Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A New Organosilicon Reagent for One-Pot Conversion of Aldehydes into Trienals

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To cite this article: Moncef Bellassoued, Emmanuelle Reboul & Malika Salemkour (1995) A New Organosilicon Reagent for One-Pot Conversion of Aldehydes into Trienals, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:20, 3097-3108, DOI: 10.1080/00397919508015458

To link to this article: http://dx.doi.org/10.1080/00397919508015458

SYNTHETIC COMMUNICATIONS, 25(20), 3097-3108 (1995)

A NEW ORGANOSILICON REAGENT FOR ONE-POT CONVERSION OF ALDEHYDES INTO TRIENALS.

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Abstract : *The 6-trimethylsilyle N-tert-butyl sorbaldimine was easily prepared from sorbaldimine throught deprotonation with LDA in THF at -60°C and subsequent trapping of the organo lithium intermediate by trimethylsilylchloride. The condensation of this new organosilicon reagent with several aldehydes, in the presence of catalytic CsF in DMSO at 100°C leads directly, after the hydrolysis of the imine function, to the expected trienals in good yields and with excellent E selectivity.*

As a matter of fact, several natural products with various activities as either fongicidal, bactericidal, antiviral or antitumoral, or some pheromones or vitamines show structure with long polyenic chains witch E configuration is essential for the biological peculiar quality of the entity.

Polyinsaturated aldehydes are very often used as intermediates in total synthesis of most of these molecules : Amphotericine B[1], Foligorubine A[2], Navenones A, B and C[3], Phytol[4] precursor of vitamines E and K1.

Since few years now, severals research teams have been challenging in finding reagent enable to introduce through few steps, one, two, three, or even four double bonds to chain issued from an aldehyde.

However, a few publications[5,6,7] deal with homologation of an aldehyde to trienal : the following reagents were used in this purpose.

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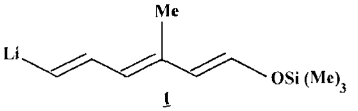
* To whom correspondence should be addressed.



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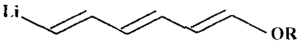

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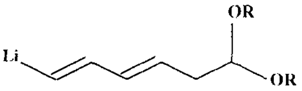

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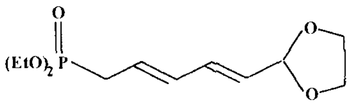

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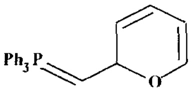


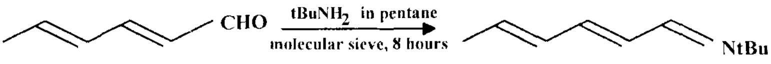
5

Except of the last one, all these reagents are ω fonctionnal derivatives with a masqued carbonyl and were described by the same team. Recently the 2-triphenylphosphoranylidimethyl-2H-pyran[7] 5 was used for the conversion of nonenolysable aldehydes into trienals.

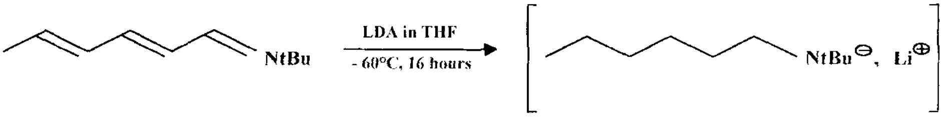
One or two steps are enought to lead them to good yields of polyenals searched for. However, these reagents have major disagreements : they are very long to obtain and process used are fastidious and costly.

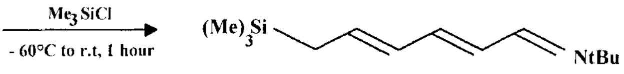
In this publication, we would like to report the preparation of the 6-trimethyl silyle N-tert-butyl sorbaldimine 6 and its use in the direct transformation of aldehydes into trienals.

To our knowledge, the organosilicon reagent 6 has not previousely been described in the literature. It is readily obtained in 74% yield from N-tert-butyl sorbaldimine through deprotonation with LDA and quentching the lithium intermediate by trimethylsilylchloride. Nevertheless, the use of the freshly in situ prepared N-tert-butyl sorbaldimine is recommended.



almost quantitative yield





6

yield = 74 %

Nucleophilic addition of 6 to benzaldehyde in the presence of catalytic amount of CsF (10%) in anhydrous DMSO at room temperature to 100°C, followed by a very mild hydrolysis of the tert-butylimine function affords the (2E, 4E, 6E) 7-phenyl heptatrienal 7a in 70% yield after purification by flash chromatography on silica gel.

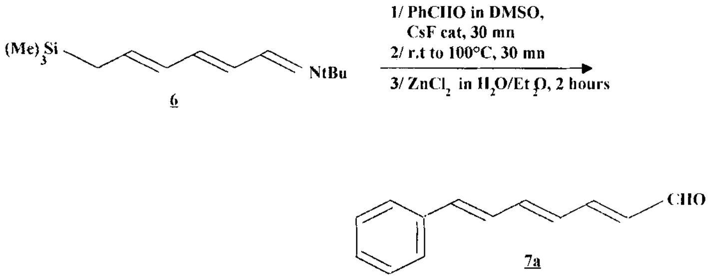
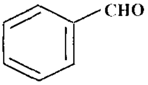
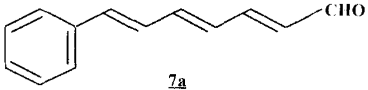
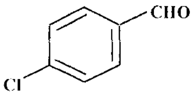
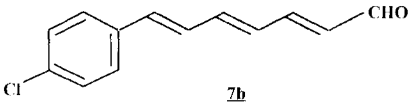


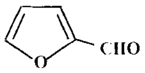
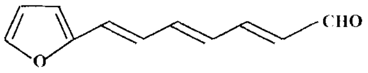
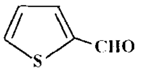
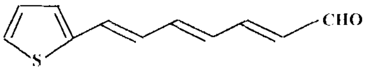
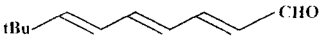
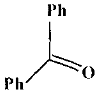
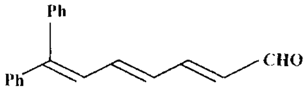
Table I shows the application of this six-carbon homologation procedure to some aldehydes.

Table I

Starting carbonyl compounds	Product	Yield^a %
	 7a	70
	 7b	90

(continued)

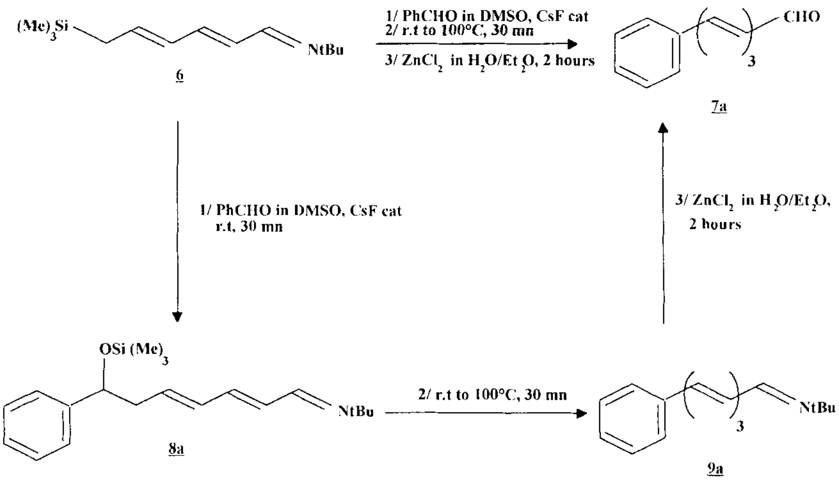
Table 1 Continued

	 7c	98
	 7d	93
tBu —CHO	 7e	72
	 7f	20[b]

(a) after purification by flash chromatography
(b) 25% if 18 hours at 100°C

In order to complete this study and to more understand the mechanism of this "one-pot" conversion of aldehydes into trienals, we have splited this addition-elimination reaction into three steps.The different intermediates have been purified and studied in the case of benzaldehyde.

We present the results in the following test scheme :



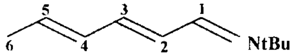
It is obvious that the first step of this reaction correspond to the condensation feedback of our silicon 6 over the benzaldehyde to convert. This condensation reaction occurs at the room temperature and is made solely by the pole ω of the reagent **6**. It leads to the siloximine **8a** and the elimination reaction which produces the trienamine **9a** occurs during the 100°C heating period. Such an emergence of this trienamine **9a** can be gradually observed by T.L.C. After a smooth hydrolysis by aqueous $ZnCl_2$ we can regenerate the aldehyde function.

Conclusion : *This work shows that the 6-trimethylsilyle N-tert-butyl sorbaldimine is a convenient reagent for stereoselectivity conversion of aldehydes into trienals (E, E, E). This reagent is much more advantageous than those already reported (1, 2 and 3). Mainly, it offers an easy route of access to trienals through the sorbaldehyde.*

EXPERIMENTAL SECTION

N-tert-butyl sorbaldimine :

To a solution of 140 mmol (10.22 g) of tert-butylamine in 18 ml of anhydrous pentane, we add a solution of 120 mmol (10.52 g) of sorbaldehyde in 18 ml of anhydrous pentane in the presence of 20 g molecular sieve. The reaction is exothermic, then an ice bath is used for stabilizing the temperature at 0°C. After 8 hours at room temperature, the mixture had filtered and the molecular sieve had washed with anhydrous pentane, the solvant is removed in vacuo and a colourless liquid is obtained.



NMR : ***^{1}H 200 MHz*** 1.5 ppm (s, 9H, tBu) ; 1.77 ppm (d.d, 3H, CH_3, $J_{CH_3-H_5} = 6.7$ Hz, $J_{CH_3-H_4} = 0.8$ Hz) ; 5.90 ppm (d.q, 1H, H_5, $J_{H_5-H_4} = 15.12$ Hz, $J_{H_5-CH_3} = 6.76$ Hz) ; 6.16 ppm (m, 2H, H_2 and H_4, $J_{H_2-H_3} = 15.4$ Hz, $J_{H_2-H_1} = 8.8$ Hz, $J_{H_4-H_5} = 14.6$ Hz, $J_{H_4-H_3} = 10.4$ Hz) ; 6.45 ppm (d.d, 1H, H_3, $J_{H_3-H_4} = 15.3$ Hz, $J_{H_3-H_2} = 10.5$ Hz) ; 7.82 ppm (d, 1H, $J_{H_1-H_2} = 8.9$ Hz). ***^{13}C 400 MHz*** : 18 ppm (CH_3) ; 29.39 ppm (CH_3, tBu) ; 56.53 ppm (C of tBu) ; 130.20 ppm (C_2) ; 130.73 ppm (C_4) ; 133.76 ppm (C_5) ; 140.89 ppm (C_3) ; 156.91 ppm (C_1). ***I.R :*** 2963 ; 1636 ; 1600 ; 1371 ; 1226. ***MS (m/z) :*** 151 ($M^{+\bullet}$, 33 %) ; 136 ($-CH_3$, 100 %) ; 121 ($-2CH_3$, 13%) ; 106 ($-3CH_3$, 8 %) ; 94 (-tBu, 28 %) ; 80 (-NtBu, 68 %).

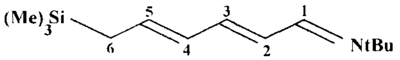
Analysis : Calculated for $C_{10}H_{17}N$: C = 79.54 ; H = 11.35 ; N = 9.28 Found : C = 79.02 ; H = 11.45 ; N = 9.20.

6-trimethylsilyle N-tert-butyl sorbaldimine 6 :

Under nitrogen atmosphere and magnetic stirring, we add drop by drop a solution of 70 mmol (10.57 g) of sorbaldimine in 10 ml of THF to LDA at - 60°C during 30 minutes.

Then the reaction is going on during 16 hours at the same temperature and after 13 ml (120 mmol) of trimethylsilyle chloride are added dropwise to the solution at - 60°C. After 15 minutes, the cold bath is taken away and the temperature is rising at room temperature. After one hour, we filtered and washed with ether the white precipitate of LiCl. Then the solvant is removed in vacuo and the product 6 is purified by distillation under low pressure ($E_{0,09}$ = 72°C, yield = 74 %).

We obtain a pale yellow liquid.



NMR : ¹H 400 MHz : -0.2 ppm (s, 9H, $Si(Me)_3$) ; 1 ppm (s, 9H, tBu) ; 1.39 ppm (d, 2H, CH_2, $J_{CH_2\text{-}H_5}$ = 7.9 Hz) ; 5.94 ppm (d.t, 1H, H_5, $J_{H_5\text{-}H_4}$ = 14.8 Hz, $J_{H_5\text{-}CH_2}$ = 8.25 Hz) ; 6.04 ppm (d.d, 1H, H_4, $J_{H_4\text{-}H_5}$ = 14.6 Hz, $J_{H_4\text{-}H_3}$ = 10.4 Hz) ; 6.18 ppm (d.d, 1H, H_2, $J_{H_2\text{-}H_3}$ = 15.4 Hz, $J_{H_2\text{-}H_1}$ = 8.8 Hz) ; 6.53 ppm (d.d, 1H, H_3, $J_{H_3\text{-}H_2}$ = 15.4 Hz, $J_{H_3\text{-}H_4}$ = 10.4 Hz) ; 7.84 ppm (d, 1H, H_1, $J_{H_1\text{-}H_2}$ = 8.8 Hz). ***¹³C 200 MHz*** : -1.99 ppm ($Si(Me)_3$) ; 24.46 ppm (C_6) ; 29.61 ppm (CH_3 of tBu) ; 56.60 ppm (C of tBu) ; 128.25 ppm (C_2) ; 128.80 ppm (C_4) ; 136.90 ppm (C_5) ; 141.78 (C_3) ; 157.32 ppm (C_1). ***IR :*** 2963 ; 1636 ; 1600 ; 1371 ; 1226 ; 1009 ; 1255 ; 850 ; 750.

Analysis : Calculated for $C_{13}H_{25}Si$: C = 70.01 ; H = 11.30 ; N = 6.28 ; Si = 12.59. Found : C = 69.00 ; H = 11.46 ; N = 6.09 ; Si = 12.65.

General procedure of conversion of aldehydes into trienals :

All the condensation process are carried out under nitrogen atmosphere, in a bicol topped by a thermometer and a bulb of bromine. It is a magnetic shaking.

A catalytic quantity of CsF (~ 10 %) in 2 ml of DMSO are mixed to a solution of 8.5 mmol of aldehyde in 2 ml of DMSO. Then 10 mmol (2.23g) of sorbic silicon imine 6 in 2 ml of DMSO are added dropwise. The temperature rises a lot (ΔT ~ 20-30°C) and a blackening of the mixture is observed. When the temperature is again at room temperature (after about 30 mn), the mixture is heated at 100°C for 20 minutes (the coming out of trienal is revealing gradually by T.L.C).

Then the mixture is letting to get cold. The acqueous layer is extracted with ether and the organic layer washed with water (3 x 10ml) and dried over $MgSO_4$.

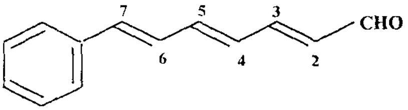
After evaporation of solvant with a rotary evaporator, we obtained the trienamine 8 which is in the form of a dark brown oil.

The hydrolysis of the imine function is executed with a solution of 2g of $ZnCl_2$ in 15 ml of water at which 8.5 mmol of 8 in 10 ml of water are added.

The mixture is shaked with magnetic small bar during 2 hours at room temperature. Then the precipitate is filtering over celite and the aqueous layer is extracted with ether (2 x 15 ml) and organics layers are washed with water (2 x 10 ml) then dried over $MgSO_4$.

After evaporation of solvant with rotary evaporator and purification of trienal 7 by flash chromatography on silica gel, we obtained, in the most of case, a crystallized solid.

(2E, 4E, 6E) 7-phenyl heptatrienal[5d] *: 7a*



m.p = 115°C

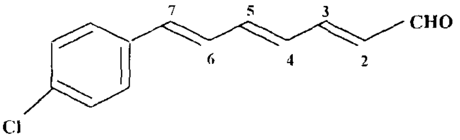
The product 7a is purified by flash chromatography on silica gel in n hexane/acetone (8/1)

We obtained an orange solid.

NMR : ¹H 400 MHz : 6.20 ppm (d.d, 1H, H_2, $J_{H_2-H_3}$ = 15.18 Hz, $J_{H_2-H_1}$ = 7.26 Hz) ; 6.56 ppm (d.d, 1H, H_4, $J_{H_4-H_5}$ = 14.38 Hz, $J_{H_4-H_3}$ = 11.24 Hz) ; 6.80 ppm (d, 1H, H_7, $J_{H_7-H_6}$ = 14.8 Hz) ; 6.82 ppm (d.d, 1H, H_5, $J_{H_5-H_4}$ = 14.46 Hz, $J_{H_5-H_6}$ = 11.3 Hz) ; 6.89 ppm (d.d, 1H, H_6, $J_{H_6-H_7}$ = 14.8 Hz, $J_{H_6-H_5}$ = 11.23 Hz) ; 7.19 ppm (d.d, 1H, H_3, $J_{H_3-H_2}$ = 15.13 Hz, $J_{H_3-H_4}$ = 11.18 Hz) ; 7.3 - 7.47 ppm (m, H aromatiques) ; 9.59 ppm (d, 1H, H of CHO, J_{CHO-H_2} = 7.89 Hz). ***^{13}C 400 MHz :*** 193.29 ppm (C_1) ; 151.58 ppm (C_3) ; 142.54 ppm (C_5) ; 138.09 ppm (C_7) ; 130.86 ppm (C_2) ; 129.89 ppm (C_4) ; 127.44 ppm (C_6) ; 136.04 ppm, 128.59 ppm, 126.77 ppm (C aromatics). ***I.R :*** 2987 ; 1700 ; 1585. ***MS (m/z) :*** 184 ($M^{+\bullet}$, 100 %) ; 155 (-CHO, 89 %) ; 91 (93 %) ; 77(48 %).

HRMS : calculated for $C_{13}H_{12}O$: 184.088842. Found 184.088860

7 - (4' chlorophenyl) hepta 2E, 4E, 6E trienal[5d] *: 7b*



m.p = 90°C

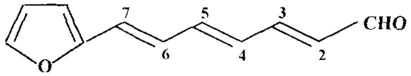
The product 7b is purified by flash chromatography on silica gel in n hexane/ethyl acetate (9/1). We obtained a yellow solid.

NMR : ^{1}H 400 MHz : 6.23 ppm (d.d, 1H, H_2, $J_{H_2\text{-}H_3}$ = 15.20 Hz , $J_{H_2\text{-}H_1}$ = 7.94 Hz) ; 6.60 ppm (d.d, 1H, H_4, $J_{H_4\text{-}H_5}$ = 13.89 Hz, $J_{H_4\text{-}H_3}$ = 11.36 Hz) ; 6.77 ppm (d, 1H, H_7, $J_{H_7\text{-}H_6}$ = 14.90 Hz) ; 6.82 ppm (d.d, 1H, H_5, $J_{H_5\text{-}H_4}$ = 13.43 Hz, $J_{H_5\text{-}H_6}$ = 10.55 Hz) ; 6.89 ppm (d.d, 1H, H_6, $J_{H_6\text{-}H_7}$ = 15.10 Hz, $J_{H_6\text{-}H_5}$ = 10.56 Hz) ; 7.20 ppm (d.d, 1H, H_3, $J_{H_3\text{-}H_2}$ = 15.18 Hz, $J_{H_3\text{-}H_4}$ = 11.20 Hz) ; 7.34 ppm (d, H_2', $J_{H_2'\text{-}H_3'}$ = 8.60 Hz) ; 7.40 ppm (d, 2H, H_3', $J_{H_3'\text{-}H_2'}$ = 8,60 Hz) ; 9.62 ppm (d, 1H, CHO, $J_{CHO\text{-}H_2}$ = 7.96 Hz). ***^{13}C 250 MHz :*** 192.41 ppm (C_1) ; 150.46 ppm (C_3) ; 141.23 ppm (C_5) ; 135.69 ppm (C_7) ; 133.80 ppm (C_4') ; 133.38 ppm (C_1') ; 130.39 ppm (C_2) ; 129.59 ppm (C_4) ; 128.00 ppm (C_3') ; 127.20 ppm (C_6) ; 127.09 ppm (C_2'). ***MS (m/z) :*** 218 ($M^{+\bullet}$, 100 %) ; 220 ($M^{+\bullet}$, 25 %) ; 189 (-CHO, 36 %).

HRMS : Calculated for $C_{13}H_{11}OCl$ = 218.04984. Found 218.04988

Analysis : Calculated for $C_{13}H_{11}OCl$: C = 71.62 ; H = 5.09 ; O = 7.34 ; Cl = 16.26. Found C = 71.51 ; H = 5.19.

7 - (2' furyl) hepta (2E, 4E, 6E) trienal : 7c



m.p = 100°C

The product 7c is purified by flash chromatography on silica gel in cyclohexane/acetone (6/1).

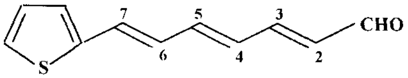
We obtained a dark brown solid.

NMR : ^{1}H 250 MHz : 5.97 ppm (d.d, 1H, H_4, $J_{H_4\text{-}H_5}$ = 14.63 Hz, $J_{H_4\text{-}H_3}$ = 11.11 Hz) ; 6.06 ppm (d.d, 1H, H_2, $J_{H_2\text{-}H_3}$ = 15.13 Hz, $J_{H_2\text{-}H_1}$ = 7.80 Hz) ; 6.17-6.14 ppm (m, 2H, H'_3 and H'_{4arom}) ; 6.23 ppm (d.d, 1H, H_5, $J_{H_5\text{-}H_4}$ = 14.78 Hz, $J_{H_5\text{-}H_6}$ = 10.80 Hz) ; 6.28 ppm (d, 1H, H_7, $J_{H_7\text{-}H_6}$ = 15.41 Hz) ; 6.56 ppm (d.d, 1H, H_3, $J_{H_3\text{-}H_2}$ = 15.13 Hz, $J_{H_3\text{-}H_4}$ = 11.16 Hz) ; 6.76 ppm (d.d, 1H, H_6, $J_{H_6\text{-}H_7}$ = 15.24 Hz, $J_{H_6\text{-}H_5}$ = 11.26 Hz) ; 7.11 ppm (s, 1H, H'_{5arom}) ; 9.56 ppm (d, 1H, CHO, $J_{CHO\text{-}H_2}$ = 7.78 Hz). ***^{13}C 250 MHz :*** 192.46 (CHO) ; 151.45 (C'_2) ; 150.73 (C_3) ; 142.53 (C'_5) ; 141.30 (C_7) ; 129.91 (C_4) ; 129.08 (C_2) ; 125.08 (C_6) ; 123.90 (C_5) ; 111.20 (C'_3) ; 110.43 (C'_4). ***MS (m/z) :*** 174 ($M^{+\bullet}$, 100 %) ; 145 (-CHO, 60 %).

HRMS : Calculated for $C_{11}H_{10}O_2$ = 174.068078. Found 174.154808

Analysis : Calculated for $C_{11}H_{10}O_2$: C = 75.93 ; H = 5.79. Found C = 75.71 ; H = 5.80.

7 - (2' thienyl) hepta (2E, 4E, 6E) trienal : 7d



m.p = 104°C

The product **7d** is purified by flash chromatography on silica gel in cyclohexane/ethyl acetate (8/1). We obtained an orange yellow solid.

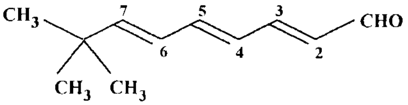
NMR : ^{1}H 250 MHz : 6.11 ppm (d.d, 1H, H_2, $J_{H_2\text{-}H_3}$ = 15.22 Hz, $J_{H_2\text{-}H_1}$ = 8.01 Hz) ; 6.47 ppm (d.d, 1H, H_4, $J_{H_4\text{-}H_5}$ = 14.11 Hz, $J_{H_4\text{-}H_3}$ = 11.40 Hz) ; 6.63 ppm (d.d, 1H, H_6, $J_{H_6\text{-}H_7}$ = 14.58 Hz, $J_{H_6\text{-}H_5}$ = 9.1 Hz) ; 6.72 ppm (d.d, 1H, H_5, $J_{H_5\text{-}H_4}$ = 14.28 Hz, $J_{H_5\text{-}H_6}$ = 10.75 Hz) ; 6.87 ppm (d, 1H, H_7, $J_{H_7\text{-}H_6}$ = 14.47 Hz) ; 6.95 ppm (d.d, 1H, H_4', $J_{H_4'\text{-}H_5'}$ = 5.05 Hz, $J_{H_4'\text{-}H_3'}$ = 3.63 Hz) ; 7.03 ppm (d, 1H, H_3', $J_{H_3'\text{-}H_4'}$ = 3.50 Hz) ; 7.10 ppm (d.d, 1H, H_3, $J_{H_3\text{-}H_2}$ = 15.13 Hz, $J_{H_3\text{-}H_4}$ = 11.00 Hz) ; 7.21 ppm (d, 1H, H_5', $J_{H_5'\text{-}H_4'}$ = 5.09 Hz) ; 9.51 ppm (d, 1H, CHO, $J_{CHO\text{-}H_2}$ = 7.98 Hz). ***^{13}C 250 MHz :*** 192.42 (CHO) ; 150.66 (C_3) ; 141.19 (C_5) ; 140.83 (C'_2) ; 129.93 (C_2) ; 129.80 (C_7) ; 128.83 (C_4) ; 127.02 ($2C'_{arom}$) ; 126.27 (C_6) ; 125.47 (C'_{arom}).

MS (m/z) : 190 ($M^{+\bullet}$, 58 %) ; 161 (-CHO, 42 %).

HRMS : Calculated for $C_{11}H_{10}OS$ = 190.045237. Found 190.045319

Analysis : Calculated for $C_{11}H_{10}OS$: C = 69.434 ; H = 5.297. Found : C = 69.19 ; H = 5.21.

(8, 8 dimethyl) nona (2E, 4E, 6E) trienal : 7e



The product **7e** is purified by flah chromatography on silica gel in cyclohexane/acetone (6/1). We obtained a dark brown oil.

The hydolysis with ZnCl2 is carrying on 3h30.

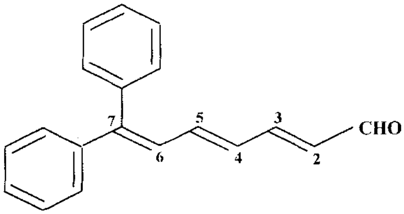
NMR : ^{1}H 250 MHz in C_6D_6 : 0.95 ppm (s, 9H, tBu) ; 5.75 ppm (d, 1H, H_7, $J_{H_7\text{-}H_6}$ = 15.49 Hz) ; 5.87 ppm (d.d, 1H, H_4, $J_{H_4\text{-}H_5}$ = 14.82 Hz, $J_{H_4\text{-}H_3}$ = 10.39 Hz) ; 5.90 ppm (d.d, 1H, H_6, $J_{H_6\text{-}H_7}$ = 15.42 Hz, $J_{H_6\text{-}H_5}$ = 10.13 Hz) ; 6.04 ppm (d.d, 1H, H_2, $J_{H_2\text{-}H_3}$ = 15.26 Hz, $J_{H_2\text{-}H_1}$ = 7.82 Hz) ; 6.18 ppm (d.d, 1H, H_5, $J_{H_5\text{-}H_4}$ = 14.88 Hz, $J_{H5\text{-}H6}$ = 10.10 Hz) ; 6.52 ppm (d.d, 1H, H_3, $J_{H_3\text{-}H_2}$ = 15.20 Hz, $J_{H_3\text{-}H_4}$ = 10.97 Hz) ; 9.47 ppm (d, 1H, CHO, $J_{CHO\text{-}H_2}$ = 7.84 Hz). ***^{13}C 250 MHz :*** 192.65 (CHO) ; 152.12 (C_3) ; 151.58 (C_7) ; 142.91 (C_5) ; 129.61 (C_2) ; 127.14 (C_6) ; 123.87 (C_4) ; 32.97 (C_8) ; 28.28 ($3CH_3$). ***I.R :*** 2963 ; 1709 ; 1650 ; 1167 ; 1120 ; 1000.

MS (m/z) : 164 ($M^{+\bullet}$, 100 %) ; 149 (-CH_3, 50 %) ; 121 (70 %) ; 105 (38 %) ; 93 (76 %).

HRMS : Calculated for $C_{11}H_{16}O$ = 164.120114. Found 164.120098

Analysis : Calculated for $C_{11}H_{16}O$: C = 80.438 ; H = 9.819. Found : C = 80.12 ; H = 9.71.

(7, 7 diphenyl) hepta (2E, 4E, 6E) trienal : 7f



m.p = 91-92°C

The product **7f** is purified by flash chromatography on silica gel in cyclohexane/ethyl acetate (12/1). We obtained an orange solid.

The hydrolysis with $ZnCl_2$ is carrying on 5h.

NMR : ^{1}H 400 MHz : 6.19 ppm (d.d, 1H, H_2, $J_{H_2\text{-}H_3}$ = 15.12 Hz, $J_{H_2\text{-}H_1}$ = 7.96 Hz) ; 6.65 ppm (d.d, 1H, H_4, $J_{H_4\text{-}H_5}$ = 15.32 Hz, $J_{H_4\text{-}H_3}$ = 11.12 Hz) ; 6.79 ppm (d.d, 1H, H_5, $J_{H_5\text{-}H_4}$ = 14.32 Hz, $J_{H_5\text{-}H_6}$ = 11.24 Hz) ; 6.88 ppm (d, 1H, H_6, $J_{H_6\text{-}H_5}$ = 11.20 Hz) ; 7.11 ppm (d.d, 1H, H_3, $J_{H_3\text{-}H_2}$ = 15.16 Hz, $J_{H_3\text{-}H_4}$ = 11.04 Hz) ; 7.28-7.24 ppm (m, 3H, H_{arom}) ; 7.35 ppm (s, 4H, H_{arom}) ; 7.46-7.45 ppm (m, 3H, H_{arom}) ; 9.54 ppm (d, 1H, CHO, $J_{CHO\text{-}H_2}$ = 7.96 Hz). ***^{13}C 250 MHz :*** 192.47 (CHO) ; 151.12 (C_3) ; 147.85 (C_7) ; 140.24 (C'_1) ; 139.76 (C_5) ; 137.85 (C'_1) ; 130.05 (C_2) ; 129.95 (C_{arom}) ; 129.40 (C_4) ; 127.53 (C_{arom}) ; 127.36 (C_{arom}) ; 127.15 (C_{arom}) ; 126.91 (C_{arom}) ; 125.76 (C_6). ***I.R :*** 2843 ; 1660 ; 1620 ; 1593 ; 1555 ; 1500 ; 1453.

MS (m/z) : 260 ($M^{+\bullet}$, 100 %) ; 231 (-CHO, 29 %).

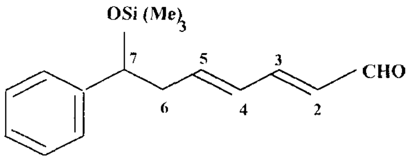
HRMS : Calculated for $C_{19}H_{16}O$ = 260.120114. Found 260.120010

Analysis : Calculated for $C_{19}H_{16}O$: C = 87.658 ; H = 6.195. Found : C = 87.41 ; H = 6.22.

7 - phényl 7-trimethyl siloxy hepta (2E, 4E) dienal :

In a bicol topped by a bulbe of bromine, by a thermometer and by a refrigerant, a catalytic quantity of CsF in 2 ml of DMSO are mixed to a solution of 9.43 mmol (1g) of benzaldehyde in 2 ml of DMSO under nitrogen atmosphere.

Then 10 mmol (2.23g) of 6 in 2 ml of DMSO are added dropwise. The temperature increases to 25°C and the reaction is carrying on to 30 mn at room temperature. The hydrolysis of imine function is the same of aboce mentioned. The product is purified by flash chromatography on silica gel in n hexane/acetone (8/1). We obtained a dark brown oil with 80 % of yield.



NMR : ^{1}H 500 MHz : 0.068 ppm (s, 9H, $Si(Me)_3$) ; 2.66 ppm (m, 1H, H_6) ; 4.83 ppm (d.d, 1H, H_7, $J_{H_7-H_{6a}}$ = 7.68 Hz, $J_{H_7-H_{6b}}$ = 7.63 Hz) ; 6.07 ppm (d.d, 1H, H_2, $J_{H_2-H_3}$ = 15.24 Hz, $J_{H_2-H_1}$ = 7.96 Hz) ; 6.21 ppm (d.t, 1H, H_5, $J_{H_5-H_4}$ = 14.7 Hz, $J_{H_5-H_6}$ = 10.1 Hz) ; 6.3 ppm (d.d, 1H, H_4, $J_{H_4-H_5}$ = 14.7 Hz, $J_{H_4-H_3}$ = 9.89 Hz) ; 7.05 ppm (d.d, 1H, H_3, $J_{H_3-H_2}$ = 15.31 Hz, $J_{H_3-H_4}$ = 9.99 Hz) ; 7.26-7.37 ppm (m, 5H, H_{arom}) ; 9.53 ppm (d, 1H, CHO, J_{CHO-H_2} = 7.79 Hz). ***I.R :*** 2987 ; 1700 ; 1637 ; 1585 ; 1082 ; 1275 ; 865 ; 760.

MS (m/z) : 273 ($M-H^{+\bullet}$, 2 %) ; 179 (100 %) ; 73 (84 %).

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(Received in the UK 13 March 1995)