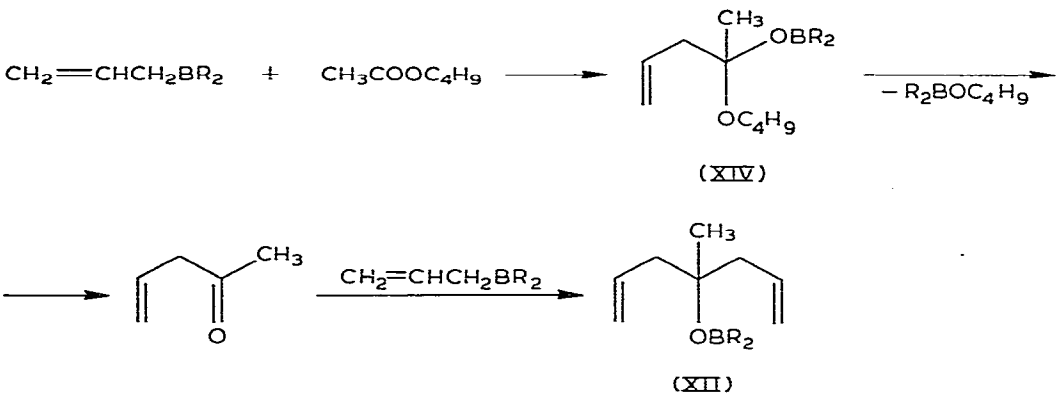
SCHEME 9



(XII a) (XIII)

latter reacts with another molecule of allyl(dialkyl)borane to form the ester XII (Scheme 10). All attempts to isolate intermediate allyl methyl ketone from

SCHEME 10

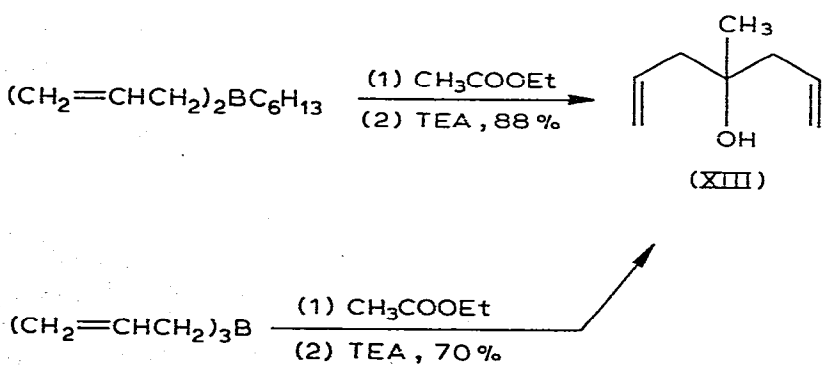


(XIV) (XII)

the reaction products met with failure. It seems to be more reactive with allyl-(dialkyl)borane than initial ester is.

Reaction of diallyl(n-hexyl)borane with ethylacetate gave carbinol (XIII) in 88% yield (Scheme 11). Tertiary alcohol XIII was also obtained, in 70% yield,

SCHEME 11



(XIII)

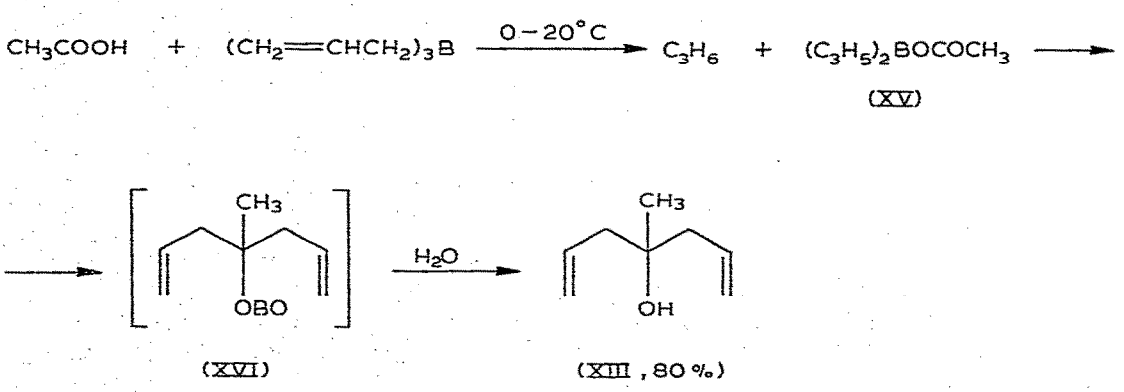
on alcoholysis with triethanolamine of the reaction product of triallylborane with ethylacetate (1 : 1). It is noteworthy that in this reaction only two allyl radicals of the three which the triallylborane molecule contains are consumed.

Not unlike esters of acetic acid, esters and other derivatives of higher organic acids can react with allylic boron compounds. These reactions offer a convenient method of synthesis of various 4-substituted-1,6-heptadien-4-ols.

As the procedure for synthesis of homoallylic alcohols, allylboration, in certain cases, gives difinite advantages when compared with organomagnesium procedures. All the reactions occur under mild conditions, easily and unambiguously to give rise to corresponding homoallylic alcohols in high yields (70—95%) whereas similar reactions of allylic derivatives of magnesium are occasionally complicated by side-reactions. Allylboration may be performed either without solvent or in any inert solvent, which is of great importance for the use of solid carbonyl compounds. Further isolation of homoallylic alcohols from boron esters is effected with the use of such neutral reagents as higher alcohols (re-esterification) or in alkaline medium (hydrolysis or oxidation with hydrogen peroxide). In contrast, the salts formed on synthesis of homoallylic alcohols using Grignard reagents, are usually hydrolyzed in acidic solution, which is at times not desirable, especially if some functional groups are present in the carbonyl compound.

Triallylborane reacts exothermally with acetic acid at 0—20°C (Scheme 12).

SCHEME 12



(XVI) (XIII, 80%)

With the ratio of reagents 1/1 one mole of propylene is evolved, and borate XVI is formed, which on hydrolysis with aqueous alkali, gives 4-methyl-1,6-heptadien-4-ol (XIII) in 80% yield. The first step of the reaction involves protolysis of one boron—allyl bond, as a result propylene evolves. Then acetoxy(diallyl)-borane (XV) undergoes intra- or inter-molecular allylboration to afford borate XVI. Benzoic and other organic acids react with triallylborane in a similar way.

Experimental

All manipulations with organoboron compounds were carried out under a stream of dry nitrogen or argon. IR spectra were recorded on a UR-20 spectrometer, PMR spectra on a DA-60-IL instrument with respect to TMS (δ 0, ppm).

Allyl-, crotyl-, 3,3-dimethylallyl(dialkyl)-boranes, and diallyl(alkyl)-boranes

were prepared from esters of alkyl- or dialkyl-boronic acids and corresponding allylic compounds of magnesium, aluminium, or boron [3]. Triallylborane and tri(2-methylallyl)borane were synthesized from aluminium, butylborate and allyl or 2-methylallylbromide [4,13]. 3-Allyl-3-borabicyclo[3.3.1]non-6-ene (IV, R = H) and 3-allyl-7-n-propyl-3-borabicyclo[3.3.1]non-6-ene (IV, R = n-C_3H_7) were obtained by heating triallylborane with acetylene or 1-pentyne, respectively [3,4,13]. 3-(2-Methylallyl)-1,5-dimethyl-3-borabicyclo[3.3.1]non-6-ene was prepared in 81% yield by heating tri(2-methylallyl)borane with acetylene in an autoclave [13].

In this work, commercial aldehydes and ketones were used; all the compounds were purified by distillation before use.

General procedure for allylboration of aldehydes and ketones

1. With the use of re-esterification with triethanolamine (a) 1-Hexen-4-ol (III, R' = H, R" = C_2H_5). To 4 g of allyl(di-n-butyl)borane was added 2 ml of propionaldehyde at —40—0°C, and warmed to room temperature. Then 4 ml of triethanolamine was added to the mixture, which on distillation gave 2.2 g (91.5%) of 1-hexen-4-ol. Other butenyl alcohols are obtained in this way, their physical constants are listed in Tables 1, 2, 3, and 4.

(b) 1,1,2-Trimethyl-3-buten-1-ol (VIII, R = R' = CH_3). 5 g of acetone was added to 4.5 g of crotyl(di-n-butyl)borane at 0—5°C and the mixture warmed to 20°C (in the IR spectrum an absorption band at 1635 cm^{-1} appeared). After adding 5 ml of triethanolamine, the mixture was distilled under reduced pressure giving 2.3 g (85%) of 1,1,2-trimethyl-3-buten-1-ol. IR-spectrum: 1635, 3080 (CH_2=CH), 3400 cm^{-1} (OH) (see Table 5).

(c) 3,3-Dimethyl-1-hepten-4-ol (X, R = H). To 9.5 g of 3,3-dimethylallyl(di-n-propyl)borane (IX) was carefully added 3.8 g of butaldehyde. The temperature of the mixture increased to 60°C and after cooling to 20°C 10 ml of triethanolamine was added. Distillation afforded 7.35 g of compound (X, R = H), b.p. 77—78°C/19 mmHg); n_D^{20} 1.4400. (Found: C, 75.53; H, 12.95. $C_9H_{18}O$ calcd.: C, 75.99; H, 12.75%.) IR spectrum: 1640, 3085 (CH_2=CH), 3990 (OH). PMR spectrum: 0.72—1.72 (m, aliphatic protons), 0.98 (s, CH_3), 3.00—3.33 (CH), 3.20 (s, OH), 4.58—5.08 (m, CH_2=C), 5.54—6.07 (m, =CH).

Using 3 g of carbinol (X, R = H) and 2 ml of acetyl chloride acetate (XI, R = H) was prepared in 62% yield (2.35 g), b.p. 77—78°C/15 mmHg, n_D^{20} 1.4305. (Found: C, 71.32; H, 11.06. $C_{11}H_{20}O_2$ calcd.: C, 71.69; H, 10.94%.) IR spectrum: 1640, 3087 (CH_2=CH), 1740 (C=O). PMR spectrum: 0.72—1.70 (m), 0.98 (s, CH_3), 3.97 (t, *J* 6 Hz, CH), 4.57—5.10 (m, CH_2=C), 5.53—6.03 (m, C=CH).

(d) 3,3,6-Trimethyl-1-hepten-4-ol (X, R = CH_3). This was synthesized in 65% yield (3 g) from 4.9 g of 3,3-dimethylallyl(di-n-propyl)borane and 4 ml of isovalaldehyde, with consequent treatment of the mixture with 8 ml of triethanolamine. B.p. 62—64°C (13 mmHg), n_D^{20} 1.4438. (Found: C, 75.90; H, 12.99. $C_{10}H_{20}O$ calcd.: C, 76.86; H, 12.90%.) IR spectrum: 1640, 3085 (CH_2=CH), 3430 cm^{-1} (OH). PMR spectrum: 0.63—1.76 (m, aliphatic protons), 0.98 (s, CH_3), 3.07—3.47 (m, OCH), 3.57 (s, OH), 4.69—5.09 (m, CH_2=C), 5.52—6.07 (m, =CH).

Acetate XI (R = CH_3) was obtained in 89% yield, b.p. 80—82°C/15 mmHg),

n_D^{20} 1.4294. (Found: C, 72.63; H, 11.30. $C_{12}H_{22}O_2$ calcd.: C, 72.68; H, 11.18%.) IR spectrum: 1638, 3090 (CH_2=CH), 1740 (C=O). PMR spectrum: 0.67—1.55 (m, aliphatic protons), 0.98 (s, CH_3), 1.95 (s, CH_3CO), 3.98 (t, *J* 6 Hz, CH), 4.59—5.11 (m, CH_2=C), 5.53—6.06 (m, =CH).

2. With the use of oxidation

To 5 g of allyl(di-n-propyl)borane was added, on cooling, (10—15°) 4.17 ml of mesityl oxide over a period of 5 min. After stirring for 10 min at 20°C, 15 ml of 3 *N* NaOH was added, followed by careful addition of 10 ml of 30% hydrogen peroxide at 10—30°C. The mixture was then heated for 10 min at 50°C, extracted with ether and dried over Na_2SO_4. Distillation gave 4.68 g (92.2%) of 2,4-dimethyl-2,6-heptadien-4-ol. The same carbinol was prepared from the same initial compounds using re-esterification with triethanolamine in 97.4% yield.

Constants of homoallylic alcohols thus obtained are listed in Tables 1 and 2.

1-Hexen-4-yloxy(diethyl)borane (II, R = C_2H_5, R′ = H, R″ = C_2H_5). 4 ml of propionaldehyde was added dropwise to 4.5 g of allyl(diethyl)borane at —50°C. On distillation of the mixture, 4.25 g (62.5%) of compound II (R = C_2H_5) was obtained, b.p. 68—70°C/20 mmHg, $n_D^{23.5}$ 1.4165. (Found: C, 71.10; H, 12.51; B, 6.43. $C_{10}H_{21}BO$ calcd.: C, 71.50; H, 12.54; B, 6.44%.) IR spectrum: 1645 and 3080 cm^{-1} (CH_2=CH). PMR spectrum (50% solution in CCl_4): 0.62—1.70 (m, aliphatic protons), 2.0—2.35 (t, CH_2C, *J* 6.5 Hz), 3.98 (m, CHO), 4.75—5.2 (m, CH_2=C), 5.4—6.2 (m, =CH).

1,1-Dimethyl-3-buten-1-yloxy(diethyl)borane (II, R = C_2H_5, R′ = R″ = CH_3). 1.2 ml of acetone was added to 1.7 g of allyl(diethyl)borane. Strong spontaneous heating (80°C) took place. Distillation of the mixture yielded 2.15 g (83.5%) of II (R = C_2H_5, R′ = R″ = CH_3), b.p. 77—78.5/30 mmHg, $n_D^{24.5}$ 1.4191. (Found: C, 70.58; H, 12.78; B, 6.47. $C_{10}H_{21}BO$ calcd.: C, 71.50; H, 12.54; B, 6.44%.) IR spectrum: 1645, 3080 (CH_2=CH). PMR spectrum (neat): 0.86 (s, C_2H_5), 1.3 (s, CH_3), 2.3 (d, *J* = 7 Hz, CH_2C=), 4.75—5.15 (m, CH_2=C), 5.4—6.2 (m, =CH).

Reactions of allylboranes with alkylacetates

1,1-Diallylethoxy(di-n-butyl)borane (XIIa). To 6.2 g of allyl(di-n-butyl)borane was added 5.2 g of butylacetate at —40°C and the mixture warmed to 20°C (there were no absorption bands in the region of 1700—1725 cm^{-1} of the IR spectrum, however an intense band at 1745 cm^{-1} was observed). To the mixture was added 6.2 g of allyl(di-n-butyl)borane, the temperature then increased spontaneously to 40°C. Distillation afforded 7 g (94%) of butyl ester of di-n-butylboronic acid, b.p. 66—68°C/3 mmHg, n_D^{20} 1.4228, together with 8.12 g (86%) of ester XIIa, b.p. 86—87°C/3 mmHg, n_D^{20} 1.4410.

IR spectrum of ester XIIa exhibits absorption bands characteristic of CH_2=CH bond (1645 and 3080 cm^{-1}). PMR spectrum: 0.62—1.75 (m, aliphatic protons), 2.30 (d, *J* 6.5 Hz, —CH_2—C=, 4H), 4.60—5.15 (m, CH_2=C, 4H), 5.45—6.20 (m, —CH=C, 2H).

4-Methyl-1,6-heptadien-4-ol (XIII) (a). Distillation of a mixture of 4.6 g of ester XIIa and 3 ml of triethanolamine gave 2.15 g (93%) of carbinol XIII, b.p. 48—50°C/12 mmHg, n_D^{20} 1.4497 (lit. b.p. 50—51°C (12 mmHg) [30], b.p. 155—156°C, n_D^{25} 1.4495 [31]). IR spectrum: 1645 and 3060 cm^{-1} (CH_2=CH).

PMR spectrum: 1.1 (s, CH_3), 2.2 (d, CH_2—C=, J 7 Hz), 3.05 (s, OH), 4.65—5.15 (CH_2=C), 5.45—6.25 (m, =CH—).

(b). To 5.3 g of allyl(diethyl)borane cooled to —30° was added 4.7 g of ethylacetate (the temperature of the mixture warmed exothermally to 60°C). 6.4 g of triethanolamine was added at 20°C, subsequent distillation yielded 2.3 g (76.5%) of alcohol XIII, b.p. 62—63°C/23 mmHg, n_D^{20} 1.4502.

(c) Reaction of 7.2 g of diallyl(n-hexyl)borane with 4 ml of ethylacetate followed by re-esterification of the mixture with triethanolamine (5.5 ml) led to 2.25 g (88%) of carbinol XIII, b.p. 64—65°C/24 mmHg; n_D^{23} 1.4497.

(d) As described above, from 8.7 g of triallylborane, 8.6 g ethylacetate, and 20 ml triethanolamine 5.6 g (70%) of carbinol XIII was synthesized, b.p. 63—64°C/23 mmHg, $n_D^{21.5}$ 1.4509.

(e) To 15.5 g of triallylborane was added, at 5—15°C, 6.6 ml of acetic acid over 0.5 h. Strong exothermic heating took place and 2.58 l of propylene was evolved. The reaction mixture was hydrolyzed by shaking with 150 ml of 10% NaOH, the organic layer was decanted and the aqueous one was twice extracted with ether (25 ml each time). After drying over Na_2SO_4 the mixture was distilled to afford 11.5 g (79.4%) of 4-methyl-1,6-heptadien-4-ol (XIII), b.p. 153—155°C/745 mmHg, n_D^{20} 1.4510.

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