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Reactivity of 3-Nitro-5,6-Dihydro-4H-Pyran with Organoalanes: Preparation of (E)-α, β-Ethylenic Aldehydes.

Rita Menicagli,* Vito Guagnano, Corrado Malanga

Dipartimento di Chimica e Chimica Industriale and Centro di Studi del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Via Risorgimento 35, 56126 Pisa - Italy

Abstract: 3-Nitro-5,6-dihydro-4H-pyran reacts with organoalanes and gives 1, 4 addition products. In suitable hydrolysis conditions, the reaction results in the formation of aldehydes that are C_1-homologues of the chain transferred by the alane.

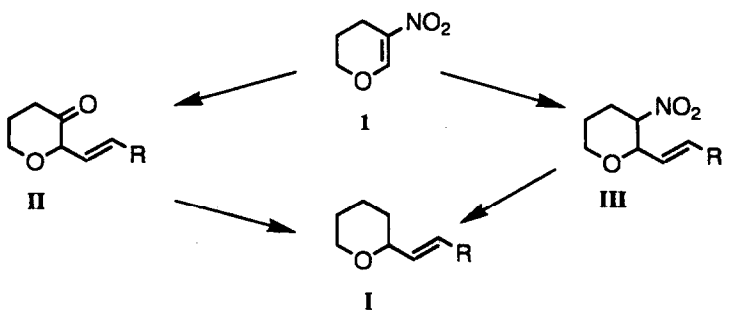
The reaction of organoaluminum compounds with α-nitroolefins provides a powerful synthetic tool in organic chemistry, allowing the preparation of a wide number of functionalized intermediates. Depending on their nature, organoalanes are able to transfer to α–nitroolefins alkyl, 1-alkenyl, 1-alkynyl, allyl, benzyl and phenyl groups.[1]

The regio- and chemocontrolled conjugate addition takes place under mild experimental conditions and gives products in very good yields.[1] Moreover, either β-substituted nitro derivatives[1a] or the corresponding carbonyl compounds[1b-d] can be obtained from the aluminum nitronate intermediates depending on the hydrolysis conditions.

The excellent results achieved in these studies prompted us to extend the investigation to β-hetero substituted α-nitroolefins and, in this context, the reactivity of 3-nitro-5,6-dihydro-4H-pyran (**1**) towards organoalanes was examined.

Such a peculiar β–nitroenolether was chosen owing to our increasing interest towards structural analogues (I) of the Rose Oxide.[2] If **1** reacted with organoalanes in the usual way, 2-[(E) alk-1'-enyl]tetrahydropyran-3-ones (**II**) or the corresponding nitro derivatives **III**, potential intermediates in the synthesis of **I**, could be obtained (Scheme).

Scheme



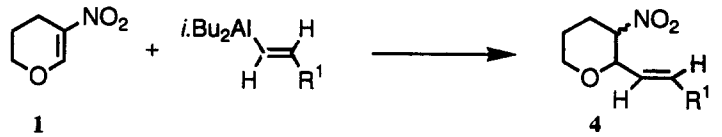
The preparation of **1** was performed (85% yield)[3] according to the procedure described by Kogan for the synthesis of 1-ethoxy-2-nitroethylene.[4]

The reaction of **1** with triisobutylaluminum (*i*.Bu3Al), followed by hydrolysis with 0.2N HCl (Procedure A),[3] provided a mixture of 2-*i*.butyl-3-nitrotetrahydropyran (**2**) and 2-*i*.butyltetrahydropyran-3-one (**3**)[3] [70 and 30% (glc) respectively]. Chemically pure **2** was obtained by (92% glc, 82% isolated yield) hydrolyzing the reaction mixture with a saturated aqueous solution of NH_4Cl.

The reactivity of **1** with dialkyl, 1-alkenylalanes was also tested in order to establish if the regio- and chemoselective transfer of the unsaturated chain occured here too.

Dialkyl, 1-alkenylalanes, prepared according to reported procedures,[5] selectively transfer to the C_2 of **1** the unsaturated chain and provide, after 0.2N HCl hydrolysis, the *cis/trans* diastereoisomeric mixtures of the corresponding 2-[(E)-alk-1'-enyl]-3-nitrotetrahydropyrans (**4a-c**) in satisfactory yields (Table 1).

Table 1. Reactions of **1** with (E)-Diisobutyl, l-alkenylalanes: Preparation of 2-[(E)-Alk-1'-enyl]-3-nitrotetrahydropyrans (**4a-c**).



1 **4**

R^1	**4**	*trans/cis* ratio[a]	Yield %[b]
n.Bu	**a**	36/64	90
t.Bu	**b**	32/68	88
n.Hex	**c**	40/60	85

[a] Glc evaluation; [b] Isolated yield.

Since these results pointed out that **1** reacts with alanes in the same fashion of α-nitroolefins, 2-[(E)-alk-1'-enyl]tetrahydropyran-3-ones seemed to be achievable from the corresponding aluminum nitronates.[1b-d]

In the experimental conditions suitable to carry out the solvolytic Nef reaction (3N HCl),[1b-d] starting from aluminum 2-*i*.butyltetrahydropyran-3-nitronate, only traces of the ketone **3** arose and the reaction resulted in the formation (70%, glc) of 3-methylbutanal.[3]

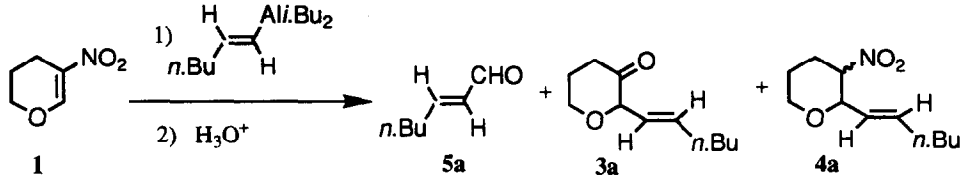
A mixture of 2-*i*.butyltetrahydropyran-3-one (**3**) and **2** was obtained when the hydrolysis was carried out with 0.8N HCl; pure **3** was recovered in 56% yield after flash chromatography. However, many attempts to convert aluminum 2-[(E)-alk-1'-enyl]tetrahydropyran-3-nitronates into the corresponding 2-[(E)-alk-1'-enyl]tetrahydropyran-3-ones, failed.

The unexpected formation of 3-methylbutanal, that arises from an indirect formylation of an Al-C bond[3] suggested gaining a deeper insight into the reaction to check its applicability to the synthesis of (E)-α, β–ethylenic aldehydes.

In order to find the best hydrolysis conditions, the conversion of aluminum 2-[(E)-hex-1'-enyl]tetrahydropyran-3-nitronate into (E)-hept-2-enal (**5a**) was investigated (Table 2). The reported data (Table 2) decidedly show that the highest yield (92% glc) in **5a** was obtained when the ethereal solution of the aluminum nitronate was treated with a mixture of 3N HCl and diethyl ether (Procedure B, see Experimental Section). This hydrolysis technique proved to be completely reproducible and was employed to prepare the aldehydes **5a-c** in satisfactory yields (70-80%) (Table 3, runs 1-3).

Surprisingly, the same procedure failed for the synthesis of (E)-non-2-enal (**5d**): here 2-[(E)-oct-1'-enyl]-

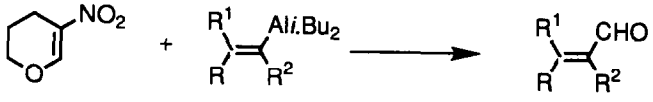
Table 2. Dependence of (E)-Hept-2-enal (**5a**) Yield on the Hydrolysis Conditions of Aluminum 2-[(E)-hex-1'-enyl]tetrahydropyran-3-nitronate.



Run	Product Distribution %[a]		
	5a	**3a**	**4a**
1[b,c]	86	5[d]	9
2[b,c]	46	13	41
8[b,e,f]	71	9	20
4[b,e,f]	73	7	20
5[b,c,g]	70	12	18
6[b,e,g]	89	8	3
7[b,e,g]	88	8	4
8[e,g,h]	92	3	-

[a] Glc evaluation; [b] 3N HCl, 0 °C; [c] The hydrolyzing solution was dropped into the reaction mixture; [d] See note 6; [e] The reaction mixture was poured into the hydrolyzing solution; [f] See ref. 3; [g] The aluminum nitronate was dissolved into ether (see Experimental Section); [h] A mixture of 3N HCl/Et_2O, cooled at 0 °C, was used (see Experimental Section).

Table 3. Reactions of **1** with (E)-Diisobutyl, 1-alkenylalanes: Preparation of (E)-α, β-Ethylenic Aldehydes (**5a-h**).



Run	5		Hydrolysis	Yield, %[a]
1	R=*n*.Bu, R^1=R^2=H	(**a**)	B	71
2	R=*t*.Bu, R^1=R^2=H	(**b**)	B	80
3	R=R^2=Et, R^1=H	(**c**)	B	72
4	R=*n*.Hex, R^1=R^2=H	(**d**)	C	70
5	R=R^2=*n*.Pr, R^1=H	(**e**)	C	70
6	R=*n*.Dec, R^1=R^2=H	(**f**)	C	73
7	R=H, R^1=*t*.Bu, R^2=SiMe3	(**g**)	C	70
8	R=H, R^1=Ph, R^2=SiMe3	(**h**)	C	85[b]

[a] Isolated yields; [b] E/Z = 87/13.

3-nitrotetrahydropyran (**4c**) was the main (80%, glc) reaction product along with a smaller amount (20%, glc) of **5d**. Since this upsetting result could be due to the more hydrophobic nature of the nitronate, in a further experiment, the reaction solvents were removed, THF was added and the nitronate was hydrolyzed with 3N HCl dissolved in the same solvent (Procedure C, see Experimental Section).

Under these conditions (E)-non-2-enal (**5d**), (E)-2-*n*.propylhex-2-enal (**5e**) and (E)-tridec-2-enal (**5f**) were obtained in good yields (70-73%) (Table 3, runs 4-6).

The *anti*-hydroalumination[7] of 1-*t*.butyl-[8] and 1-phenyl-2-trimethylsilylacetylene followed by reaction with **1** and by hydrolysis according to procedure C, provided an interesting approach to stereoisomerically pure (E)-2-trimethylsilyl-4,4-dimethylpent-2-enal (**5g**)[10] and 87% stereoisomerically pure (E)-2-trimethylsilyl-3-phenylpropenal (**5h**)[10, 11] (Table 3, runs 7, 8).

It is noteworthy that these last reactions could provide an elegant route to the synthesis of (Z)-4,4-dimethylpent-2-enal and (Z)-cinnamaldehyde by a stereocontrolled protodesilylation of **5g** and (E)-**5h** respectively.[12]

Since in comparable experimental conditions, no formylated products arise by reacting 1-ethoxy-2-nitroethylene[4] rather than **1** with alanes,[3] it is reasonable to join the success of the described reaction to the structure of **1**.

Experimental Section

Materials and Instruments

Hexane, diethyl ether, benzene and tetrahydrofuran were purified by standard methods and distilled from $LiAlH_4$ before use; methylene chloride was distilled from P_2O_5. Hex-1-yne, hex-3-yne, 3,3-dimethylbut-1-yne, oct-1-yne, oct-4-yne, 1-phenyl-2-trimethylsilylacetylene (Fluka) and dodec-1-yne (Aldrich) were used without further purification. *i*.Bu_3Al and the 1.0 M hexane solution of *i*.Bu_2AlH (DIBAH) are commercially available (Fluka).

Glc analyses were performed on a Perkin Elmer 8500 instrument (both a DB1, 12m x 0.22mm and a DBWAX, 30m x 0.32mm capillary columns were used) equipped with a flame ionization detector and using He as carrier gas. ^1H and ^{13}C NMR (200 and 50 MHz respectively) spectra were recorded on a Varian Gemini 200 spectrometer; all NMR data were obtained using $CDCl_3$ solutions. Chemical shifts (δ ppm) are referred to tetramethylsilane (TMS) (^1H NMR), if not otherwise stated, or $CDCl_3$ (^{13}C NMR) as internal reference. IR spectra (ν, cm^{-1}) were recorded on a Perkin Elmer FT-IR 1760X spectrophotometer, using liquid films. Mass spectra (m/z, I%) were taken on VG-Analytical 7070 GC-MS instrument. All isolated compounds gave satisfactory elemental analyses (± 0.4%). Analytical TLC were performed on silica gel (Merck, SiO_2 60); purifications *via* flash chromatography were carried out on silica gel (Merck, SiO_2 60, 230-400 mesh). All the reactions were carried out in dry apparatus under Argon.

Reaction of 1 with i.Bu3Al. A CH_2Cl_2 solution of **1** (7.6 mmol) was added dropwise to a cooled (0 °C) hexane solution (30 ml) of *i*.Bu_3Al (9.9 mmol). After 15 min. at 0 °C and 45 min. at room temperature, the reaction mixture was rapidly poured into a stirred saturated solution of NH_4Cl. Organic products were extracted into CH_2Cl_2, washed with brine and dried (Na_2SO_4). After the removal of the solvent, pure *trans*- **2** and 64% stereoisomerically pure *cis*- **2**, obtained by flash chromatography (petroleum ether/ethyl acetate 95/5), showed:

trans-**2**: ^1H NMR, 4.29 (ddd, 1H, J=11.5, 9.4, 4.4 Hz, >CH-NO_2), 3.98-3.90 (m, 1H, >CH-*i*.Bu), 3.68 (td, 1H, J=9.6, 2.2 Hz, -C*H*H-O-), 3.56-3.36 (m, 1H, -CH*H*-O-), 2.50-1.10 (m, 10H), 0.90 (t, 6H, J=6.7 Hz, 2-CH_3); ^{13}C NMR, 86.98, 76.83, 67.51, 41.21, 29.40, 24.40, 23.97, 23.54, 21.22; m/z (I%), 141(M^+-46, 4), 140(7), 131(6), 125(9), 102(26), 98(64), 84(36), 71(100), 57(23), 55(41), 43 (59), 41(75), 39(30).

cis-**2**: m/z (I%), 141(M^+-46, 6), 130(6), 114(9), 102(14), 98(16), 83(19), 84(31), 71(96), 57(45), 55 (41), 43 (61), 41(100), 39(42).

cis/trans-**2**: (64/36): ^1H NMR, 4.60-4.51 (m, 0.64H, >CH-NO_2), 4.29 (ddd, 0.36H, J=11.5, 9.4, 4.4 Hz, >CH-NO_2), 4.15-3.90 (m, 1H, >CH-*i*.Bu), 3.79-3.60 (m, 1H, -C*H*H-O-), 3.56-3.36 (m, 1H, -CH*H*-O-), 2.60-1.20 (m, 7H), 0.90 (t, 2.16 H, J=6.7 Hz, 2 -CH_3), 0.89 (t, 3.84 H, J=6.8 Hz, 2 -CH_3); ^{13}C NMR, (86.98, 82.76), (76.82, 74.89), (67.50, 67.30), (41.20, 40.06), (29.38, 26.28), (24.40, 24.26), (23.97, 23.10), (23.53, 21.87), (21.24, 20.53); IR, 1547, 1325, 1051, 1029.

Reaction of 1 with (E)-diisobutyl, 1-alkenylaluminum. In a typical run, a CH_2Cl_2 solution of **1** was added dropwise to a cooled (0 °C) hexane solution of the suitable organoalane (1 molar equivalent). The resulting mixture was stirred at 0 °C for 10 min., at room temperature for additional 45 min. and then hydrolyzed according to the following (A, B, or C) procedures.

Procedure A: The reaction mixture was poured into a flask containing a cooled (0 °C), vigorously stirred 0.2N HCl solution. Organic products were extracted into CH_2Cl_2, washed with brine and dried (Na_2SO_4). The solvent was evaporated and the crude reaction products were purified by flash chromatography; this technique allowed to obtain >80% diastereoisomerically pure samples of *trans*-

4a-c and *cis*-**4b-c** but it failed for *cis*-**4a**.

Procedure B: The reaction solvents were evaporated under reduced pressure (20 and then 10^{-2} Torr) and the residue nitronate was dissolved into Et_2O. The solution was poured into a cooled (0 °C) vigorously stirred 3N HCl/Et_2O (2.5/1, v/v) mixture and then extracted with pentane. The organic phase was washed with brine and dried. The solvent was evaporated and distillation of the residue gave chemically pure samples of **5a-c**.

Procedure C: Likewise procedure B but THF was used instead of Et_2O. Crude **5d-h** were purified by flash chromatography.

The pure products (hydrolysis procedure, yield, flash chromatography eluent or bp) showed:

2-(E)-Hex-1'-enyl-3-nitrotetrahydropyran (**4a**) (A, 90%, petroleum ether/ethyl acetate 90/10);

trans-**4a**: ^{1}H NMR, 5.80 (dt, 1H, J=15.4, 6.7 Hz, =CH-*n*.Bu), 5.40 (ddt, 1H, J=15.4, 7.5, 1.4 Hz, -C*H*=CH-*n*.Bu), 4.36 (ddd, 1 H, J=11.6, 9.4, 4.3 Hz, >CH-NO_2), 4.16-3.94 (m, 2H, >C*H*-CH=, -C*H*H-O-), 3.66-3.44 (m, 1H, -CH*H*-O-), 2.50-1.60 [m, 6H, -(CH_2)$_2$-CH_2-O-, =CH-CH_2-], 1.50-1.10 [m, 4H, -(CH_2)$_2$-Me], 0.87 (t, 3H, J=7.1 Hz, -CH_3); ^{13}C NMR, 137.82, 124.80, 86.64, 79.82, 67.35, 31.61, 30.55, 28.68, 23.92, 21.75, 13.48; m/z (I%), 213(M^+, 2), 183(4), 167(30), 166(100), 137 (21), 123(12), 111(16), 109(43), 102(33), 97(29), 83(39), 71(31), 69(27), 55(72), 41(88); IR, 1673, 1550, 1078, 1029, 972.

cis-**4a**: m/z (I%), 167(M^+-46, 12), 166(44), 137(16), 123(13), 109(34), 97(21), 83(28), 67(24), 57(34), 55 (71), 43(44), 41(100).

2-[(E)-3,3-Dimethylbut-1-enyl]-3-nitrotetrahydropyran (**4b**) (A, 88%, petroleum ether/ethyl acetate 90/10);

trans-**4b**: ^{1}H NMR, 5.80 (d, 1H, J=15.7 Hz, =CH-*t*.Bu), 5.31 (dd, 1H, J=15.7, 7.5 Hz, -C*H*=CH-*t*.Bu), 4.34 (ddd, 1H, J=11.6, 9.3, 4.3 Hz, >CH-NO_2), 4.12-3.94 (m, 2H, >C*H*-CH=, -C*H*H-O), 3.62-3.40 (m, 1H, -CH*H*-O-), 2.50-1.60 [m, 4H, -(CH_2)$_2$-CH_2-O-], 0.97 [s, 9H, -C(CH_3)$_3$]; ^{13}C NMR, 148.28, 120.02, 86.87, 80.18, 67.45, 32.89, 28.91, 28.65, 23.98; m/z (I%), 183(M^+-30, 16), 167(17), 166 (50), 152(46), 151(56), 137(52), 113(66), 97(71), 83(81), 69(51), 57(66), 55(100).

cis-**4b**: ^{1}H NMR, 5.85 (dd, 1H, J=15.8, 0.8 Hz, =CH-*t*.Bu), 5.43 (dd, 1H, J= 15.8, 6.2 Hz, -C*H*=CH-*t*.Bu), 4.61 (dt, 1H, J=4.0, 3.8 Hz, >CH-NO_2), 4.30-4.18 (m, 1H, >C*H*-CH=), 4.16-4.00 (m, 1H, -C*H*H-O-), 3.68-3.46 (m, 1H,-CH*H*-O-), 2.48-1.46 [m, 4H, -(CH_2)$_2$-CH_2-O-], 1.00 [s, 9H, -C(CH_3)$_3$]; ^{13}C NMR, 146.42, 119.30, 83.17, 76.87, 66.55, 32.92, 29.04, 25.58, 20.52; m/z (I%), 167(M^+-46, 16), 166(100), 151(64), 137(49), 132(41), 129(39), 111(34), 97(56), 83(76), 69(39), 67(37), 55 (76); IR, 1667, 1548, 1091, 1053, 976.

2-[(E)-Oct-1'-enyl]-3-nitrotetrahydropyran (**4c**) (A, 85%, petroleum ether/ ethyl acetate 90/10);

trans-**4c**: ^{1}H NMR, 5.80 (dt, 1H, J=15.4, 6.7 Hz, =CH-*n*.Hex.), 5.40 (ddt, 1H, J=15.4, 7.4, 1.4 Hz, -C*H*=CH-*n*.Hex.), 4.35 (ddd, 1H, J=11.6, 9.4, 4.3 Hz, >CH-NO_2), 4.14-3.92 (m, 2H, >C*H*-CH=, -C*H*H-O-), 3.64-3.42 (m, 1H, -CH*H*-O-), 2.50-1.00 [m, 14H, -(CH_2)$_2$-CH_2-O-, -(CH_2)$_5$-Me], 0.98 (t, 3H, J=6.9 Hz, -CH_3); ^{13}C NMR, 138.10, 124.89, 86.77, 79.99, 67.52, 32.12, 31.51, 28.83, 28.67, 28.58, 24.06, 22.42, 13.89; m/z (I%), 195(M^+-46, 24), 194(81), 137(26), 123(14), 109(51), 97(35), 81(29), 71(42), 55(96), 43(74), 41(100);

cis-**4c**: ^{1}H NMR, 5.82 (dtd, 1H, J=15.5, 6.6, 1.0 Hz, =CH-*n*.Hex.), 5.52 (ddt, J=15.5, 6.3, 1.4 Hz, -C*H*=CH-*n*.Hex.), 4.61 (dt, 1H, J=4.3, 3.7 Hz, >CH-NO_2), 4.30-4.18 (m, 1H, >C*H*-CH=), 4.16-4.00 (m, 1H, C*H*H-O-), 3.68-3.44 (m, 1H, -CH*H*-O-), 2.50-1.10 [m, 14H, -(CH_2)$_2$-CH_2-O-, -(CH_2)$_5$-Me], 0.88 (t, 3H, J=6.8 Hz, -CH_3); ^{13}C NMR, 136.45, 123.83, 83.04, 76.79, 66.22, 32.14, 31.47, 28.57, 25.48, 22.37, 20.72, 13.83; m/z (I%), 211(M^+-30, 14), 195(24), 194(35), 149 (9), 137(14), 123(11), 111(20), 109(24), 102(28), 97(37), 81(30), 71(45), 69(45), 67(39), 55(100), 41(100); IR, 1672, 1548, 1090, 1051, 970.

(E)-Hept-2-enal (**5a**)[14] (B, 71%, bp 120 °C/128 Torr); ^{1}H NMR, 9.51 (d, 1H, J= 7.9 Hz, -CHO), 6.87 (dt, 1H, J=15.6, 6.8 Hz, =C*H*-CH_2-), 6.12 (ddt, 1H, J=15.6, 7.9, 1.5 Hz, -C*H*=CH-CH_2-), 2.34 (dtd, 2H, J= 6.8, 6.8, 1.5 Hz, =CH-CH_2-), 1.62-1.20 [m, 4H, -(CH_2)$_2$-Me), 0.93 (t, 3H, J=7.0 Hz, -CH_3); ^{13}C NMR, 194.30, 159.02, 133.08, 32.17, 29.71, 21.95, 13.46; m/z (I%), 112(M^+, 2), 97(3), 83(23), 70(16), 69(14), 57(19), 56(21), 55(41), 53(16), 43(29), 41(100), 39(86); IR, 3014, 2734, 1694, 1637, 1153, 1105, 978.

(E)-4,4-Dimethylpent-2-enal (**5b**)[14] (B, 80%, bp 91°C/150 Torr); ^{1}H NMR, 9.53 (d, 1H, J=7.8 Hz, -CHO), 6.82 (d, 1H, J=15.9 Hz, =CH-*t*.Bu), 6.05 (dd, 1H, J=15.9, 7.8 Hz, -C*H*=CH-*t*.Bu), 1.13 [s, 9H, -C(CH_3)$_3$]; ^{13}C NMR, 195.07, 168.99, 128.51, 34.33, 28.35; m/z (I%), 112(M^+, 30), 111(8), 97(100), 83(90), 79(14), 69(28), 65(7), 55(71); IR, 2712, 1688, 1641, 1189, 1082, 966.

(E)-2-Ethylpent-2-enal (**5c**)[15] (B, 72%, bp 92 °C/155 Torr); ^{1}H NMR, 9.38 (s, 1H, -CHO), 6.43 (t, 1H, J=7.4 Hz, =CH-Et), 2.50-2.30 (m, 2H, =CH-CH_2-Me), 2.26 [q, 2H, J=7.4 Hz, =C(CHO)CH_2-Me], 1.13 (t, 3H, J=7.7 Hz, -CH_3), 0.97 (t, 3H, J=7.6 Hz, -CH_3); ^{13}C NMR, 195.36, 156.10, 144.91, 21.82, 16.95, 13.13, 12.91; m/z (I%), 112(M^+, 78), 111(8), 97(51), 83(37), 79(21), 69(16), 67(18), 55(100); IR, 2711, 1723, 1688, 1644, 1100, 1060, 1019, 728.

(E)-Non-2-enal (**5d**)[16] (C, 70%, petroleum ether/ethyl acetate 90/10); ^{1}H NMR, 9.52 (d, 1H, J=7.9 Hz, -CHO), 6.87 (dt, 1H, J=15.6, 6.8 Hz, =CH-*n*.Hex.), 6.12 (ddt, 1H, J=15.6, 7.9, 1.5 Hz, -C*H*=CH-*n*.Hex.), 2.34 (dtd, 2H, J=6.8, 6.8, 1.4 Hz, =CH-CH_2-), 1.70-1.10 [m, 8H,-(CH_2)$_4$-CH_3], 0.90 (t, 3H. J=6.8 Hz, -CH_3); ^{13}C NMR, 194.38, 159.21, 133.02, 32.49, 31.29, 28.55, 27.54, 22.24, 13.72; m/z (I%), 122(M^+-18, 9), 111(12), 96(39), 83(96), 70(100), 69(58), 57(86), 56(59), 55(100), 43(97), 41(98); IR, 3010, 2731, 1696, 1654, 1100, 726.

(E)-2-n.Propylhex-2-enal (**5e**)[17] (C, 70%, petroleum ether/ethyl acetate 95/5); ^{1}H NMR, 9.38 (s, 1H, -CHO), 6.47 (t, 1 H, J=7.4

Hz, =CH-*n*.Pr), 2.35 (dt, 2H, J=7.4, 7.4 Hz, =CH-C*H*$_2$-), 2.23 [t, 2H, J=7.5 Hz, =C(CHO)-C*H*$_2$-], 1.70-1.20 (m, 4H, 2 -CH$_2$-Me), 0.99 (t, 3H, J=7.3 Hz, -CH$_3$), 0.90 (t, 3H, J=7.3 Hz, -CH$_3$); ^{13}C NMR, 195.36, 155.26, 143.75, 30.91, 25.95, 21.96(2C), 14.03, 13.87; m/z (I%), 140(M^+, 98), 125(19), 111(53), 97(100), 93(37), 83(23), 79(17), 77(17), 69(56), 67(43), 55(82); IR, 3049, 2727, 1693, 1633, 980.

(E)-Tridec-2-enal (**5f**) (C, 73%, petroleum ether/ethyl acetate 90/10); ^{1}H NMR, 9.51 (d, 1H, J+7.9 Hz, CHO), 6.87 (dt, 1H, J=15.6, 6.8 Hz, =CH-Dec.), 6.12 (ddt, 1H, J=15.5, 7.9, 1.5 Hz, -C*H*=CH-Dec.), 2.34 (dtd, 2H, J=6.8, 6.8, 1.5 Hz, =CH-C*H*$_2$-), 1.62-1.20 [m, 16H, -(C*H*$_2$)$_8$-CH$_3$], 0.90 (t, 3H, J=7.0 Hz, -CH$_3$); ^{13}C NMR, 194.44, 159.21, 133.15, 32.58, 31.75, 29.41, 29.35, 29.19(2C), 28.99, 27.70, 22.50, 13.91; IR, 3012, 2722, 1695, 1648, 1100, 730.

(E)-2-Trimethylsilyl-4,4-dimethylpent-2-enal (**5g**) (C, 70%, petroleum ether/ethyl acetate 95/5); ^{1}H NMR, 10.57 (s, 1H, -CHO), 6.54 (s, 1H, =CH-*t*.Bu), 1.25 [s, 9H, -C(CH$_3$)$_3$], 0.13 [(s, 9H, -Si(CH$_3$)$_3$]; ^{13}C NMR, 197.47, 165.28, 152.93, 31.84, 29.37, -1.07; m/z (I%), 184(M^+, 8), 169(68), 131(8), 127(10), 111(8), 83(9), 75(98), 73(100), 69(36), 59(17), 57(21).

2 -Trimethylstlyl-3-phenylpropenal (**5h**)(C, 85%, petroleum ether/ethyl acetate 90/10, E/Z=87/13);

(E)-**5h**: ^{1}H NMR,[18] 10.00 (s, 1H, CHO), 7.80 (s, 1H, =CH-), 7.52-7.26 (m, 5H, -C$_6$H$_5$), 0.28 [s, 9H, -Si(CH$_3$)$_3$]; ^{13}C NMR, 197.48, 155.02, 144.84, 135.48, 130.05, 129.61, 128.49, -1.63; m/z (I%), 204(M^+, 41), 189(60), 161(14), 145 (10), 129(7), 115(100), 103(£), 89(15), 83(21), 73(31), 59(13), 45(45); IR, 3035, 3018, 2720, 1680, 1671, 1100, 809, 730, 658.

(Z)-**5h**: ^{1}H NMR,[18] 9.75 (s, 1H, -CHO), 8.08 (s, 1H, =CH-), 7.50-7.26 (m, 5H, -C$_6$H$_5$), 0.12 [s, 9H, Si(CH$_3$)$_3$]; ^{13}C NMR, 199.85, 164.72, 151.87, 137.25, 129.49, 128.80, 128.29, -0.12; m/z (I%), 204(M^+, 37), 189(61), 161(9), 145(4), 129(4), 115(100), 103(1), 89(13), 83(9), 73(17), 59(5), 45(26).

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References and Notes

1. a) Pecunioso, A.; Menicagli, R. *Tetrahedron*, **1987**, *43*, 5411; b) Idem *J. Org. Chem.*, **1988**, *53*, 45; c) Idem *ibid.*, **1988**, *53*, 2614; d) Idem *ibid.*, **1989**, *54*, 2391.
2. a) Naves, Y. R.; Lamparsky, D.; Ochsner, P. *Bull. Soc. Chim. Fr.*, **1961**, 645; b) Vidari, G.; De Bernardi, M.; Pavon, M.; Ragozzino, L. *Tetrahedron Lett.*, **1973**, 4065; c) Thomas, A. F. *Total Synthesis of Natural Products*; J. Wiley and Sons: N. Y., 1973; 167; d) Naves, Y. R. *Soap, Perfumery and Cosmetics*, **1961**, *34*, 1025.
3. Menicagli, R.; Malanga, C.; Guagnano, V. *Tetrahedron Lett.*, **1992**, *33*, 2867.
4. Kogan, T. P.; Gaeta, F. C. A. *Synthesis*, **1988**, 706.
5. Zweifel, G.; Miller, J. A. *Org. Reac.*, **1984**, *32*, 375, and references cited therein.
6. Compound **3a** showed: m/z (I%), 182(M^+, 1), 154(2), 139(1), 137(3), 125(2), 111(19), 97(100), 84(12), 69(16), 55(34), 41 (56).
7. Eisch, J. J.; Foxton, M. W. *J. Org. Chem.*, **1971**, *36*, 3520.
8. Prepared in 74% yield according to a reported procedure.[9]
9. Benkeser, R. A.; Hickner, R. A. *J. Am. Chem. Soc.*, **1958**, *80*, 5298.
10. The E configuration was confirmed by the evidences obtained in NOE experiments.
11. Since, in the experimental conditions adopted,[7] the *anti*-hydroalumination occurs with a 96% diastereocontrol, the (Z)-**5h** observed (13%) could arise *via* acid catalyzed isomerization of (E)-**5h**.
12. a) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.*, **1975**, 2825; Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Ibid.*, **1983**, *24*, 2877; Idem *Tetrahedron*, **1985**, *41*, 3257.
13. Menicagli, R.; Guagnano, V.; Malanga, C. *Gazz. Chim. Ital.*, **1992**, *122*, 487.
14. Jutz, C. *Chem. Ber.*, **1958**, *91*, 1867.
15. Green, M. B.; Hickinbottom, W. J. *J. Chem. Soc.*, **1957**, 3262.
16. Surber, W.; Theus, V.; Colombi, L.; Schinz, H. *Helvetica Chimica Acta*, **1956**, *39*, 1299.
17. Breslow, R.; Altaman, L. J.; Krebs, A.; Mohacsi, E.; Murata, I.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.*, **1965**, *87*, 1326.
18. Chemical shifts are referred to $CHCl_3$ (δ, 7.24 ppm).

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