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Polyvinylogation Reagents : 1-Lithio-4-trimethylsiloxy-penta-1,3-diene and 1-Lithio-4-ethoxy-2-methyl-buta-1,3-diene

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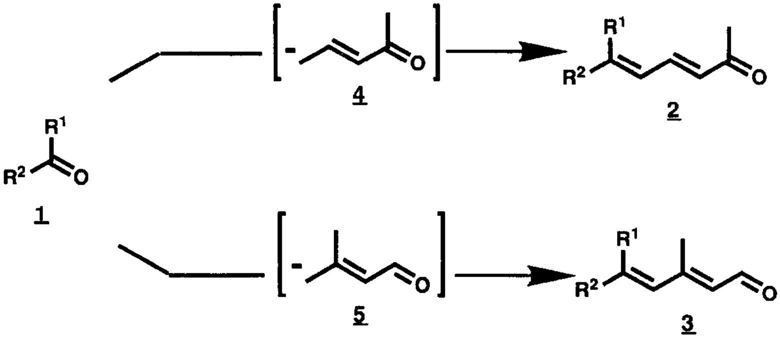
Abstract : *Title products, lithiodienol ethers 6a and 7a, synthetic equivalents of 4-lithio pent-3-ene-2-one and 4-lithio-senecialdehyde were obtained by bromine-lithium exchange. They are choice reagents for the transformations 1 → 2 and 1 → 3, respectively.*

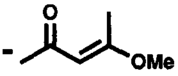
INTRODUCTION

The transformations of carbonyl compounds 1 into ketones 2 or aldehydes 3 are very useful processes in the terpene area. These transformations, including the introduction of five carbon atoms and two double bonds, involve synthons 4 and 5.

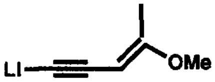


The use of enolates directly prepared from the pent-3-ene-2-one (1) and the senecialdehyde (2) being excluded, and the utilization of the corresponding imine anions leading to, at least, a partial condensation in α (3) (4), the synthetic equivalents 4a-f and 5a-e have been proposed in the literature :

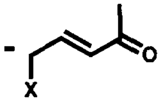
For the reaction 1 -> 2, their use involves a multistep process (4a-b), the yields are modest (4a,b,f) and the condensation of some of them (4c-e) has not been described with the ketones. Moreover, the 4-bromo-pent-3-ene-2-one, the precursor of 4c-f is not easily prepared and is very unstable (7).

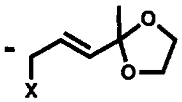


4a (5)



4b (6)





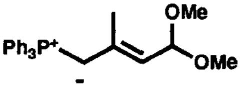
4c X = Ph_3P^+ (7)

4d X = Ph_3As^+ (9)

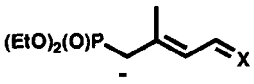
4e X = Ph_3P^+ (8)

4f X = $(EtO)_2P(O)$ (8)

Most of the reagents used for the reaction 1 -> 3 have been described recently. (5b-e) and are ambident anions such as the anions of phosphonium salts (5a), the anions of phosphonates (5b,c) and the dienolate 5d prepared from the corresponding trimethylsilylether or acetate.

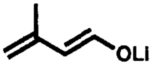


5a (10)

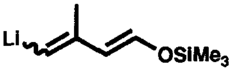


5b X = N-C_6H_{11} (11)

5c X =  (12)

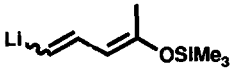


5d (13)

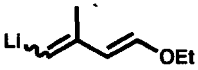


5e (14)

In order to carry out the two reactions considered in one pot, and to have at our disposal a choice of reagents, we prepared the lithiodienol ethers 6a and 7a.



6a

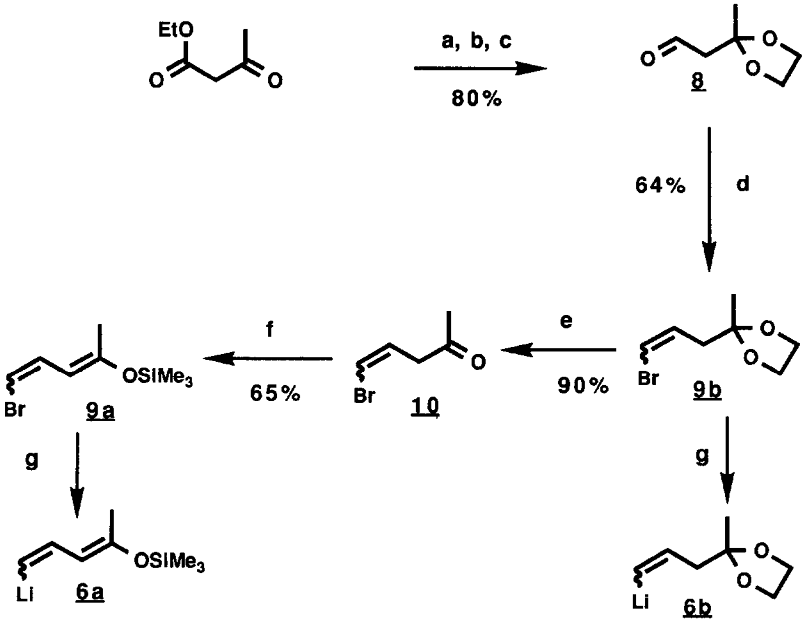


7a

RESULTS

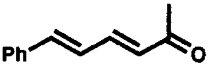
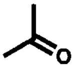
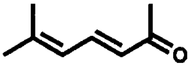
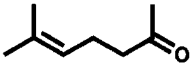
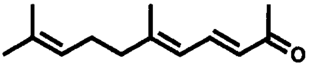
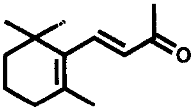
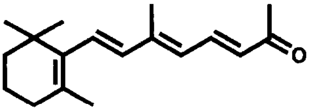
I. Lithio dienol ether 6a : synthetic equivalent of the 4-lithio-pent-3-ene-2-one

The preparation of the lithio dienol ether 6a is given in the following scheme. The aldehyde 8 was obtained from methyl or ethyl acetylacetate in three steps : ketalization followed by reduction and oxidation, with a global yield of 80 % (15).Its condensation with the bromomethylene triphenylphosphorane led to the bromodioxolane 9b which was hydrolyzed under controlled conditions, into the bromo ketone 10 (16). The corresponding bromo trimethylsilyl enol ether 9a (17) was transformed into 6a by bromine - lithium exchange using *tert*-butyllithium in ether at -70°C (18). For comparison, we have also studied the lithiodioxolane 6b, prepared from 9b in the same conditions.



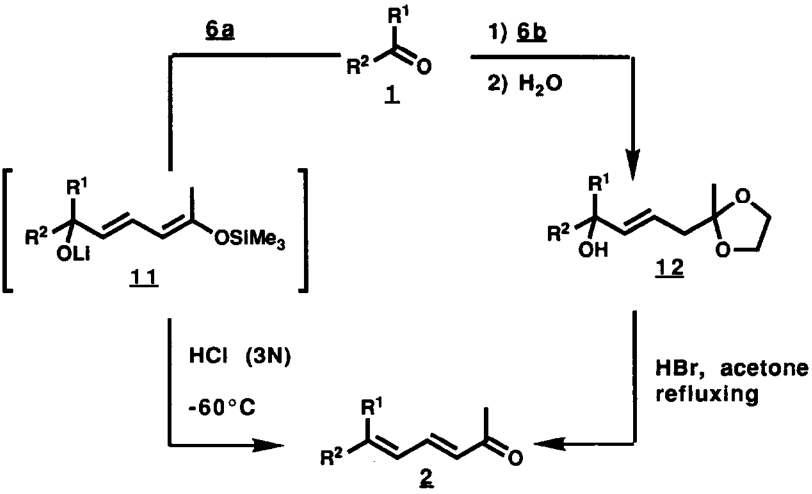
a) ethyleneglycol, benzene, PTSA ; b) $LiAlH_4$, Et_2O ; c) PCC, SiO_2, CH_2Cl_2 ; d) $BrCH_2PPh_3^+$, Br^-, tBuOK, THF ; e) PTSA (1eq), acetone, 40°C ; f) Me_3SiBr, NEt_3, CH_3CN, RT, distillation or chromatography ; g) tBuLi, Et_2O, -70°C

Table 1 : Ketones 2 from Carbonyl Compounds 1 and Reagents 6a,b

Starting material 1	Ketone 2	Yield %^{a} from 6a (one step)	Yield %^{a} from 6b (two steps)
 1a	 2a	73	36
 1b	 2b	70	
 1c	 2c	63	
 1d	 2d	71	37

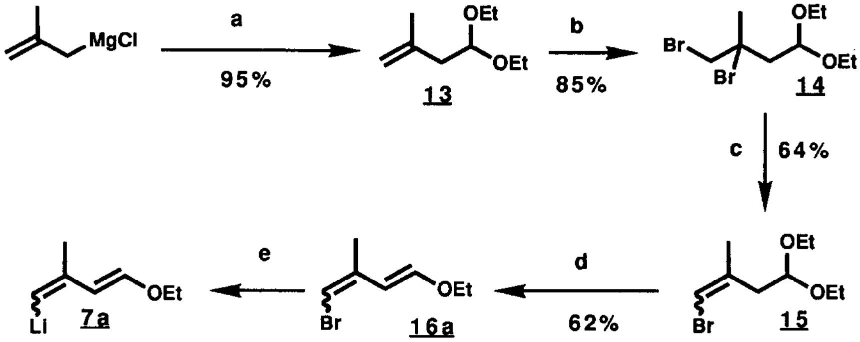
a) yield of chromatographed product

The condensation of the reagent 6a with carbonyl compounds 1a-d, in ether at -70°C leads to adducts 11 which are transformed directly into ketones 2a-d when treated at low temperature with a mildly acidic solution (table 1). Thus, from acetone, methylheptenone and β-ionone we have obtained in one step the dehydromethylheptenone 2b, the ψ-ionone 2c and the C_{18} ketone 2d, respectively. Starting from lithiodioxolane 6b, the adducts 12a-d were isolated, then transformed into ketones 2a,d by refluxing with an acidic acetone solution.



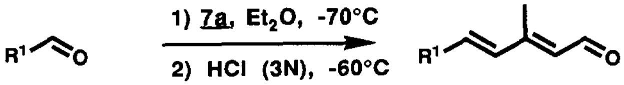
II. Lithio dienol ether 7a : synthetic equivalent of the 4-lithio senecialdehyde

Condensation of methallylmagnesium chloride with diethyl phenyl orthoformate (19) led to the eneacetal 13. After bromination (14), dehydrohalogenation (15) according to (20), and ethanol elimination according to (21), the obtained bromo-dienol ether 16a was submitted to bromine lithium exchange.



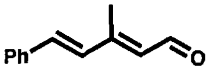
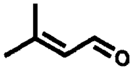
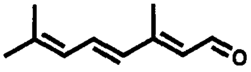
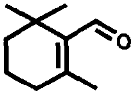
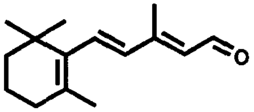
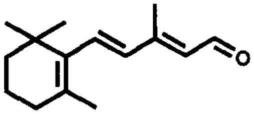
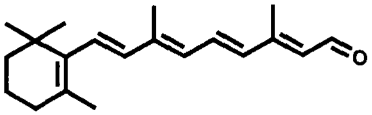
a) $(EtO)_2CH(OPh)$, THF ; b) Br_2, CCl_4, 0°C ; c) NaOH 50 % ; d) HMDS, $ISiMe_3$, CCl_4 ;
e) tBuLi, Et_2O, -70°C

The lithio dienol ether 7a was condensed with aldehydes 1a,e-g leading in one pot to polyconjugated aldehydes 3 such as dehydrocitral 3e, β-ionylideneacetaldehyde 3f, retinal 3g (table 2).



1a,e-g 3a,e-g

Table 2 : Aldehydes 3 from Carbonyl Compounds 1 and Reagent 7a

Starting material 1	Aldehydes 3	Yield % [a]
 1a	 3a	56
 1e	 3e	80
 1f	 3f	71
 3f	 3g	82

a) yield of chromatographed product

CONCLUSION

Results of tables 1 and 2 show that lithio dienol ethers 6a and 7a are choice reagents for convergent syntheses of 2 and 3 from 1. Their condensation with conjugated carbonyl compounds occurs exclusively 1-2 and the hydrolysis of the intermediate adducts could be performed under very mild conditions. To our knowledge, 6a is the first reagent able to transform ketones 1 into ketones 2 in one pot, in good yields. Superiority of lithio enol ether 6a compared to lithiodioxolane 6b is pointed out in table 1. Lithio enol ether 7a seems to have prenylating properties similar to those of lithio trimethylsilylenol ether 5e (14).

EXPERIMENTAL SECTION

All ^1H NMR spectra were recorded at 80 MHz. unless otherwise indicated (internal reference TMS) ^{13}C spectra were recorded on a Bruker apparatus at 50MHz. Mass spectra were recorded on a JEOL AX500 apparatus. IR spectra were recorded on Perkin Elmer 233 apparatus. Anhydrous ether and THF were prepared by distillation over sodium and benzophenone. Flash chromatographies were performed with SiO_2 230-400 mesh. HPLC analysis was done with a HibarMerck Lichrosorb Si-60 column (λ = 254 nm, 70 Atm., 1,5 ml/ mn). *Tert*-butyllithium solutions were titrated according to (22).

3-(1.3-dioxolane)-2yl-butanal 8

A mixture of ethyl acetylacetate (30 g, 231 mmol), ethyleneglycol (16 g, 254 mmol), paratoluenesulfonic acid monohydrate (0.5 g) in 50 mL of benzene was refluxed. Water formed during reflux was removed with a Dean-Stark apparatus. Evaporation of the solvent and distillation yielded ethyl 3-(1.3-dioxanne)-2yl-butanoate (92 %).

$BP_{12\ mmHg}$ = 98°C

^1H NMR ($CDCl_3$) : 1.2 (t, 3H ; J = 6.4 Hz) ; 1.5 (s, $3H_4$) ; 2.6 (s, $2H_2$) ; 3.9 (s, 4H) ; 4.1 (q, 2H, J = 6.4 Hz)

IR : 2980, 1735

A solution of the preceding ester (3 g, 17 mmol), in 10 mL of dry ether was added to a suspension of lithium aluminohydride (1 g, 25 mmol) in 100 mL of ether cooled to 0°C. The reaction mixture was stirred for 2.5 hours at room temperature then 12 mL of saturated aqueous sodium sulfate were added. The organic layer was separated by filtration and dried over magnesium sulfate. Evaporation of the solvent afforded 3-(1.3-dioxolane)-2yl-buten-1-ol (97 %).

^1H NMR ($CDCl_3$) : 1.35 (s, $3H_4$) ; 1.95 (t, $2H_2$, J = 6.1 Hz) ; 2.8 (1H, exchanged with D_2O) ; 3.75 (t, $2H_1$, J = 6,1 Hz) ; 3.95 (s, $4H_5$)

IR : 3400, 1380, 1050

The preceding alcohol (5 g, 37.9 mmol) was rapidly added at room temperature to a mixture of pyridinium chlorochromate (16.4 g, 76,1.mmol) and 500 mL of dichloromethane. After 2h (TLC monitoring) the solution was filtered on a mixture of Florisil and Celite 545 and the residue was washed with 500 mL of ether. The combined organic layers were concentrated and the residue was distilled providing aldehyde 8 as an oil (90 %). $BP_{0.4\ mmHg}$: 35°C

^1H NMR (CCl_4) : 1.35 (s, $3H_4$) ; 2.55 (d, $2H_2$, J = 3.3 Hz) ; 3.9 (s, 4H) ; 9.6 (t, $1H_1$, J = 3.3 Hz)

IR : 2980, 1735, 1380

1-Bromo-4-(1,3-dioxolane)-2yl-but-1-ene 9b :

To a mixture of bromomethyl triphenyl phosphonium bromide (25 g, 57.3 mmol) and 230 mL of THF was added, at -70°C, under argon, potassium terbutylate (7.7 g, 68.8 mmol) After stirring for 1.5 h at -70°C, a solution of aldehyde 8 (6.0 g, 46 mmol) in 25 mL of THF was slowly added. The mixture was stirred at 0°C for 1 h and at room temperature for 1.5 h. After addition of water (130 mL), the mixture was energetically stirred for 15 min, then extracted twice with 100 mL of ether, washed with water and dried over $MgSO_4$. Filtration and evaporation yielded 9b which was distilled (64 %).

$BP_{0,7\ mmHg}$: 63°C 9b was a mixture of Z (80 %) and E (20 %) isomers.

^1H NMR (CCl_4) : 1.25 (s, $3H_5$) ; 2.45 (d, $2H_3$, J = 6 Hz) ; 3.9 (s, 4H) ; 5.95-6.33 m, $2H_{1,2}$)

IR : 2990, 1625, 1380

^{13}C NMR (C_6D_6) : 129.6 (C_2) ; 109.4 and 108.5 (C_1) ; 65.2 and 64.2 ; 39.1 (C_3) ; 23.4 (C_4) ; 14.7 (C_5)

MS (EI) m/e 193 ($M-CH_3$)

Anal. calcd for $C_7H_{11}BrO_2$: C, 40.60 ; H, 5.35. Found : C, 40.47 ; H, 5.30

5-Bromo-pent-4-ene-2-one 10

To a solution of bromoacetal 9b (4.3 g, 20.8 mmol) in 40 mL of acetone, a solution of paratoluensulfonic acid monohydrate (4.3 g, 22.9 mmol) in 10 mL of water was rapidly added. The reaction mixture was stirred for 1 h at 40°C, poured onto 50 g of ice, extracted twice with 50 mL of ether, washed with 20 mL of water, and dried on $MgSO_4$. Evaporation of the solvents afforded crude bromo-enone 10 (90 %) as an oil which was immediatly used as such.

^1H NMR (CCl_4) : 2.05 (s, $3H_1$) ; 3.05 (d, $0.5H_3$, J = 6 Hz) ; 3.25 (d, $1.5H_3$), jJ= 6 Hz) ; 6.05-6.5 (m, $2H_{4,5}$)

IR : 2990, 1720, 1625

1-Bromo-4-trimethylsiloxy-penta-1,3-diene 9a

To a mixture of 12 mL of dry pentane and 12 mL of acetonitrile, was successively added, under argon, bromoenone 10, (1.52 g, 9.3 mmol), triethylamine (1.7 mL, 12 mmol) and bromotrimethylsilane (1.85 g, 12 mmol). After stirring for 20 h at room temperature, the solution of pentane was removed with a syringe and replaced by 20 mL of pure pentane. The operation was repeated four times. The combined pentane solutions were concentrated and the residue was distilled (43 %) or chromatographed on neutral alumina (petroleum ether) (65 %) affording enol ether 9a as an oil (one isomer).

^{1}H NMR (CCl_4) : 0.1 (s, 9H) ; 1.85 (s, $3H_5$) ; 4.3-5.4 (d, $1H_3$, J = 10.7 Hz) ; 5.4-5.7 (d, $1H_1$, J = 6.7 Hz) ; 6,15-6.65 (dd, $1H_2$, J1 = 10.7 Hz, J2 = 6.7 Hz)

IR : 3090, 1640, 1620, 1580

4,4-Diethoxy-2-methyl-but-1-ene 13 :

A solution of metallyl chloride (6.0 g, 66.3 mmol) in 50 mL of THF was added dropwise to magnesium (2.0 g, 83 mmol) and 10 mL of THF (so that the temperature did not exceed 30°C). The mixture was stirred for 2 h at room temperature and a solution of (1,1-diethoxy)-methoxy benzene (5.0 g, 26.5 mmol) in 30 mL of THF was added dropwise over 15 min (exothermic reaction). The mixture was stirred at room temperature for 20 h. After addition of 5 % NH_4Cl (10 mL), and extraction with ether (150 mL x 2), the organic layer was washed with 2N NaOH (50 mL x 2) and dried over $MgSO_4$. After evaporation the residue was distilled (95 %) giving acetal 13 as an oil.

BP $_{50\ \mathrm{mmHg}}$ = 86°C

^{1}H NMR ($CDCl_3$) : 1.1 (t, 6H, J = 8 Hz) ; 1.7 (s, $3H_5$) ; 2.3 (d, $2H_3$, J = 6 Hz) ; 4.55 (dq, 4H, J1 = $J2_{app}$ = 8 Hz); 4.6 (t, $1H_4$, J = 6 Hz) ; 4.85 (s, $2H_1$).

IR : 3080, 2990, 1645, 1445

^{13}C NMR ($CDCl_3$) : 140 (C_2) ; 112 (C_1) ; 102 (C_5) ; 61 (C_4) ; 42 (C_6) ; 22 (C_3) ; 15 (C_7)

1,2-Dibromo-4,4-diethoxy-2-methyl-butane 14

Sodium carbonate (8.0 g, 76.3 mmol) was added to a solution of acetal 13 (7.1 g, 44.9 mmol) in 75 mL of carbon tetrachloride. After cooling at 0°C, a solution of bromine (7.2 g, 45 mmol) in 10 mL of carbone tetrachloride was added dropwise. The reaction mixture was stirred at 0°C for 15 min and filtered. Solvent was removed under vacuum and the residue was chromatographed on Florisil (petroleum ether) giving dibromoacetal 14 (85 %) which was immediatly used.

^{1}H NMR (CCl_4) : 1.15 (t, 6H, J = 10 Hz) ; 1.85 (s, $3H_5$) ; 2.15 (d, $2H_3$, J = 6 Hz) ; 3.2-3.75 (m, 4H) ; 3.9 (q, 2H, J = 10 Hz); 4.8 (t, $1H_4$, J = 6 Hz)

IR : 2990, 2930, 1445

1-Bromo-4,4-diethoxy-2-methyl-but-1-ene 15

A mixture of dibromoacetal 14 (12.6 g, 39,6 mmol), 50 % NaOH (23 mL) and 40 % tetrabutylammonium hydroxide (0.7 mL) was warmed at 100°C for 4 h, cooled and extracted with ether (40 mL x 4). The extract was washed with water (30 mL) and dried over $MgSO_4$. Distillation afforded bromoacetal 15 as an oil (64 %). **E/Z** : 35/65. $BP_{0.8\ mmHg}$ = 70°C

^{1}H NMR ($CDCl_3$) : 1.15 (t, 6H, J = 8 Hz) ; 1.8 (s, $3H_5$) ; 2.35 (d, 0.7 H_3, J = 6 Hz) ; 2.5 (d, 1.3 H_3, J = 6 Hz) ; 3.2-3.8 (m, 4H) ; 4.4-4.8 (dt, $1H_4$, J1 = J2 = 6 Hz) ; 5.95 (s, $1H_1$).

IR : 3070, 2990, 1630, 1440

^{13}C NMR ($CDCl_3$) : 137.59 and 137 (C_2) ; 103.29 and 102 (C_1) ; 100.74 (C_4) ; 61.10 and 60.83 (C_6) ; 41.89 and 38.41 (C_3) ; 22.91 and 19.26 (C_5) ; 14.73 (C_7).

Anal. Calc. for $C_9H_{16}BrO_2$: C, 45.59 ; H, 7.23. Found : C, 45.45 ; H, 7.30

1-Bromo-4-ethoxy-2-methyl-buta-1,3-diene 16a

To a solution of bromoacetal 15 (2.0 g, 8.44 mmol) in carbone tetrachloride (15 mL), were successively added at 0°C under argon, hexamethyldisilazane (2.7 mL, 12.7 mmol) and iodotrimethylsilane (1.56 mL, 11.0 mmol). After 2 h at 0°C and 15 h at room temperature, pentane (15 mL) was added and the mixture was stirred for 15 min. The precipitate was filtered and washed with pentane (50 mL). The combined filtrates were washed with 5 % $NaHCO_3$ (20 mL x 4) and dried over $MgSO_4$. The solvent was removed, avoiding moisture, and the residue was distilled under argon yielding bromoenol ether 16a (62 %).

BP_{15mmHg} : 70°C

1H NMR (CCl_4) : 1.05 (t, 1.5 H, J = 8 Hz) ; 1.10 (t, 1.5 H, J = 8 Hz) ; 1.65 (s, $3H_5$) ; 3.6 (dq, 2H, J1 = 8 Hz ; $J2_{app}$ = 8 Hz) ; 4.95-6.6 (m, $3H_{1,3,4}$)

IR (CCl_4) : 3040, 2980, 1650, 1635, 1585

General conditions for the obtention of carbonyl compounds 2 and 3 via lithiodienols ethers 6a and 7a

To a solution of bromodienol ether 9a or 16a (2.26 mmol) in ether (8 mL) in a dry flash equipped with a magnetic stirrer and a septum cap, was added at -70°C, under argon, tertiobutyllithium (1.6 M in pentane titrated according to (22), 4.1 mmol) via a syringe in 15 min. The mixture was stirred for 90 mn at -70°C, then the carbonyl compound (0.8 to 0.9 eq) in dry ether (1 mL) was added via a syringe. After 1 h at -70°C and 1.5 h at -30°C, the reaction mixture was cooled to -60°C and 2.5 N HCl (15 mL) was added. The mixture was warmed to 0°C in 10 min then ether (15 mL) was added while stirring. The organic solution was washed with water (8 mL x 2) dried and on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography (silica gel, 96/4 petroleum ether/ether) to give carbonyl compound 2 or 3.

6-phenyl-hexa-3,5-dien-2-one 2a (6) was obtained starting from 9a (0.30 g, 1.27 mmol) and benzaldehyde 1a (0.11 g, 1,04 mmol, 0.85 eq) (yield : 73 %).

^{1}H NMR ($CDCl_3$) : 2.2 (3, 3H) ; 6.43 (m, 1H) ; 7.20-7.70 (m, 7H) ; 8.25 (1, $1H_6$, J = 16 Hz)

IR : 3080, 3060, 1685, 1670, 1610, 1600, 1585

6-methyl-hepta-3,5-dien-2-one 2b (23) was obtained starting from 9a (0.40 g, 1.7 mmol) and acetone (1 mL) (yield : 70 %).

^{1}H NMR ($CDCl_3$) : 1.9 (s, $6H_7$) ; 2.25 (s, $3H_1$) ; 6(d, $1H_5$, J = 12 Hz) ; 6.05 (d, $1H_3$, J = 14.7 Hz) ; 7.4 (dd, $1H_4$, J_1 = 12 Hz), J_2 = 14.7 Hz)

IR : 2990, 1720, 1630

Pseudo-ionone 2c was obtained starting from 9a (0.52 g, 2.21 mmol) and 6-methyl-5-hepten-2-one 1c (0.22 g, 1,75 mmol) (yield : 63 %)

^{1}H NMR ($CDCl_3$) : 1.5-1.7 (m, 9H) ; 1.85 (m, 4H) ; 2.1 (s, 3H) ; 5.05 (m, 1H) ; 5.9 (d, 1H, J = 12 Hz) ; 5.95 (d, 1H, J = 16 Hz) ; 7.25 (dd, 1H, J_1 = 12 Hz), J_2 = 16 Hz)

IR : 1680, 1650, 1620, 1580

HPLC : 2 isomers identified by comparison with an authentic sample (all trans : 68 %; areas ratio).

C_{18} Ketone 2d was obtained starting from 9a (0.52 g, 2.21 mmol) and β-ionone 1d (0.32 g, 1,67 mmol) (yield : 71 %).

^{1}H NMR ($CDCl_3$) : 1 (s, 6H) ; 1.4-2.1 (m, 12H) ; 2.25 (s, 3H) ; 5.9-6.7 (m, 4H) ; 7.2-7.8 (m, 1H)

IR : 2960, 1680, 1590, 1570

HPLC : 2 isomers identified by comparison with an authentic sample (all trans : 71 %).

3-Methyl-5-phenyl-penta-2,4-dienal 3a (14) was obtained starting from 16a (0.28 g, 1.43 mmol) and benzaldehyde (0,129 g, 0.9 eq) (yield : 56 %).

^{1}H NMR ($CDCl_3$) : 2.3 (s, 3H) ; 6 (d, $1H_2$, J = 8.4 Hz) ; 7 (d, $1H_4$, J = 6.3 Hz) ; 7.1-7.6 (m, 6H) ; 10.15 (d, $1H_1$, J = 8.4 Hz)

IR ($CDCl_3$) : 3030, 2980, 1670, 1650, 1640, 1610, 1595

Dehydrocitral 3e (14) was obtained starting from 16a (0.40 g, 2.26 mmol) and senecialdehyde (2.03 mmol, 0.9 eq)

^{1}H NMR (400 MHz, $CDCl_3$) All trans (70 %) : 1.77 (s, $6H_8$) ; 2.18 (s, 3H) ; 5.8 (d, H_2, J = 8.3 Hz) ; 5.88 (d, H_6, J = 9.9 Hz) ; 6.12 (d, H_4, J = 15.2 Hz) ; 6.86 (dd, H_5, J_1 = 9.9 Hz, J_2 = 15.2 Hz) ; 9.97 (d, H_1, J = 8.3 Hz)

2Z,4E (30 %) : 1.77 (s, $6H_8$) ; 2 (s, 3H) ; 5.7 (d, H_2, J = 8 Hz) ; 5.75 (d, H_6, J = 7.1 Hz) ;
7.05 (d, H_4, J = 15.3 Hz) ; 6.77 (dd, H_5, J_1 = 7.1 Hz, J_2 = 15.3 Hz) ; 10.07 (d, H_1, J = 8 Hz)

IR : 3050, 2970, 1650, 1595

β-ionylidene acetaldehyde 3f (14) was obtained starting from 16a (0.60 g, 3.14 mmol) and β-cyclocitral 1f. The product isolated after flash chromatography was a mixture of 3f (70 %) and 1f (30 %).

^1H NMR (400 MHz, $CDCl_3$) : 1.05 (s, 6H) ; 1.2-2.4 (m, 12H) ; 5.9 (d, 1H, J = 7.8 Hz) ;
6.15 (d, 1H, J = 16.8 Hz) ; 6.75 (d, 1H, J = 16.8 Hz) ; 10.05 (d, 1H, J = 7.8 Hz)

IR : 1670, 1610

Retinal 3g (14) was obtained starting from 16 a (0.65 g, 3.40 mmol) and β-ionylideneacetaldehyde (0.63 g, 2.9 mmol) (yield : 82 %).

HPLC (90/10 hexane/ether) : All trans 65 %, 9 cis : 22 % ; 13 cis : 13 % (areas ratio), by comparison with an authentic sample.

Preparation of hydroxyacetals 12

For the preparation of lithiodioxolane 6b from bromodioxolane 9b, see the general procedure. After addition of the carbonyl compound at -70°C, the mixture was warmed to 0°C and stirred for 1.5 h. Then saturated $NaHCO_3$ (5 mL) was added. After 10 min, the aqueous solution was extracted with ether (5 mL) and the combined organic solutions were washed with water (5 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvents, the residue was chromatographed on silicagel (85/15 petroleum ether/ether).

1-Hydroxy-1-phenyl-5-(1,3 dioxolane)-2yl-hex-2-ene 12a was obtained starting from bromodioxolane 9b (0.34 g, 1.16 mmol) and benzaldehyde (0.123 g, 1.16 mmol) (yield : 50 %).

^1H NMR ($CDCl_3$) : 1.25 (s, 1.2 H_6) ; 1.35 (s, 1.8H_6) ; 2.55 (m, 2H_4) ; 3 (m, 1H, exchanged with D_2O) ; 3.95 (s, 4H) ; 4.20 (m, 1H_1) ; 5.35-6 (m, 2$H_{2,3}$) ; 7.2-7.65 (m, 5H)

IR : 3420, 2990, 1630, 1445

6-Hydroxy-6-methyl-1,3-(dioxolane)-2yl-7-(2,6,6-trimethylcyclohex-1-en)-2yl-octa-4,7-diene 12d was obtained starting from bromodioxolane 9b (0.40 g, 1.36 mmol) and β-ionone 1d (0.30 g, 1.09 mmol) (yield : 50 %)

^1H NMR ($CDCl_3$) : 0.9 (s, 6H) ; 1.2-2.05 (m, 15H) ; 2.70 (d, 1H, J = 4Hz) ; 2.80 (d, 1H, J = 4Hz) ; 3.6 (m, 1H, exhanged with D_2O) ; 3.95 (s, 4H) ; 6.1 (d, 1H, J = 16 Hz) ; 5.3-5.9 (m, 3H)

IR : 3440, 2960, 1440, 1375

^{13}C NMR ($CDCl_3$) : 18.21 ; 21.20 ; 24.48 ; 28.63 ; 30.69 ; 32.55 ; 33.94 ; 37.41 ; 39.31 ; 64.83 ; 73.18 ; 109.78 ; 123.83 ; 124.05 ; 127.75 ; 136.87 ; 139.19 ; 140.29

6-phenyl-hexa-3,5-dien-2-one 2a from hydroxydioxolane 12a

A solution of hydroxydioxolane 12a (0.120 g, 0.51 mmol), acetone (5 mL) and 1N HCl (0.5 mL) was heated at reflux (1h., TLC monitoring). The reaction mixture was poured on ice and extracted with ether (15 mL x 2). The organic layer was separated and washed with water (7 mL x 2). The residue was chromatographed on silica gel (94/6 petroleum ether/ether) yielding ketone 2a 72%).

Ketone C_{18} 2d from hydroxy dioxolane 12d

A solution of hydroxy dioxolane 12d (0.10 g, 0.31 mmol) acetone (7 mL) and water (60 microlitres) was warmed at reflux for two minutes and 80 microlitres of a 3/141 HBr 48 % / acetone was added. After stirring for one hour at reflux (TLC monitoring), the mixture was poured onto ice and treated as before, yielding ketone 12d 74 %).

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