Aliphatic Claisen Rearrangement Promoted by Organoaluminium Reagents

Kazuhiko Takai, Ichiro Mori, Koichiro Oshima,* and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

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Organoaluminium compounds, R_3Al, promote the Claisen rearrangement of allyl vinyl ether derivatives at room temperature under transfer of R or H as a nucleophile to the aldehydic carbon. Treatment of 1-butyl-2-propenyl vinyl ether with a hexane solution of Me_3Al (1.0 M†, 2.2 equiv) in CH_2ClCH_2Cl at 25 °C afforded 5-decen-2-ol (91% yield, $E/Z=47/53$), which was produced by the [3,3] sigmatropic rearrangement and successive methylation. The rearrangements with alkynylation, alkenylation, and hydrogenation are also achieved. The regular Claisen rearrangement products, or γ,δ-unsaturated aldehydes (ketones), are obtained at 25 °C in good to excellent yields with Et_2AlSPh (2.5 equiv) or the combination of Et_2AlCl (2.0 equiv) and PPh_3 (2.2 equiv).

Although aliphatic Claisen rearrangement[1] provides a means of introducing a carbon-carbon bond in a stereo- and regiospecific manner, higher temperature and longer reaction time limit the synthetic use of this reaction. Some modifications, such as amide-acetal,[2] orthoester,[3] and ester enolate method,[4] have been reported to overcome this difficulty. We report here that the treatment of simple allyl vinyl ether substrates with organoaluminium amphoteric reagents results in the [3,3] sigmatropic rearrangements under mild conditions.[5]

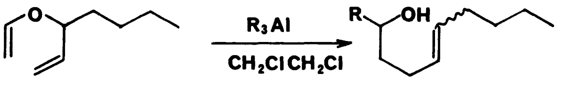
Addition of Lewis acid has been recently well documented as accelerating Diels-Alder reaction,[6] ene reaction,[7] and aromatic Claisen rearrangement.[8] The attempted aliphatic Claisen rearrangement in the presence of common Lewis acid, however, failed. For example, treatment of 1-butyl-2-propenyl vinyl ether (**1**) with $BF_3 \cdot OEt_2$, $TiCl_4$,[9] $SnCl_4$, or $ZnBr_2$ resulted in formation of complex mixtures containing 1-hepten-3-ol but none of the desired rearrangement products. In contrast, organoaluminium reagent, R_3Al or R_2AlSPh, proved to bring about the rearrangement at room temperature under transfer of R, H, or SPh[10] as a nucleophile to the aldehydic carbon.

Treatment of 1-butyl-2-propenyl vinyl ether (**1**) with 2.2 equiv of trimethylaluminium in 1,2-dichloroethane at 25 °C under an argon atmosphere gave 5-decen-2-ol (**2a**) in 91% yield ($E/Z=47/53$), this was apparently produced by the rearrangement and successive methylation. The use of triethylaluminium resulted in formation of a mixture of the corresponding ethylated alcohol **2b** (75% yield, $E/Z=42/58$) as well as a hydrogenated one **2c** (19% yield, $E/Z=42/58$). Meanwhile, the hydrogenated product was obtained exclusively with triisobutylaluminium or diisobutylaluminium hydride. The reactions between triisobutylaluminium and allyl vinyl ether substrates are shown in Table 1.

The E/Z ratios of newly developed double bonds were close to 1/1 and not affected by such solvents as hexane, benzene, dichloromethane, and 1,2-dichloroethane. In ethereal solvents like ether and THF, the reaction did not take place.

Neither methyllithium nor diethylzinc was effective for the transformation. Methylmagnesium iodide was marginal; for example, the reaction of **1** with 3 equiv of MeMgI took 2 h to be completed, affording **2a** in 78% yield ($E/Z=52/48$).

Because allyl vinyl ether substrates **3** and **4** gave the corresponding [3,3] sigmatropic products respectively



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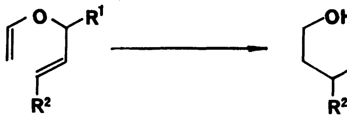
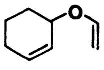
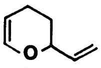
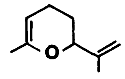
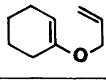
2a: R = CH_3
2b: R = CH_2CH_3
2c: R = H (i-Bu_3Al)

Scheme 1.

Table 1. Reactions between Bu_3Al and allyl vinyl ether substrates[a)]



Run	Ether[b)] R¹	Ether[b)] R²	Conditions Temp/°C	Conditions Time/h	Yield[c)] %	E/Z[d)]
1	n-Bu	H	25	0.25	82	38/62
2	n-Bu	Me	25	0.25	89	45/55
3	Ph	H (**3**)	25	0.25	93	E only
4	H	Ph (**4**)	25	0.25	91	—
5			25	0.25	90	—
6			60	2	95	—
7			60	2	97	—
8			25	0.25	78	trans/cis 23/77

a) The substrates (2.0 mmol) dissolved in 1,2-dichloroethane (10 ml) were treated with a hexane solution of i-Bu_3Al (1.0 M, 4.4 mmol). b) Prepared by the mercury(II) acetate-catalyzed transetherification with ethyl vinyl ether (Runs 1—5). See Ref. 3b. c) Isolated yields. d) the crude prodcts were transformed into trimethylsilyl ethers whose isomeric ratios were determined by GLPC.

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† 1 M = 1 mol dm^{-3}.

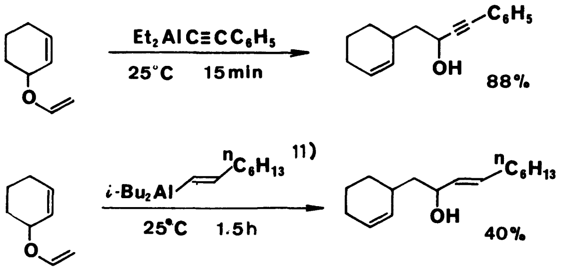
(Runs 3 and 4), the possibility of the following sequence of reactions was rejected: (1) A Lewis acid promoting C-O bond fission to give the ion pair of allylic cation and enolate ion, (2) recombination of the ion pair to afford the aldehyde, and (3) reduction of the aldehyde by i-Bu_3Al.10)

Table 2 summarizes the reaction between trimethylaluminium and allyl vinyl ether derivatives.

Alkynyl and alkenyl groups were introduced in preference to an alkyl group, as shown in Scheme 2.

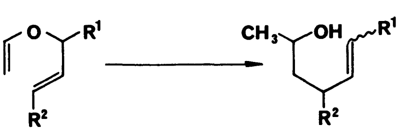
The reagent Et_2AlSPh12) (method A) or a combination of Et_2AlCl and PPh_3 (method B) turned out to be effective for the rearrangement giving regular Claisen products, or γ,δ-unsaturated aldehydes (ketones), as shown in Table 3. The rearrangement did not occur in the presence of Et_2AlSEt, Et_2AlS^tBu, or $^iBu_2AlOPh$. Triphenylphosphine plays an important role in method B, since the reaction of **1** with diethylaluminium chloride alone afforded the same mixture of **2b** (56%, E/Z=46/54) and **2c** (12%, E/Z=48/52) as that with triethylaluminium. A similar combination of Et_2AlI and Et_3N was effective, but the yields were not so good as the yield of Et_2AlCl and PPh_3.

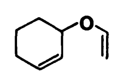
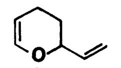
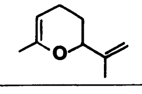
Almost the same yields and selectivities were obtained with Et_2AlSPh and Et_2AlCl-PPh_3 reagents.



Scheme 2.

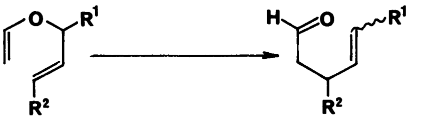
TABLE 2. REACTIONS BETWEEN Me_3Al AND ALLYL VINYL ETHER SUBSTRATES$^{a)}$

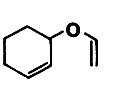
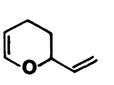
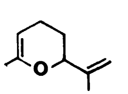
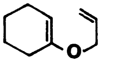


Run	Ether		Conditions		Yield$^{b)}$	$E/Z^{c)}$
	R^1	R^2	Temp/°C	Time/h	%	
1	n-Bu	H	25	0.25	91	47/53
2	Ph	H	25	0.25	78	E only
3	H	Ph	25	0.25	71	—
4			25	0.5	81	—
5			60	2	86	—
6			60	2	87	—

a) The substrates (2.0 mmol) dissolved in 1,2-dichloroethane (10 ml) were treated with a hexane solution of Me_3Al (1.0 M, 4.4 mmol). b) Isolated yields. c) The isomeric ratios of the corresponding trimethylsilyl ethers were determined by GLPC.

TABLE 3. CLAISEN REARRANGEMENT PROMOTED BY ORGANOALUMINIUM REAGENTS$^{a)}$



Run	Ether		Method	Time	Yield	E/Z
	R^1	R^2		h	%	
1	n-Bu	H	A$^{b)}$	0.25	84	39/61$^{c)}$
2			B$^{d)}$	0.25	81	43/57
3	n-Bu	Me	A	0.25	77	52/48$^{c)}$
4	Ph	H	A	0.5	67	E only
5	H	Ph	A	0.25	86	—
6			B	0.25	87	—
7			A	0.25	78	—
8			B$^{e)}$	1	61	—
9			B$^{e)}$	0.5	69	—
10			A$^{e)}$	0.5	76	—

a) Reactions were carried out in 1,2-dichloroethane at 25 °C. b) The substrates (2.0 mmol) were treated with Et_2AlSPh (5.0 mmol). c) The crude products were reduced with $LiAlH_4$ and transformed into trimethylsilyl ethers. The E/Z ratios of trimethylsilyl ethers were determined by GLPC. d) The substrates (2.0 mmol) were treated with a mixture of Et_2AlCl (4.0 mmol) and PPh_3 (4.4 mmol). e) Dichloromethane was used as a solvent.

It is worth noting that the rearrangement of 2-vinyl-3,4-dihydro-2H-pyran derivatives took place under extremely mild conditions (Runs 8 and 9) as compared with the pyrolysis (410—425 °C) without the catalyst described in the literature.13)

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer; the mass spectra, on a Hitachi M-80 machine; and the NMR spectra, on a Varian EM-360 spectrometer. The chemical shifts are given in δ, with TMS as the internal standard. The microanalyses were carried out at the Elemental Analyses Center of Kyoto University. 1,2-Dichloroethane and dichloromethane were dried over P_2O_5 and distilled. All the experiments were carried out under an argon atmosphere. Purification of products was performed by preparative thin-layer chromatography (TLC) or column chromatography on silica gel (Merck Kieselgel 60). Analytical GLPC was performed with a Yanagimoto GCG-550-F or Shimadzu GC-4CPT. Preparative GLPC was performed with a JEOL-JGC-20K apparatus.

*Preparation of Allylic Vinyl Ethers by Transetherification.*3b) Mercury(II) acetate and ethyl vinyl ether were purified according to the literature.14) Allylic alcohol (30 mmol), mercury(II) acetate (6.4 g, 20 mmol), and freshly distilled ethyl vinyl ether (150 ml) were boiled under reflux for 20—30 h under an argon atmosphere. The mixture was poured into 5% potassium hydroxide solution (30 ml) and extracted with hexane. After being dried over anhydrous potassium carbonate, the solvent was evaporated. In order to remove the mercury compounds and the unreacted starting alcohol, the remaining liquid was purified by column chromatography on alumina (Merck Aluminiumoxid 90 aktiv neutral (Aktivitätsstufe III)) using hexane as an eluent.

1-Butyl-2-propenyl Vinyl Ether (1): Bp 52 °C (bath temp, 2 Torr, 1 Torr≈133.322 Pa); IR (neat): 2975, 2945, 1635, 1615, 1320, 1195, 1180, 1045, 990, 923, 825 cm^{-1}; NMR (CCl_4): δ=0.73—1.06 (m, 3H), 1.10—1.75 (m, 6H), 3.83 (d, J=6 Hz, 1H), 3.85—4.18 (m, 1H), 4.13 (d, J=15 Hz, 1H), 5.06 (d, J=11 Hz, 1H), 5.10 (d, J=15 Hz, 1H), 5.68 (ddd, J=15, 11, 6 Hz, 1H), 6.15 (dd, J=15, 6 Hz, 1H); MS m/z (%): 140 (M$^+$, 1), 97 (12), 96 (15), 81 (9), 55 (100), 54 (13); Found: C, 77.17; H, 11.72%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

(E)-1-Butyl-2-butenyl Vinyl Ether: Bp 53 °C (bath temp, 4 Torr); IR (neat): 2940, 2860, 1634, 1455, 1320, 1180, 1033, 960, 818 cm^{-1}; NMR (CCl_4): δ=0.92 (bt, J=6 Hz, 3H), 1.10—1.63 (m, 6H), 1.72 (d, J=5 Hz, 3H), 3.80 (d, J=6 Hz, 1H), 3.75—4.08 (m, 1H), 4.09 (d, J=15 Hz, 1H), 5.25 (dd, J=6, 15 Hz, 1H), 5.55 (dq, J=15, 5 Hz, 1H), 6.13 (dd, J=6, 15 Hz, 1H); MS m/z (%): 154 (M$^+$, trace), 111 (41), 69 (96), 55 (100); Found: C, 77.74; H, 11.94%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

1-Phenyl-2-propenyl Vinyl Ether (3): Bp 75 °C (bath temp, 2 Torr); IR (neat): 1645, 1620, 1500, 1462, 1320, 1188, 1172, 990, 930, 700 cm $^{-1}$; NMR (CCl_4): δ=3.90 (dd, J=2, 7 Hz, 1H), 4.17 (dd, J=2, 14 Hz, 1H), 5.00—5.30 (m, 3H), 5.87 (ddd, J=6, 10, 15 Hz, 1H), 6.23 (dd, J=6, 14 Hz, 1H), 7.15—7.30 (m, 5H); MS m/z (%): 160 (M$^+$, 7), 117 (100), 115 (24), 104 (17), 91 (40); Found: C, 82.60; H, 7.72%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.54%.

(E)-3-Phenyl-2-propenyl Vinyl Ether (4): Bp 77 °C (bath temp, 1 Torr); IR (neat): 3040, 2870, 1640, 1620, 1500, 1457, 1320, 1194, 964, 820, 742, 692 cm^{-1}; NMR (CCl_4): δ=3.92 (dd, J=2, 6 Hz, 1H), 4.12 (dd, J=2, 15 Hz, 1H), 4.29 (d, J=5 Hz, 2H), 6.15 (dt, J=15, 5 Hz, 1H), 6.36 (dd, J=10, 15 Hz, 1H), 6.53 (d, J=15 Hz, 1H), 7.06—7.40 (m, 5H); MS m/z (%): 160 (M$^+$, 3), 117 (100), 115 (29), 91 (19); Found: C, 82.60; H, 7.67%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

2-Cyclohexenyl Vinyl Ether:[14] Bp 53 °C (bath temp, 18 Torr); IR (neat): 2940, 1635, 1612, 1190, 1065, 1012, 810 cm^{-1}; NMR (CCl_4): δ=1.00—2.23 (m, 6H), 3.97 (dd, J=1, 6 Hz, 1H), 4.22 (dd, J=1, 17 Hz, 1H), 4.20—4.47 (m, 1H), 5.70—5.98 (m, 2H), 6.36 (dd, J=6, 17 Hz, 1H); MS m/z (%): 124 (M$^+$, 6), 82 (13), 81 (100), 80 (37), 79 (43), 53 (23).

*2-Vinyl-3,4-dihydro-2*H*-pyran*:[13] Dry DMSO (50 ml) was added at 25 °C by a syringe to the washed sodium hydride (4.0 g of a 60% mineral oil dispersion, 0.10 mol). The mixture was heated at 75 °C and stirred until the hydrogen evolution ceased (*ca.* 1 h). Then, a solution of methyltriphenylphosphonium bromide (35.7 g, 0.10 mol) in warm DMSO (100 ml) was added to the methylsulfinylmethanide ion solution at 0 °C. The resulting greenish red solution was stirred at 25 °C for 15 min before freshly distilled acrylaldehyde dimer (11.2 g, 0.10 mol) was added at 25 °C. An immediate color change was observed. After stirring at 25 °C for 1 h, the reaction mixture was diluted with cold water (300 ml). The solids were removed by filtration and washed with pentane (3×100 ml). The concentrated crude product was distilled to afford the title compound (3.7 g, 34%) as a colorless liquid: Bp 57 °C (20 Torr); IR (neat): 3060, 2920, 2850, 1650, 1428, 1235, 1060, 985, 918, 900, 722 cm^{-1}; NMR (CCl_4): δ=1.47—2.13 (m, 4H), 4.09—4.32 (m, 1H), 4.45—4.63 (m, 1H), 5.03 (ddd, J=11, 10 Hz, 1H), 5.17 (ddd, J=1, 1, 15 Hz, 1H), 5.79 (ddd, J=4, 10, 15 Hz, 1H), 6.23 (d, J=6 Hz, 1H); MS m/z (%): 110 (M$^+$, 75), 95 (21), 92 (20), 81 (41), 79 (50), 54 (100).

*2-Isopropenyl-6-methyl-3,4-dihydro-2*H*-pyran*:[13] This material was prepared from methacrylaldehyde dimer as described for 2-vinyl-3,4-dihydro-2*H*-pyran in 63% yield as a colorless liquid: Bp 74 °C (28 Torr); IR (neat): 3080, 2960, 1722, 1684, 1655, 1462, 1440, 1380, 1238, 1045, 890, 800 cm^{-1}; NMR (CCl_4): δ=1.20—2.20 (m, 4H), 1.69 (s, 3H), 1.74 (s, 3H), 4.10 (dd, J=3, 8 Hz, 1H), 4.27—4.40 (bt, J=3 Hz, 1H), 4.78 (s, 1H), 4.89 (s, 1H); MS m/z (%): 138 (M$^+$, 12), 98 (20), 95 (90), 71 (49), 68 (100).

Allyl 1-Cyclohexenyl Ether:[15] To a stirred solution of Et_2AlI (1.2 M of a toluene solution, 4.2 ml, 5.0 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (20 ml) was added at 0 °C a dichloromethane solution of cyclohexanone diallyl acetal (0.98 g, 5.0 mmol). After stirring at 25 °C for 5 h, the resulting mixture was poured into 6 M sodium hydroxide solution (20 ml) and extracted with ether. The ethereal layer was washed with sat. sodium hydrogencarbonate (20 ml), dried over potassium carbonate, and concentrated. The crude product was purified by column chromatography on alumina (hexane–ether, 10 : 1) to give the ether (0.40 g, 58%) as a colorless liquid: Bp 72 °C (bath temp, 9 Torr); IR (neat): 2970, 1685, 1382, 1338, 1270, 1084, 910, 778 cm^{-1}; NMR (CCl_4): δ=1.33—1.80 (m, 4H), 1.80—2.14 (m, 4H), 4.05 (d, J=5 Hz, 2H), 4.44 (bt, J=4 Hz, 1H), 5.05 (d, J=10 Hz, 1H), 5.20 (d, J=15 Hz, 1H), 5.86 (ddt, J=10, 15, 5 Hz, 1H); MS m/z (%): 138 (M$^+$, 21), 109 (19), 105 (38), 95 (20), 94 (35), 79 (26), 55 (35), 41 (100).

Reactions between Triisobutylaluminium and Allyl Vinyl Ether Derivatives. A hexane solution of triisobutylaluminium (1.0 M, 5.0 ml, 5.0 mmol) was added to a solution of an allyl vinyl ether (2.0 mmol) in 1,2-dichloroethane (15 ml) at 25 °C under an argon atmosphere and the whole was stirred at 25 °C (60 °C) for 15 min (2 h). The mixture was diluted with ether (15 ml) and poured into 1 M hydrochloric acid (20 ml). The separated organic layer was washed with brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate).

(E)- and (Z)-4-Nonen-1-ol (2c): The crude product generated from 1-butyl-2-propenyl vinyl ether (**1**) and triisobutylaluminium was transformed into trimethylsilyl ether with *N*-(trimethylsilyl)imidazole (1.2 equiv) in dichloromethane. GLPC (5% PEG 20M, 2 m, 65 °C) indicated two peaks, T_r=16.0 min ((*Z*)-isomer, 62%) and T_r=17.5 min ((*E*)-isomer, 38%). The analytically pure samples of both isomers were prepared by preparative GLPC (20% PEG 20 M). These samples were identical to the authentic samples.[16] (*E*)-Alcohol: Bp 76 °C (bath temp, 5 Torr); IR (neat): 3350, 2940, 1470, 1380, 1055, 965 cm^{-1}; NMR (CCl_4); δ=0.90 (bt, J=6 Hz, 3H), 1.16—1.70 (m, 7H), 1.80—2.18 (m, 4H), 3.53 (t, J=7 Hz, 2H), 5.23—5.42 (m, 2H); MS m/z (%): 124 (M$^+-H_2O$, 17), 96 (27), 95 (42), 82 (51), 81 (100), 69 (32), 68 (97), 67 (65), 55 (69). (*Z*)-Alcohol: Bp 80 °C (bath temp, 5 Torr); IR (neat): 3350, 2950, 1475, 1380, 1060 cm^{-1}; NMR (CCl_4); δ=0.90 (bt, J=6 Hz, 3H), 1.04—1.78 (m, 7H), 1.80—2.23 (m, 4H), 3.52 (t, J=7 Hz, 2H), 5.05—5.48 (m, 2H); MS m/z (%): 124 (M$^+-H_2O$, 11), 96 (26), 95 (40), 82 (45), 81 (90), 68 (87), 67 (78), 55 (95), 41 (100).

(E)- and (Z)-3-Methyl-4-nonen-1-ol: GLPC analysis (10% PEG 20 M, 2 m, 100 °C) of the corresponding trimethylsilyl ethers indicated two peaks, T_r=20.0 min ((*E*)-isomer, 45%), T_r=17.9 min ((*Z*)-isomer, 55%). (*E*)-Alcohol: Bp 78 °C (bath temp, 1 Torr); IR (neat): 3350, 2990, 2950, 1460, 1376, 1050, 970 cm^{-1}; NMR (CCl_4): δ=0.88 (bt, 3H), 0.98 (d, J=6 Hz, 3H), 1.23—1.65 (m, 7H), 1.90—2.10 (m, 2H), 2.12—2.35 (m, 1H), 3.50 (t, J=7 Hz, 2H), 5.10—5.40 (m, 2H); MS m/z (%): 156 (M$^+$, 2), 138 (4), 109 (30), 95 (38), 81 (100), 69 (89); Found: C, 76.69; H, 13.20%. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%. (*Z*)-Alcohol: Bp 75 °C (bath temp, 2 Torr); IR (neat): 3360, 2980, 2940, 1462, 1052, 1000, 968 cm^{-1}; NMR (CCl_4):

δ=0.78—1.05 (m, 6H), 1.10—1.55 (m, 7H), 1.80—2.18 (m, 2H), 2.35—2.85 (m, 1H), 3.46 (t, *J*=6 Hz, 2H), 4.85—5.40 (m, 2H); MS *m/z* (%): 156 (M^+, 3), 138 (5), 109 (32), 95 (33), 81 (100), 69 (84); Found: *m/z* 156.1572. Calcd for $C_{10}H_{20}O$: M, 156.1515.

(E)-5-Phenyl-4-penten-1-ol:[17] Bp 123 °C (bath temp, 1 Torr); IR (neat): 3325, 2940, 1600, 1498, 1450, 1050, 960, 735, 688 cm^{-1}: NMR (CCl_4); δ=1.70 (tt, *J*=7, 7 Hz, 2H), 1.83 (s, 1H), 2.25 (dt, *J*=6, 7 Hz, 2H), 3.57 (t, *J*=6 Hz, 2H), 6.06 (dt, *J*=15, 6 Hz, 1H), 6.33 (d, *J*=15 Hz, 1H), 7.00—7.33 (m, 5H); MS *m/z* (%): 162 (M^+, 43), 144 (22), 143 (23), 129 (100), 117 (59), 91 (46).

3-Phenyl-4-penten-1-ol: Bp 103 °C (bath temp, 2 Torr); IR (neat): 3350, 2950, 1642, 1608, 1500, 1460, 1048, 1026, 915, 702 cm^{-1}; NMR (CCl_4): δ=1.23 (s, 1H), 1.87 (dt, *J*=6, 6 Hz, 2H), 3.23—3.65 (m, 3H), 4.94 (ddd, *J*=1.5, 1.5, 10 Hz, 1H), 4.95 (ddd, *J*=1.5, 1.5, 17 Hz, 1H), 5.89 (ddd, *J*=7, 10, 17 Hz, 1H), 6.90—7.50 (m, 5H); MS *m/z* (%): 162 (M^+, 60), 144 (40), 143 (27), 129 (89), 117 (100), 115 (49), 91 (44); Found: C, 81.20; H, 8.74%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

3-(2-Hydroxyethyl)-1-cyclohexene:[18] Bp 80 °C (bath temp, 1 Torr); IR (neat): 3325, 2920, 1650, 1450, 1045, 784, 715 cm^{-1}; NMR (CCl_4); δ=1.03—2.33 (m, 10H), 3.74 (t, *J*=6 Hz, 2H), 5.33—5.70 (m, 2H); MS *m/z* (%): 126 (M^+, 1), 108 (48), 93 (78), 81 (45), 80 (33), 79 (100), 67 (30).

4-Hydroxymethyl-1-cyclohexene: Bp 75 °C (bath temp, 2 Torr); IR (neat): 3340, 3040, 2925, 1658, 1440, 1090, 1020, 965, 784 cm^{-1}; NMR (CCl_4); δ=1.10—2.53 (m, 8H), 3.40 (d, *J*=6 Hz, 2H), 5.56 (s, 2H); MS *m/z* (%): 112 (M^+, 1), 94 (28), 81 (24), 79 (100), 53 (23); Found: *m/z* 112.0904. Calcd for $C_7H_{12}O$: M, 112.0888.

4-(1-Hydroxyethyl)-2-methyl-1-cyclohexanol: Bp 75 °C (bath temp, 2 Torr); IR (neat): 3360, 2920, 1445, 1380, 1080, 930, 782 cm^{-1}; NMR (CCl_4); δ=1.14 (d, *J*=6 Hz, 3H), 1.00—2.15 (m, 8H), 1.62 (s, 3H), 3.54 (dq, *J*=6, 6 Hz, 1H), 5.30 (s, 1H); MS *m/z* (%): 140 (M^+, 2), 122 (10), 107 (35), 93 (100), 79 (36), 67 (31); Found: *m/z* 140.1209. Calcd for $C_9H_{16}O$: M, 140.1202.

cis- and trans-2-Allyl-1-cyclohexene: TLC analysis (hexane–ethyl acetate, 5 : 1) of the product derived from the reaction of allyl 1-cyclohexenyl ether and triisobutylaluminium showed two spots, R_f=0.42 (cis-isomer, 77%) and R_f=0.33 (trans-isomer, 23%). Analytically pure samples of both isomers were prepared by preparative TLC (hexane–ethyl acetate, 5 : 1). *cis*-Isomer:[19] Bp 90 °C (bath temp, 12 Torr); IR (neat): 3400, 3100, 2940, 1647, 1452, 1260, 975, 906, 785 cm^{-1}; NMR (CCl_4): δ=1.03—1.87 (m, 10H), 1.87—2.20 (m, 2H), 3.72—3.87 (bm, 1H), 4.90 (d, *J*=10 Hz, 1H), 4.93 (d, *J*=16 Hz, 1H), 5.71 (ddt, *J*=10, 16, 6 Hz, 1H); MS *m/z* (%): 140 (M^+, trace), 122 (54), 107 (35), 98 (79), 93 (45), 81 (100). *trans*-Isomer:[19] Bp 94 °C (bath temp, 12 Torr); IR (neat): 3350, 3075, 2940, 1640, 1450, 1055, 1030, 990, 902 cm^{-1}; NMR (CCl_4): δ=0.90—2.10 (m, 11H), 2.25—2.60 (m, 1H), 2.97—3.32 (m, 1H), 5.90 (d, *J*=10 Hz, 1H), 5.93 (d, *J*=16 Hz, 1H), 5.95 (ddt, *J*=10, 16, 6 Hz, 1H); MS *m/z* (%): 140 (M^+, trace), 122 (41), 107 (17), 98 (55), 93 (43), 81 (100), 67 (43).

Reactions between Trimethylaluminium and Allyl Vinyl Ether Derivatives. A solution of an allyl vinyl ether substrate (2.0 mmol) in 1,2-dichloroethane (15 ml) was treated with a hexane solution of trimethylaluminium (1.0 M, 4.4 ml, 4.4 mmol) at 25 °C (60 °C) for 15 min (2 h). The resulting mixture was diluted with ether (15 ml), and poured into 1 M hydrochloric acid (20 ml). The ethereal extracts were washed with brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate).

*(E)- and (Z)-5-Decen-2-ol (**2a**)*: The product was converted into trimethylsilyl ether, whose *E*/*Z* ratio was determined by GLPC (5% PEG 20 M, 2 m, 75 °C). GLPC showed a peak at 11.2 min, corresponding to (*Z*)-1-methyl-3-nonenyl trimethylsilyl ether (53%) and a peak at 12.3 min, corresponding to the (*E*)-isomer (47%). The authentic samples of both isomers were prepared by methylation of (*E*)- and (*Z*)-4-nonenal with MeMgI in THF. (*E*)-Alcohol: Bp 83 °C (bath temp, 5 Torr); IR (neat): 3350, 2940, 1470, 1460, 1375, 1120, 1080, 966 cm^{-1}; NMR (CCl_4); δ=0.89 (bt, *J*=5 Hz, 3H), 1.13 (d, *J*=6 Hz, 3H), 1.10—1.60 (m, 7H), 1.80—2.18 (m, 4H), 3.66 (tq, *J*=6, 6 Hz, 1H), 5.23—5.42 (m, 2H); MS *m/z* (%): 156 (M^+, 12), 138 (19), 109 (26), 95 (88), 82 (82), 81 (72), 71 (54), 68 (57), 67 (100); Found: C, 76.81; H, 13.09%. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%. (*Z*)-Alcohol: Bp 59 °C (bath temp, 1 Torr); IR (neat): 3370, 2950, 1465, 1378, 1124, 1078, 955 cm^{-1}; NMR (CCl_4): δ=0.90 (bt, *J*=5 Hz, 3H), 1.13 (t, *J*=6 Hz, 3H), 1.10—1.53 (m, 7H), 1.80—2.20 (m, 4H), 3.68 (tq, *J*=6, 6 Hz, 1H), 5.07—5.47 (m, 2H); MS *m/z* (%): 156 (M^+, 9), 138 (11), 109 (17), 95 (58), 82 (58), 81 (56), 67 (90), 55 (79), 45 (100); Found: C, 76.74; H, 13.07%. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%.

(E)-6-Phenyl-5-hexen-2-ol:[20] Bp 118 °C (bath temp, 1 Torr); IR (neat): 3375, 2950, 1602, 1498, 1452, 1125, 1068, 960, 740, 690 cm^{-1}; NMR (CCl_4): δ=1.13 (d, *J*=6 Hz, 3H), 1.40—1.70 (m, 2H), 1.80 (s, 1H), 2.15—2.43 (m, 2H), 3.74 (tq, *J*=6, 6 Hz, 1H), 6.05 (dt, *J*=15, 6 Hz, 1H), 6.30 (d, *J*=15 Hz, 1H), 7.00—7.30 (m, 5H); MS *m/z* (%): 176 (M^+, 30), 158 (13), 143 (32), 129 (100), 118 (31), 117 (45).

4-Phenyl-5-hexen-2-ol: Bp 86 °C (bath temp, 1 Torr); IR (neat): 3350, 3150, 3050, 1602, 1496, 1125, 910, 705 cm^{-1}; NMR (CCl_4): δ=1.08, 1.14 (d, *J*=6 Hz, total 3H diastereomeric mixture), 1.20 (bs, 1H), 1.73 (t, *J*=7 Hz, 2H), 3.16—3.90 (m, 2H), 4.80—5.20 (m, 2H), 5.60—6.25 (m, 1H), 6.88—7.30 (m, 5H); MS *m/z* (%): 176 (M^+, 1), 158 (13), 143 (50), 132 (53), 129 (23), 118 (26), 117 (100), 91 (16); Found: C, 81.88; H, 9.21%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

1-(2-Cyclohexenyl)-2-propanol: Bp 78 °C (bath temp, 1 Torr); IR (neat): 3350, 2940, 1650, 1450, 1372, 1126, 1014, 716, 672 cm^{-1}; NMR (CCl_4): δ=1.18 (d, *J*=6 Hz, 3H), 1.08-2.43 (m, 10H), 3.70—4.00 (m, 1H), 5.38—5.70 (m, 2H); MS *m/z* (%): 140 (M^+, 1), 122 (86), 107 (91), 93 (52), 81 (100), 79 (74); Found: C, 76.90; H, 11.79%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

4-(1-Hydroxyethyl)-1-cyclohexanol: Bp 70 °C (bath temp, 1 Torr); IR (neat): 3360, 3040, 2910, 1658, 1440, 1370, 1136, 1060, 942, 854, 650 cm^{-1}; NMR (CCl_4): δ=1.15 (d, *J*=6 Hz, 3H), 1.10—2.30 (m, 8H), 3.50 (q, *J*=6 Hz, 1H), 5.57 (s, 2H); MS *m/z* (%): 126 (M^+, trace), 108 (27), 93 (32), 79 (100), 78 (20), 67 (28); Found: C, 75.94; H, 11.44%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

4-(1-Hydroxy-1-methylethyl)-2-methyl-1-cyclohexanol: Bp 97 °C (bath temp, 2 Torr); IR (neat): 3390, 2980, 2925, 1440, 1378, 1150, 940, 910, 785 cm^{-1}; NMR (CCl_4): δ=1.13 (s, 6H), 1.10—2.27 (m, 8H), 1.60 (s, 3H), 5.30 (s, 1H); MS *m/z* (%): 154 (M^+, trace), 136 (16), 121 (21), 93 (86), 92 (36), 81 (32), 59 (100); Found: *m/z* 154.1352. Calcd for $C_{10}H_{18}O$: M, 154.1358.

*(E)- and (Z)-6-Undecen-3-ol (**2b**)*: The reaction was carried out with triethylaluminium as described for trimethylaluminium to give the mixture of (*E*)- and (*Z*)-4-nonen-1-ol (**2c**) and the ethylated alcohols **2b**. The crude product was separated by preparative TLC (hexane–ether, 5 : 1). The isomeric alcohols **2b** were transformed into trimethylsilyl ethers. GLPC analysis (5% PEG 20 M, 2 m, 75 °C) of the trimethylsilyl ethers showed two peaks, T_r=19.8 min ((*E*)-isomer, 42%) and T_r=18.2 min ((*Z*)-isomer, 58%). The authentic samples of both isomers were prepared by ethylation of (*E*)- and (*Z*)-4-nonenal with EtMgBr in THF. (*E*)-Alcohol: Bp 79 °C (bath temp, 3 Torr); IR (neat): 3360, 2960, 1470, 970 cm^{-1}; NMR (CCl_4); δ=0.91 (t, *J*=7 Hz, 6H), 1.15—1.58 (m,

8H), 1.68 (s, 1H), 1.80—2.23 (m, 4H), 3.39 (tt, J=6, 6 Hz, 1H), 5.23—5.43 (m, 2H); MS m/z (%): 170 (M^+, 2), 152 (11), 123 (14), 109 (25), 96 (42), 81 (74), 67 (100); Found: C, 77.49; H, 13.24%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%. (Z)-Alcohol: Bp 68 °C (bath temp, 1 Torr); IR (neat): 3350, 2940, 1460, 1114, 964 cm^{-1}; NMR (CCl_4): δ=0.93 (t, J=7 Hz, 6H), 1.06—1.62 (m, 9H), 1.83—2.24 (m, 4H), 3.44 (tt, J=6, 6 Hz, 1H), 5.10—5.46 (m, 2H); MS m/z (%): 170 (M^+, 1), 123 (10), 109 (18), 96 (33), 81 (61), 67 (100); Found: C, 77.36; H, 13.30%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%.

1-(2-Cyclohexenyl)-4-phenyl-3-butyn-2-ol: To a stirred hexane solution of PhC≡CLi prepared from phenylacetylene (0.51 g, 5.0 mmol) and butyllithium (1.5 M of a hexane solution, 3.3 ml, 5.0 mmol) was added at 0 °C a hexane solution of diethylaluminium chloride (1.0 M, 5.0 ml, 5.0 mmol) and the whole was stirred at 25 °C for 20 min. After addition of 1,2-dichloroethane (15 ml), a solution of 2-cyclohexenyl vinyl ether (0.25 g, 2.0 mmol) in 1,2-dichloroethane (4 ml) was added to the aluminium reagent at 25 °C and the mixture was stirred for 15 min. After the usual workup, the crude product was purified by preparative TLC (hexane–ether, 5 : 1) to give the desired adduct in 88% yield (0.40 g) as a pale yellow liquid: Bp 130 °C (bath temp, 0.1 Torr); IR (neat): 3320, 2920, 2350, 1650, 1600, 1490, 1442, 1012, 750, 686 cm^{-1}; NMR (CCl_4): δ=1.05—2.62 (m, 10H), 4.16 (t, J=7 Hz, 1H), 5.46—5.74 (m, 2H), 7.13—7.50 (m, 5H); MS m/z (%): 226 (M^+, 1), 225 (12), 183 (19), 167 (19), 131 (100), 103 (25), 95 (35); Found: C, 84.87; H, 8.01%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%.

1-(2-Cyclohexenyl)-3-decen-1-ol: A solution of 2-cyclohexenyl vinyl ether (0.25 g, 2.0 mmol) in 1,2-dichloroethane (15 ml) was treated at 25 °C for 1.5 h with a hexane solution of (E)-1-octenyldiisobutylaluminium prepared from 1-octyne (0.60 g, 5.5 mmol) and diisobutylaluminim hydride (3.2 ml of a 1.7 M toluene solution, 5.5 mmol). After the usual workup and purification by silica-gel column chromatography gave the title alcohol in 40% yield (0.19 g) as a colorless liquid: Bp 95 °C (bath temp, 0.05 Torr); IR (neat): 3350, 2925, 1450, 960, 715 cm^{-1}; NMR (CCl_4); δ=0.89 (bt, J=6 Hz, 3H), 1.06—2.35 (m, 20H), 4.06 (dt, J=6, 6 Hz, 1H), 5.33—5.70 (m, 4H); MS m/z (%): 236 (M^+, 14), 218 (33), 151 (66), 134 (46), 109 (41), 95 (87), 94 (69), 81 (100); Found: C, 81.21; H, 12.05%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

Claisen Rearrangement of Allyl Vinyl Ether Derivatives Promoted by Et_2AlSPh (Method A). A solution of thiophenol (0.55 g, 5.0 mmol) in hexane (3 ml) was added at 25 °C to a hexane solution of triethylaluminium (1.0 M, 5.0 ml, 5.0 mmol) and the mixture was stirred at the same temperature for 20 min. After an addition of 1,2-dichloroethane (5 ml), a solution of allyl vinyl ether substrate (2.0 mmol) in 1,2-dichloroethane (3 ml) was added to the aluminium reagent at 25 °C and the whole was stirred for an appropriate time, as listed in Table 3. The reaction mixture was diluted with ether (20 ml) and poured into 1 M hydrochloric acid. The organic layer was separated, combined with three additional extracts of the aqueous layer, and washed with brine (2×20 ml). The ethereal layer was dried over anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography or preparative TLC (hexane–ethyl acetate).

Claisen Rearrangement of Allyl Vinyl Ether Derivatives Promoted by Et_2AlCl-PPh_3 System (Method B). A mixture of Et_2AlCl (1.0 M of hexane solution, 4.0 ml, 4.0 mmol) and triphenylphosphine (1.2 g, 4.4 mmol) was dissolved in 1,2-dichloroethane (5 ml) at 25 °C and stirred for 10 min. A solution of allyl vinyl ether substrate (2.0 mmol) in 1,2-dichloroethane (10 ml) was added to the reagent at 25 °C and the whole was stirred at the same temperature for an appropriate time, as listed in Table 3. The resulting mixture was diluted with ether (20 ml) and poured into 1 M hydrochloric acid (20 ml). The separated organic layer was washed with brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography or preparative TLC (hexane–ethyl acetate).

A small aliquot was treated with diisobutylaluminium hydride to yield the alcohols. The E/Z ratios of these aldehydes were calculated from GLPC peak area of the corresponding trimethylsilyl ethers of the alcohols.

(E)-*4-Nonenal*:[16] Bp 80 °C (bath temp, 2 Torr); IR (neat): 2940, 2725, 1730, 1470, 968 cm^{-1}; NMR (CCl_4); δ=0.91 (t, J=6 Hz, 3H), 1.06—1.50 (m, 4H), 1.76—2.13 (m, 2H), 2.13—2.53 (m, 4H), 5.20—5.43 (m, 2H), 9.66 (s, 1H); MS m/z (%): 140 (M^+, trace), 122 (8), 98 (20), 96 (35), 84 (100), 83 (49), 67 (43).

(Z)-*4-Nonenal*:[16] Bp 76 °C (bath temp, 2 Torr); IR (neat): 2970, 2940, 2720, 1730, 1470, 1415, 1055 cm^{-1}; NMR (CCl_4): δ=0.93 (t, J=6 Hz, 3H), 1.10—1.50 (m, 4H), 1.80—2.16 (m, 2H), 2.16—2.52 (m, 4H), 5.15—5.45 (m, 2H), 9.69 (s, 1H); MS m/z (%): 140 (M^+, trace), 122 (5), 98 (12), 96 (19), 84 (49), 67 (33), 55 (64), 41 (100).

(E)-*3-Methyl-4-nonenal*: Bp 72 °C (bath temp, 2 Torr); IR (neat): 3010, 2960, 2750, 1740, 1466, 1385, 976 cm^{-1}; NMR (CCl_4): δ=0.75—1.05 (m, 3H), 1.03 (d, J=6 Hz, 3H), 1.05—1.40 (m, 4H), 1.83—2.00 (m, 2H), 2.17—2.33 (m, 2H), 2.40—2.87 (m, 1H), 5.20—5.40 (m, 2H), 9.60 (t, J=2 Hz, 1H); MS m/z (%): 154 (M^+, 4), 111 (22), 110 (20), 98 (74), 97 (99), 69 (89), 55 (100); Found: C, 77.97; H, 11.86%. Calcd for $C_{10}H_{18}O$: C, 77.87, H, 11.76%.

(Z)-*3-Methyl-4-nonenal*: Bp 70 °C (bath temp, 2 Torr); IR (neat): 2960, 2700, 1728, 1455, 1255, 725 cm^{-1}; NMR (CCl_4): δ=0.76—1.08 (m, 3H), 1.04 (d, J=6 Hz, 3H), 1.13—1.60 (m, 4H), 1.90—2.07 (m, 2H), 2.30 (dd, J=2, 7 Hz, 2H), 2.75—3.18 (m, 1H), 5.08—5.45 (m, 2H), 9.57 (t, J=2 Hz, 1H); MS m/z (%): 154 (M^+, 2), 139 (10), 111 (20), 110 (20), 98 (67), 97 (83), 69 (85), 55 (100); Found: C, 77.94; H, 11.98%. Calcd or $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

(E)-*5-Pheyl-4-pentenal*: Bp 118 °C (bath temp, 2 Torr); IR (neat): 3050, 2920, 2840, 2740, 1725, 1602, 1498, 1452, 962, 742, 690 cm^{-1}; NMR (CCl_4): δ=2.40—2.60 (m, 4H), 6.03 (m, 1H), 6.34 (d, J=15 Hz, 1H), 7.00—7.30 (m, 5H), 9.70 (s, 1H); MS m/z (%): 160 (M^+, 38), 132 (11), 129 (11), 117 (37), 104 (100), 91 (39). The compound was identical with the authentic sample.[21]

3-Phenyl-4-pentenal: Bp 86 °C (bath temp, 3 Torr); IR (neat): 3050, 2840, 2740, 1730, 1498, 1460, 915, 758, 700 cm^{-1}; NMR (CCl_4): δ=2.69 (dd, J=2, 6 Hz, 2H), 3.85 (dq, J=6, 6 Hz, 1H), 4.93 (d, J=16 Hz, 1H), 4.98 (d, J=10 Hz, 1H), 5.90 (ddd, J=6, 10, 16 Hz, 1H), 6.97—7.30 (m, 5H), 9.57 (s, 1H); MS m/z (%): 160 (M^+, 24), 142 (32), 132 (24), 131 (27), 117 (100), 115 (36), 91 (43); Found: C, 82.62; H, 7.59%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

3-Cyclohexene-1-carbaldehyde:[13] Bp 97 °C (bath temp, 20 Torr); IR (neat): 2940, 2710, 1732, 1662, 1442, 1372, 1240, 1044 cm^{-1}; NMR (CCl_4): δ=1.00—2.53 (m, 6H), 5.57 (s, 1H), 9.55 (s, 1H); MS m/z (%): 110 (M^+, 72), 95 (28), 92 (37), 81 (78), 79 (100), 67 (41), 54 (51), 53 (52).

4-Acetyl-2-methyl-1-cyclohexene:[13] Bp 88 °C (bath temp, 25 Torr); IR (neat): 2940, 1718, 1445, 1358, 1168, 775 cm^{-1}; NMR (CCl_4): δ=1.10—2.60 (m, 7H), 1.63 (s, 3H), 2.06 (s, 3H), 5.28 (s, 1H); MS m/z (%): 138 (M^+, 10), 95 (100), 79 (16), 67 (28), 43 (65).

2-Cyclohexene-1-acetaldehyde:[18] Bp 75 °C (bath temp, 20 Torr); IR (neat): 3040, 2950, 2740, 1730, 1445, 720 cm^{-1}; NMR (CCl_4): δ=1.03—2.10 (m, 6H), 2.30 (dt, J=1, 6 Hz, 1H), 2.38 (d, J=1 Hz, 1H), 2.43—2.83 (m, 1H), 5.25—5.80 (m, 2H), 9.70 (d, J=1 Hz, 1H); MS m/z (%): 124 (M^+, 21), 96 (19), 95 (40), 81 (56), 80 (100), 79 (51), 67 (71).

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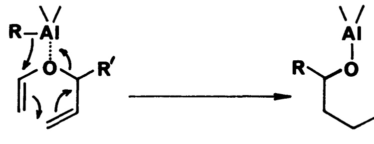
10) We are tempted to assume the following mechanism (Scheme 3): (1) The oxygen atom of an allyl vinyl ether coordinates to an organoaluminium compound, and (2) [3,3] sigmatropic rearrangement occurs and a nucleophilic moiety R or H on the aluminium atom adds to the aldehydic carbon concomitantly.



5

Scheme 3.

In the case of Et_2AlSPh, both diethylaluminium and SPh parts are eliminated from **5** (R=SPh) upon acidic workup to afford the regular Claisen rearrangement product, or γ,δ-unsaturated aldehyde.

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