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REACTIONS OF LITHIUM ALUMINUM HYDRIDE OR ALANE WITH OLEFINS CATALYZED BY TITANIUM TETRACHLORIDE OR ZIRCONIUM TETRACHLORIDE. A CONVENIENT ROUTE TO ALKANES, 1-HALOALKANES AND TERMINAL ALCOHOLS FROM ALKENES

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Summary

Titanium tetrachloride or zirconium tetrachloride catalyzes the addition of lithium aluminum hydride or alane to olefinic double bonds to afford the corresponding organoaluminate or organoalane, respectively. This reaction shows the following characteristics: 1. The success of this addition reaction is dependent on the solvent. 2. The main products of the reaction of $LiAlH_4$ and olefins are 1-alkylaluminum derivatives. 3. Relative rates for reactions of olefin with $LiAlH_4$ are in the order: $RCH{=}CH_2 > R_2C{=}CH_2 > RCH{=}CHR$. 4. Relative rates for aluminum hydride reactions with 1-hexene are in the order: $LiAlH_4 > AlH_3 > AlH_2Cl > AlHCl_2$. 5. $LiAlH_4$ or AlH_3 selectively adds to the least hindered C=C bond of nonconjugated diolefins. 6. $LiAlH_4$ and α,ω-dienes give dialumino or monoalumino derivatives, depending on the molar ratio of the reactants. This facile reaction offers a convenient laboratory method for (1) the hydrogenation of olefins or the preparation of 1-haloalkanes or terminal alcohols from olefins, (2) the selective reduction of nonconjugated diolefins or the selective preparation of haloolefins or unsaturated alcohols from diolefins, and (3) the preparation of α,ω-dihaloalkanes from α,ω-dienes.

Introduction

It has long been recognized that organoaluminum compounds are useful and versatile reagents and intermediates in organic synthesis [1]. However, their application as sources of organic groups in organic synthesis has largely been restricted to reactions of alkenylalanes which are readily obtainable by hydroalumination of alkynes [2]. Organoaluminums are not obtainable by the hydroalumination of alkenes under mild conditions and so they are most commonly prepared from organolithium or Grignard reagents. Also, reaction using organoaluminums often give less satisfactory results than the corresponding reactions of analogous derivatives of Li or Mg. If the reaction of aluminum hydride and olefins could be made to proceed under mild conditions, the corresponding organoaluminums would be readily available for applications in organic synthesis, on the bench scale, which would renew interest in the organoaluminums as intermediates. We report here that some transition metal halides, e.g. $TiCl_4$ and $ZrCl_4$, catalyze the addition of lithium aluminum hydride or alane to olefinic double bonds to afford the corresponding organoaluminums in excellent yield under mild conditions, thus making them as readily available as the organoboranes.

Results and discussion

Reactions of $LiAlH_4$ and olefins

As mentioned in preliminary papers [3], titanium(IV) and zirconium(IV) compounds are effective catalysts for the addition of lithium aluminum hydride to 1-alkenes to give lithium tetraalkylaluminum compounds. $TiCl_4$ and $ZrCl_4$ are particularly effective. The mechanisms of these reactions very likely involve intermediate transition metal hydrides.

Further investigations have revealed that this reaction is not restricted to 1-alkenes, but that internal olefins also react with $LiAlH_4$ in an appropriate solvent. The results of the reactions of olefins with $LiAlH_4$ in various solvents are shown in Table 1. Tetrahydrofuran, ethylene glycol, dimethyl ether, diglyme

TABLE 1

YIELDS AND PRODUCTS OF ADDITION REACTIONS OF OLEFINS

Olefin	Reaction conditions [a]		Hydrolysis or halogenolysis	Product (Yield (%)) [b]
	Solvent	Time (h)		
1-Hexene	Ethyl ether	20	H_2O	n-Hexane (trace)
	Tetrahydrofuran	0.5	H_2O	n-Hexane (99)
	Ethylene glycol dimethyl ether	3	H_2O	n-Hexane (100)
	Diglyme	3	H_2O	n-Hexane (100)
	Triglyme	3	H_2O	n-Hexane (100)
2-Hexene [c]	Diglyme	80	H_2O	n-Hexane (98)
			Br_2	1-Bromohexane (79)
				2- and 3-Bromohexane (14)
	Triglyme	120	Br_2	1-Bromohexane (79)
				2- and 3- Bromohexane (13)
3-Hexene	Diglyme	120	H_2O	n-Hexane (96)
			Br_2	1-Bromohexane (63)
				2- and 3-Bromohexane (12)
	Triglyme	190	Br_2	1-Bromohexane (66)
				2- and 3-Bromohexane (13)
cis-2-Octene	Diglyme	96	H_2O	n-Octane (98)
			Br_2	1-Bromooctane (84)
				2- and 3-Bromooctane (7)
Cyclohexene	Diglyme	150	H_2O	Cyclohexane (46)

[a] 29 mmol of olefin. 7.9 mmol of $LiAlH_4$ and 0.45 mmol of $TiCl_4$. Temp. 20°C. [b] Yields were determined by GLC and are based on olefin. [c] *Trans/cis* = 1.6.

and triglyme are effective solvents for this reaction, while diethyl ether was essentially ineffective. Internal olefins, such as 2-hexene, 3-hexene and 2-octene, have been found to react with $LiAlH_4$ in the presence of $TiCl_4$ in diglyme or triglyme to give 1-alkylaluminum derivatives as the main products. This observation is not entirely unprecedented: (1) zirconium(IV) and titanium(IV) salts are known to catalyze the isomerization of secondary alkyl Grignard [4] and aluminum [5] reagents to give primary alkyl organometallics. Moreover, stable 1-alkylzirconium compounds were prepared recently by the hydrozirconation of internal olefins [6]; (2) it was noted that alkyl-titanium- or -zirconiumcompounds play an important role in the present reaction [3].

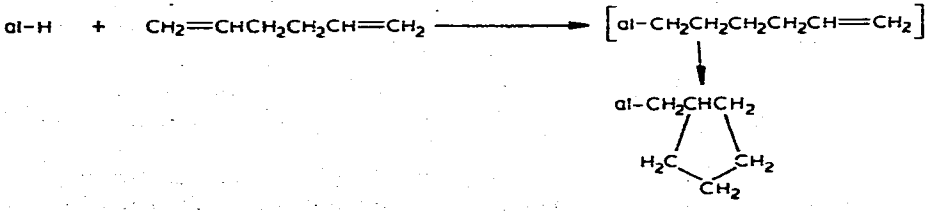
Thus, in view of the proposed mechanism for the $ZrCl_4$-catalyzed 1-alkene—$LiAlH_4$ reaction, it is probable that the reaction of $LiAlH_4$ with internal olefins and $TiCl_4$ proceeds via hydrotitanation of the internal double bond followed by rapid rearrangement prior to the occurrence of titanium—aluminum exchange.

With regard to the function of the solvents, it can be assumed that the solvents play a role as ligands and stabilize the titanium hydride which is supposed to be the actual catalytic species, because good donor solvents are effective for these reactions.

In summary, we should point out that $TiCl_4$- or $ZrCl_4$-catalyzed olefin—$LiAlH_4$ reactions proceed readily in a number of cases, with the decrease of the reaction rate in the order: $RCH{=}CH_2 > R_2C{=}CH_2 > RCH{=}CHR$. This facile reaction provides a satisfactory synthetic route from olefins to alkanes or 1-haloalkanes.

Reaction of $LiAlH_4$ with nonconjugated dienes

The $TiCl_4$-catalyzed olefin—$LiAlH_4$ reaction permitted the selective addition of $LiAlH_4$ to the less hindered C=C bond of nonconjugated dienes. Thus, as summarized in a preliminary report [3b], 4-vinyl-1-cyclohexene, 1,4-hexadiene and 2-methyl-1,5-hexadiene react with $LiAlH_4$ giving the corresponding organoaluminate in which aluminum is connected to the less hindered double bond of diolefins. We have extended this reaction to α,ω-dienes. $TiCl_4$-catalyzed α,ω-diene—$LiAlH_4$ reactions have been found to proceed readily at room temperature to generate dialumino or monoalumino derivatives, depending on the molar ratio of the reactants. Up to the present time, efforts to prepare monoalumino derivatives by the direct reaction of aluminum hydride with α,ω-dienes have been unsuccessful. Thus 1,5-hexadiene and triisobutylaluminum or diisobutylaluminum hydride did not give the 1,6-dialuminohexane derivative nor the 6-alumino-1-hexene derivative, but cyclopentylmethylaluminum compounds were formed as shown in eq. 1 [7].



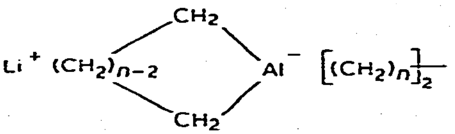
(1)

We have succeeded in producing α,ω-dialuminoparaffins and ω-alumino-1-olefins by the following procedure. $LiAlH_4$ (16 mmol) was added to a mixture of $TiCl_4$ (0.82 mmol) and 1,5-hexadiene (26 mmol) in 60 ml of tetrahydrofuran. A gray precipitate, apparently a polymeric substance, appeared gradually and the solution became clear while the reaction mixture was stirred at room temperature. After 24 h, the reaction product was hydrolyzed and gas chromatographic analysis indicated the quantitative formation of n-hexane. In another experiment, the product was treated with bromine to give 1,6-dibromohexane in 80% yield with no other dibromo derivatives being formed. A similar reaction of equimolar amounts of the reactants (10.6 mmol of $LiAlH_4$ = 42.4 mmol of hydride and 41 mmol of 1,5-hexadiene) produced 53% yield of 1-hexene and 23% yield of n-hexane, along with 24% recovery of 1,5-hexadiene. These results clearly indicated that the reaction proceeds as shown in eq. 2.

$$\begin{aligned} &\text{al–H} + CH_2{=}CHCH_2CH_2CH{=}CH_2 \xrightarrow{TiCl_4} \text{al-}CH_2CH_2CH_2CH_2CH{=}CH_2 \\ &2\ \text{al-H} + CH_2{=}CHCH_2CH_2CH{=}CH_2 \xrightarrow{TiCl_4} \text{al-}CH_2CH_2CH_2CH_2CH_2CH_2\text{-al} \end{aligned} \qquad (2)$$

A similar reaction of $LiAlH_4$ (16 mmol) and 1,7-octadiene (29 mmol) gave a gray precipitate from which 1,8-dibromooctane was obtained in 67% yield on treatment with bromine.

These results lead us to propose that the α,ω-dialuminoalkane derivative is best formulated as $Li^+Al^-[(CH_2)_n]_4Al^-Li^+$ (n = 6 or 8), which, of course, is a three dimensional, cross-linked, high molecular weight compound. Its insolubility in tetrahydrofuran is thus not surprising. Other possible formulas which contain cyclic structures, such as, seem unfavorable because they involve 7- or 9-membered rings. This cyclization must be an important path when 1,4-pentadiene is used as the α,ω-diene, because the reaction product of $LiAlH_4$ with 1,4-pentadiene is soluble in tetrahydrofuran and 1,4- and 1,5-dibromopentanes are obtained in 1/12 ratio by treating the product with bromine. The production of 1,4-dibromopentane can be understood on the basis of the formation of a 5-membered cyclic organoaluminum compound.



The results of the reaction of α,ω-dienes with $LiAlH_4$ are shown in Table 2. This reaction thus provides a satisfactory synthetic route to α,ω-dihaloalkanes or to the corresponding haloolefins from α,ω-dienes.

Reaction of AlH_3, AlH_2Cl or $AlHCl_2$ with olefins

Organoalanes and organoaluminates differ from one another in their reactivity. It is therefore, desirable to find an easy method for the preparation of organoalanes. AlH_3, AlH_2Cl and $AlHCl_2$ are obtained readily by the reaction of $LiAlH_4$ and $AlCl_3$ [8]. This result encourages us to investigate the reaction of olefins with alane.

AlH_3, AlH_2Cl and $AlHCl_2$, which had been obtained from the reaction of $LiAlH_4$ with $AlCl_3$ in the ratios 3/1, 1/1 and 1/3, respectively, reacted with 1-hexene in the presence of $TiCl_4$ with decreasing reaction rate (see Table 3). Organoalanes are well-known to react with oxygen to give alcohols on subse-

TABLE 2

YIELDS AND PRODUCTS OF ADDITION REACTION OF α,ω-DIENES[a]

Dienes (mmol)	$LiAlH_4$ (mmol)	Hydrolysis or halogenolysis	Product (yield (%))[b]
1,4-Pentadiene			
27	16	Br_2	1,5-Dibromopentane (59)
			1,4-Dibromopentane (5)
40	10.6	H_2O	1-Pentene (35)
			n-Pentane (27)
			1,4-Pentadiene (38)
		Br_2	5-Bromo-1-pentene (47)[c]
			1-Bromopentane (7)[c]
			1,5-Dibromopentane (18)[c]
			1,4-Dibromopentane (2)[c]
1,5-Hexadiene			
26	16	H_2O	n-Hexane (100)
		Br_2	1,6-Dibromohexane, (80)
41	10.6	H_2O	1-Hexene (53)
			n-Hexane (23)
			1,5-Hexadiene (24)
		Br_2	6-Bromo-1-hexene (48)[c]
			1-Bromohexane (6)[c]
			1,6-Dibromohexane (17)[c]
1,7-Octadiene			
29	16	Br_2	1,8-Dibromooctane (67)
38	10.6	H_2O	1-Octene (47)
			n-Octane (30)
			1,7-Octadiene (23)
		Br_2	8-Bromo-1-octene (41)[c]
			1-Bromooctane (16)[c]
			1,8-Dibromooctane (13)[c]

[a] 0.82 mmol of $TiCl_4$, in 60 ml of tetrahydrofuran, reaction time 24 h at room temperature. [b] Yields were determined by GLC and are based on diene. [c] Based on reacted diene.

TABLE 3

YIELD OF n-HEXANE AFTER HYDROLYSIS OF THE REACTION MIXTURE OF ALANE AND 1-HEXENE

Alane[a]		1-Hexene (mmol)	Reaction conditions[b]		n-Hexane, yield (%)[c]
$LiAlH_4$ (mmol)	$AlCl_3$ (mmol)		Temperature (°C)	Time (h)	
7.9	2.8 (AlH_3)	26	10—15	3	88
7.9	8.3 (AlH_2Cl)	26	10—15	3	62
				6	90
7.9	24 ($AlHCl_2$)	26	10—15	3	43
				16	90

[a] Alane was prepared by stirring the mixture of $LiAlH_4$ and $AlCl_3$ at −10°C for 1 h. [b] The reaction was carried out in the presence of 0.45 mmol of $TiCl_4$. [c] Yields were determined by GLC analysis and are based on 1-hexene.

TABLE 4

YIELDS AND PRODUCTS OF OXIDATION OF ALKYLALUMINUM

Olefin	Method[a]	Product	Yield[b] (%)
1-Hexene	A	Hexan-1-ol	82
	B		90
2-Hexene	A	Hexan-1-ol	71
		Hexan-2-ol	10
		Hexan-3-ol	5
1-Heptene	A	Heptan-1-ol	85 (78)[c]
4-Vinyl-1-cyclohexene	A	2-(4-Cyclohexenyl)ethanol	85 (71)[c]
	B		95
1,4-Hexadiene	A	4-Hexen-1-ol	80
	B		83
2-Methyl-1,5-hexadiene	A	5-Methyl-5-hexen-1-ol	90
	B		92

[a] A: AlR_3 was obtained by the treatment of $LiAlR_4$ with 1/3 $AlCl_3$. B: AlR_3 was obtained by the treatment of AlH_3 with olefin. [b] GLC analysis and based on olefin. [c] Isolated yield.

quent hydrolysis in almost quantitative yield [1] *.

To show the availability of this facile reaction in organic synthesis on the bench scale, the preparation of alcohols from olefins were investigated. A typical experimental procedure is illustrated by the reaction of 1-hexene with AlH_3. After the mixture of $LiAlH_4$ (7.9 mmol) and $AlCl_3$ (2.8 mmol) in 30 ml of tetrahydrofuran had been stirred at −10°C, 1-hexene (26 mmol) and $TiCl_4$ (0.45 mmol) were added. The mixture was stirred for 10 h at 10~15°C, oxygen was passed through it, and hexan-1-ol was obtained in 85% yield after hydrolysis. The reaction of nonconjugated dienes with AlH_3, catalyzed by $TiCl_4$, proceeded in a similar manner as in the case of $LiAlH_4$ and gave unsaturated alcohols in excellent yields.

Alcohols also were obtained in excellent yields by converting $LiAlR_4$ to AlR_3 by treatment with 1/3 $AlCl_3$ [1] prior to the oxidation. Yields of alcohols obtained by the above two methods are given in Table 4.

Two useful methods for the preparation of primary alcohols from olefins are known: (1) reactions of borane and olefins followed by oxidation with alkaline hydrogen peroxide [9] and (2) oxidation of alkylzirconiums derived from $(\eta^5\text{-}C_5H_5)_2Zr(Cl)H$ and olefins [10]. The AlH_3—$TiCl_4$ system is an attractive alternative to these methods.

Experimental

All solvents used were distilled from lithium aluminum hydride. Lithium aluminum hydride and aluminum chloride were commercial available and used without purification. The olefins were products available from commercial sources and were distilled from lithium aluminum hydride prior to their utilization. All operations were conducted under nitrogen or argon. The products were iden-

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* $LiAl(C_6H_{13})_4$, prepared by the $TiCl_4$-catalyzed reaction of $LiAlH_4$ with 1-hexene, reacted with oxygen to give hexan-1-ol only in 35 ~ 45% yield.

tified by GLC and ^{1}H NMR. ^{1}H NMR spectra were obtained with JEOL-JNM-4H 100 NMR spectrometers with TMS as internal standard.

Some typical procedures are shown below, while the data are summarized in Tables 1—4 or have been given in the preliminary papers [3].

$TiCl_4$-catalyzed $LiAlH_4$-1-hexene reaction

1-Hexene (2.4 g, 29 mmol), $TiCl_4$ (86 mg, 0.45 mmol) and 30 ml of THF were placed in a 100 ml flask. $LiAlH_4$ (0.3 g, 7.9 mmol) was added to the 1-hexene at room temperature. The flask was permitted to remain at 20°C for 30 min. The organoaluminum thus formed was hydrolyzed by adding ice. GLC analysis indicated the formation of n-hexane in 99% yield with small amounts of *trans*- and *cis*-2-hexene.

Preparation of 1-bromohexane

After reaction of 1-hexene (2.4 g, 29 mmol) and $LiAlH_4$ (0.3 g, 7.9 mmol) for 30 min as described above, bromine (5.3 g, 33 mmol) in 40 ml of benzene was added dropwise at 5°C. After completion of the bromine addition, the flask was permitted to remain 30 min at room temperature. Then the reaction mixture was washed with 10% sodium hydroxide solution, washed with saturated sodium chloride solution and dried over magnesium sulfate. GLC analysis indicated the formation of 1-bromohexane in 91% yield. Distillation yielded 4.0 g (84%) of 1-bromohexane, b.p. 55—57°C/35 mmHg.

Preparation of 1-chlorohexane

After reaction of 1-hexene (3.2 g, 38.1 mmol) and $LiAlH_4$ (0.4 g, 11 mmol) for 24 h in the presence of $ZrCl_4$ (150 mg, 0.64 mmol), the solvent was removed under vacuum and the residue was dissolved in n-hexane (30 ml) and pyridine (5 ml) mixture. Chlorine was bubbled into this solution at —20°C. GLC analysis indicated the formation of 1-chlorohexane in 89% yield.

$TiCl_4$-catalyzed $LiAlH_4$—2-hexene reaction

2-Hexene (*trans/cis* = 1.6, 2.4 g, 29 mmol), $TiCl_4$ (86 mg, 0.45 mmol) and 30 ml of diglyme were placed in a 100 ml flask. $LiAlH_4$ (0.3 g, 7.9 mmol) was added at room temperature. Then the flask was kept at 20°C for 80 h. The organoaluminum thus obtained was hydrolyzed by adding ice to give n-hexane in quantitative yield (GLC analysis).

In another experiment, the reaction mixture was treated with bromine (5.1 g, 32 mmol) to give 1-bromohexane (79%) and 2- and 3-bromo hexane (13%) (GLC analysis).

$TiCl_4$-catalyzed $LiAlH_4$—4-vinyl-1-cyclohexene reaction

4-Vinyl-1-cyclohexene (3.0 g, 28 mmol) and $TiCl_4$ (57 mg, 0.3 mmol) were dissolved in 30 ml of THF and to this solution $LiAlH_4$ (0.3 g, 7.9 mmol) was added After 12 h of standing at room temperature, the mixture was hydrolyzed by adding ice. GLC analysis indicated the presence of a 97% yield of 4-ethyl-1-cyclohexene [11]. 4-Ethyl-1-cyclohexene [2.65 g (86%)] was isolated by distillation, b.p. 59—60°C/80 mmHg. ^{1}H NMR; δ 5.5 (2H, d, olefin), 0.85 ppm (3H, t, CH_2—$C\underline{H}_3$)

Preparation of 2-(4-cyclohexenyl)ethyl iodide [12]

After reaction of 4-vinyl-1-cyclohexene (3.0 g, 28 mmol) and $LiAlH_4$ (0.3 g, 7.9 mmol) as described above, iodine (8.0 g, 31 mmol) in 100 ml of benzene was added dropwise at 5°C. After the addition was completed, the mixture was permitted to remain for 1 h at room temperature. The reaction mixture was then washed with 100 ml of water containing 2 g of sodium thiosulfate, dried over magnesium sulfate and distilled. 2-(4-Cyclohexenyl)ethyl iodide [3.8 g (58%)] was obtained, b.p. 55—56°C/1 mmHg. ^1H NMR; δ 5.6 (2H, d, olefin), 3.2 ppm (2H, t, CH_2—$\underline{CH_2}I$).

Reaction of 1,5-hexadiene with $LiAlH_4$

$LiAlH_4$ (0.6 g, 16 mmol) was added to a solution containing 1,5-hexadiene (2.1 g, 26 mmol) and $TiCl_4$ (0.16 g, 0.82 mmol) in 60 ml of THF. The solution was stirred at room temperature for 24 h. A precipitate appeared gradually, but the solution became clear again when stirring was continued. The organoaluminum compound thus obtained was hydrolyzed by adding ice to give n-hexane quantitatively.

Preparation of 1,6-dibromohexane

After reaction of $LiAlH_4$ (0.6 g, 16 mmol) and 1,5-hexadiene (2.1 g, 26 mmol) in 60 ml of THF for 24 h, bromine (10.2 g, 64 mmol) was added dropwise at 5°C. GLC analysis of the reaction mixture indicated the presence of 1,6-dibromohexane in 80% yield. Distillation yielded 4.4 g (69%) of 1,6-dibromohexane, b.p. 78—82°C/2 mmHg. ^1H NMR; δ 3.36 ppm (4H, t, CH_2—Br)

Preparation of 6-bromo-1-hexene

$LiAlH_4$ (0.4 g, 10.6 mmol) was added to a solution containing 1,5-hexadiene (3.4 g, 41 mmol) and $TiCl_4$ (0.16 g, 0.82 mmol) in 50 ml of THF at room temperature. After standing of the reaction mixture for 24 h, *N*-bromosuccinimide (7.6 g, 42.7 mmol) was added at 0°C and the mixture was stirred at room temperature for 3 h. GLC analysis indicated the formation of 6-bromo-1-hexene (48% based on diene), 1-bromohexane (6%) and 1,6-dibromohexane (17%).

$TiCl_4$-catalyzed AlH_3—1-hexene reaction

After stirring a mixture of $LiAlH_4$ (0.3 g, 7.9 mmol) and $AlCl_3$ (0.37 g, 2.8 mmol) in 30 ml of THF at —10°C for 1 h, the mixture was warmed to 10°C and 1-hexene (2.2 g, 26 mmol) and $TiCl_4$ (86 mg, 0.45 mmol) were added. The mixture was stirred for 10 h at 10—15°C and hydrolyzed by adding ice to give n-hexane in 88% yield.

Preparation of 2-(4-cyclohexenyl)ethanol [13]

Method A. After reaction of 18.9 g (0.175 mol), of 4-vinyl-1-cyclohexene and 1.9 g (0.05 mmol) of $LiAlH_4$ for 12 h in the presence of $TiCl_4$ (0.3 g, 1.6 mmol) in 30 ml of THF at room temperature, 2.25 g (0.017 mol) of $AlCl_3$ was added to the reaction mixture. The mixture was refluxed for 4 h, cooled and then oxygen was passed through during 1.5 h. During this operation the temperature rose to 50—60°C, then fell again. When the temperature leveled off, the oxygen stream was discontinued and 50 ml of dilute (10%) hydrochloric acid was added, first dropwise and later in large portions. The product was extracted with 100 ml of ether and distillation of the extract gave 15.6 g (71%) of product, b.p. 92—94°C/10 mmHg. Anal. Found: C, 76.0; H, 10.8. $C_8H_{14}O$ calcd.: C, 76.2; H, 11.1%. ^1H NMR; δ 5.64 (2H, d, olefin), 4.64 (1H, s, OH), 3.62 ppm (2H, t, $CH_2{-}OH$)

Method B. 4-Vinyl-1-cyclohexene (3.8 g, 35 mmol) was treated with AlH_3 prepared from $LiAlH_4$ (0.4 g, 10 mmol) and $AlCl_3$ (0.45 g, 3.3 mmol) in 30 ml of THF at room temperature for 20 h. Then oxygen was passed through and the mixture was hydrolyzed to give the product in 95% yield (GLC analysis).

Preparation of 4-hexene-1-ol

Method A. After reaction of 1,4-hexadiene (1.5 g, 18.5 mmol) and $LiAlH_4$ (0.2 g, 5 mmol) for 40 h in the presence of $TiCl_4$ (0.08 g, 0.41 mmol) in 30 ml of THF at room temperature, 0.3 g (2.2 mmol) of $AlCl_3$ was added and the mixture was refluxed for 8 h. After oxidation with oxygen and isolation as described above, 4-hexen-1-ol (80% yield, analyzed by GLC) was obtained, b.p. 65—68°C/8 mmHg. Anal. Found: C, 72.0; H, 12.4. $C_6H_{12}O$ calcd.: C, 72.0; H, 12.0%. ^1H NMR; δ 5.40 (2H, m, olefin), 4.5 (1H, s, OH), 3.55 ppm (2H, t, $C\underline{H}_2{-}OH$)

Method B. 1,4-Hexadiene (1.5 g, 18.5 mmol) was treated with AlH_3, prepared from $LiAlH_4$ (0.2 g, 5 mmol) and $AlCl_3$ (0.3 g, 2.2 mmol), in 30 ml of THF for 20 h at room temperature. After oxidation with oxygen, 4-hexen-1-ol was obtained 83% yield, analyzed by GLC). Distillation yielded 1.3 g of 4-hexen-1-ol (72%).

Preparation of 5-methyl-5-hexen-1-ol [14]

From 3.0 g of 2-methyl-1,5-hexadiene (31 mmol) a 92% yield of 5-methyl-5-hexen-1-ol (GLC analysis) was obtained by Method B. Distillation gave 2.8 g of the alcohol (78% yield), b.p. 83—84°C/13 mmHg. Anal. Found: C, 73.1; H, 11.9. $C_7H_{14}O$ calcd.: C, 73.7; H, 12.3%. ^1H NMR: δ 4.68 (2H, s, $=CH_2$), 4.2 (1H, s, OH), 3.55 (2H, t, $C\underline{H}_2{-}OH$), 2.73 ppm (3H, s, $>C{-}CH_3$).

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