

# From allylic alcohols to saturated carbonyls using $\text{Fe}(\text{CO})_5$ as catalyst: scope and limitation studies and preparation of two perfume components

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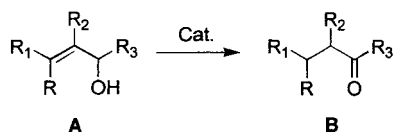
Received 4 December 2000; revised 12 January 2001; accepted 26 January 2001

**Abstract**—The direct conversion of allylic alcohols to saturated carbonyls, using  $\text{Fe}(\text{CO})_5$  as a catalyst, offers good synthetic potential. Mono-, di- and even trisubstituted alkenes bearing various alkyl, aryl and electronwithdrawing groups on the allylic system give good to excellent yields of rearranged products. Limitations occur mainly with polyunsaturated derivatives. This reaction was applied to a short and efficient synthesis of cyclamen aldehyde and foliaver. © 2001 Elsevier Science Ltd. All rights reserved.

The conversion of allylic alcohols to saturated carbonyl compounds is a useful synthetic process, usually requiring a two-step sequence of oxidation (reduction) followed by reduction (oxidation). A one pot catalytic transformation of allylic alcohols to saturated carbonyl compounds by internal redox processes (Scheme 1) is an attractive alternative strategy: it is a complete atom economy process, which may also minimise the number of protection–deprotection steps often required for such transformations.<sup>1a</sup>

Various transition metal complexes derivatives, including Ru, Rh, Co, Ni, Mo, Ir, Pt, have been already used for the transformation of A into B.<sup>1</sup> However, many of them are expensive and (or) not easily accessible; furthermore, they are often of restricted scope with regard to the degree of substitution of the double bond. Harsh reaction conditions are also often required.

Iron carbonyl derivatives have been known for a long time as being able to perform this transformation.<sup>2</sup> Furthermore, labelling experiments have clearly established a mechanism



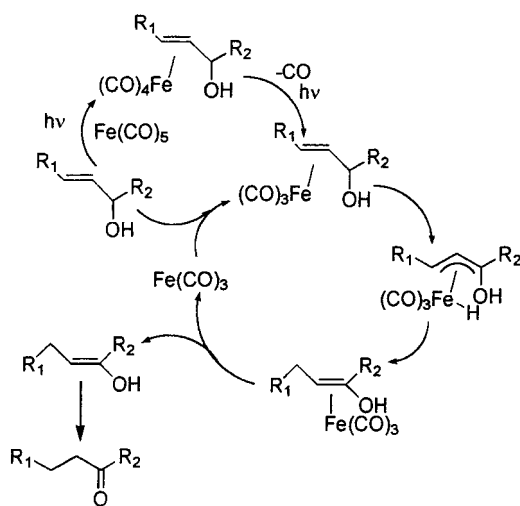
**Scheme 1.** Isomerization of allylic alcohols to ketones.

**Keywords:** allylic alcohols; isomerization; catalysis; iron.

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involving in the key step, an hydride migration in the coordination sphere of the metal (Scheme 2).<sup>2c,e</sup>

However, only limited studies have been reported later regarding the possible synthetic uses of this transformation. Simple alkyl derivatives<sup>2b</sup> and bicyclic systems<sup>2d–g</sup> have been examined. Extension to some ethers and esters have also been reported.<sup>2f,g</sup> As part of our program of novel preparation and synthetic applications of transition metal enolates,<sup>3</sup> we felt it necessary to perform a systematic study on the scope and limitations of this transformation induced by iron carbonyls.  $\text{Fe}(\text{CO})_5$  was selected for our



**Scheme 2.** Mechanism of  $\text{Fe}(\text{CO})_5$  induced isomerization.

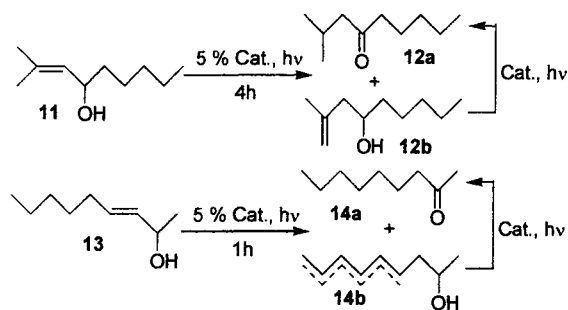
**Table 1.** Isomerization of simple models with alkyl and aryl groups

Alcohol	Fe(CO) <sub>5</sub> %	Time (h)	Yield %	Ketone
	1	1	95	
	2	2	86	
	2	2	95	
	5	1.5	84	
	5	5	64	

studies, as it is the most economical and easily accessible member of this family of reagents. Furthermore, it is also very efficient for the preparation of diene tricarbonyl iron complexes under irradiative conditions.<sup>4</sup>

Allylic alcohols with hydrogens or alkyl substituents on the double bond were studied first (Table 1). The reaction was found to be very efficient in the case of alcohols having methyl groups in  $\alpha$  or  $\beta$  position on the double bond and alkyl chains or aromatic groups on the secondary alcohol function. In each case, good to excellent yields were obtained using 1–5% catalyst.

Allylic alcohols bearing two alkyl substituents in geminal position on the double bond are known to be among the most difficult compounds with regards to this isomerization process.<sup>1a</sup> The reported examples were performed mainly with geraniol: low yields were obtained with Ir complexes,<sup>5</sup> low to moderate yields with Ni derivatives,<sup>1c</sup> while TPAP proved to be recently successful in this rearrangement.<sup>1c</sup> For the *gem*-dimethyl derivative **11**, the reaction is complete after 4 h, giving a mixture of **12a** and **12b** separated by chromatography (Scheme 3). For this sterically more hindered molecule, competition for hydride migration occurs between one hydrogen from the methyl group and the other hydrogen from the secondary alcohol. Such migrations of double bonds along alkyl chains and induced by iron carbonyls are well known in the literature.<sup>6</sup> However, from a synthetic point of view it is important to notice that pure homoallylic alcohol **12b**, under previously described reaction conditions, also isomerized slowly to the desired ketone **12a**.

**Scheme 3.** Isomerization of allylic alcohols **11** and **13**.

Another competitive double bond migration was observed in the case of alcohol **13**. Reaction of **13** gave the desired ketone **14a** (59% yield) together with a mixture of unsaturated alcohols **14b** resulting from the migration of the double bond along the pentyl chain (Scheme 3). The NMR data indicated a complex mixture of regio- and stereoisomers, which could not be separated by chromatography. However, here again, under the same reaction conditions, this mixture of isomers slowly isomerized to desired ketone **14a**.

The second family of allylic alcohols studied were compounds possessing an aromatic group on the double bond. As indicated in Table 2, all secondary alcohols gave the desired ketones in excellent yields.

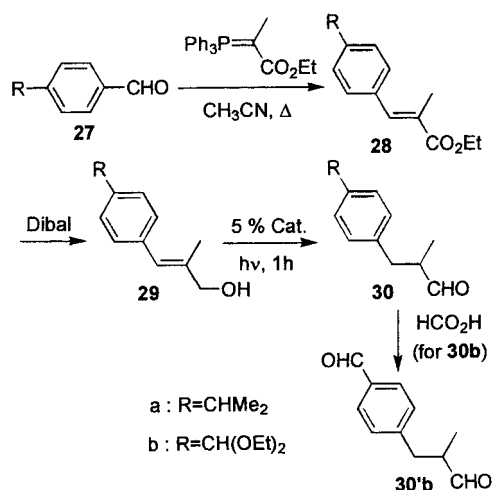
For primary alcohols, the results depend upon substitution: cinnamyl alcohol gave a complex reaction mixture with the desired aldehyde **24** isolated in only 38% yield. It was established that this derivative is not stable under the reaction conditions, giving a mixture of unidentified products. A completely different result was obtained in the case of alcohol **25**, giving **26** in excellent yield. Due to the steric hindrance by the methyl group, the corresponding aldehyde is probably more stable. It is interesting to notice that **25** is the first example of an allylic alcohol with substituents both in  $\alpha$  and  $\beta$  position on the double bond which could be isomerized under transition metal mediated catalysis. Since several perfume components have this general structure **26**, two of them were selected in order to test the applicability of this methodology: cyclamen aldehyde and foliaver.<sup>7</sup>

The starting alcohols **29** were prepared from commercially available aldehydes by standard procedures and in good overall yields (Scheme 4).

Using 5% molar catalyst, the isomerization of **29a** gave **30a** in quantitative yield. In the case of **29b**, the isomerization followed by the ketal deprotection using formic acid<sup>8</sup> gave foliaver **30'b**. Both perfume components were obtained

**Table 2.** Isomerization of cinnamyl type derivatives

Alcohol	Fe(CO) <sub>5</sub> %	Time (h)	Yield %	Ketone/Aldehyde
	5	2	93	
	10	1.5	90	
	5	1.5	85	
	5	5	80	
	5	2	38	
	5	1	90	



Scheme 4.

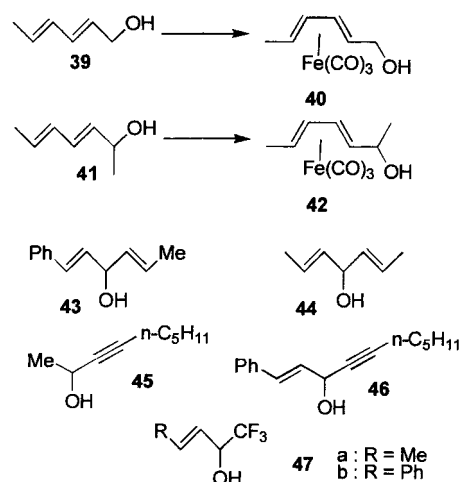
easily and in excellent overall yields (93% for **30a** and 85% for **30'b**) from aldehydes **27**.

Studies were then extended to alkenes functionalized with electron withdrawing groups; the corresponding results are given in Table 3. The reaction was found compatible with an ester group either in  $\alpha$  or  $\beta$  position on the alkene. In both cases, good yields of the desired ketoesters were obtained. More surprisingly, the  $\alpha,\beta$  unsaturated ketone **35** gave, with only 5% catalyst and after 3 h, the diketone **36** in 70% yield. It is well established that conjugated enones give easily stable  $\eta^2$  or  $\eta^4$  complexes on reaction with iron carbonyls.<sup>9</sup> Therefore, it is of note that in the case of **35**, hydride migration from the allylic alcohol portion of the molecule occurs preferentially. To the best of our knowledge, such a competition has not been observed previously.

The cyano group is also compatible with this isomerization, however 10% catalyst was necessary to obtain good rates for this reaction. The *Z* isomer **37b** reacted faster and gave ketone **38** in excellent yield. However, the corresponding *E* isomer **37a** exhibited a slower rate for the transformation and gave a lower yield. Furthermore, after 6 h it was possible to characterize (by TLC and NMR) in the reaction mixture, about 6% of the *Z* isomer. This indicates that *E*–*Z*

Table 3. Isomerization of derivatives with electron withdrawing substituents

Alcohol	Fe(CO) <sub>5</sub> %	Time (h)	Yield %	Ketone/Aldehyde
	5	1	70	
	5	1	87	
	5	3	70	
	10	6	40	
	10	1.5	90	

Scheme 5. Allylic alcohols which do not rearrange under Fe(CO)<sub>5</sub> catalysis.

isomerization occurs under the reaction conditions and that the *Z* isomer is, at least in part, an intermediate in the rearrangement of **37a**. The reason for this peculiar behaviour of latter derivative has not yet been established.

Finally, several examples of polyunsaturated alcohols were studied (Scheme 5).

Not surprisingly, in the case of  $\alpha,\beta$  unsaturated dienols **39** or **41**, no transformation to carbonyl derivatives was observed. The only isolated compounds (in yields corresponding to the amount of catalyst used) were the known  $\eta^4$  complexes **40** and **42** (as a mixture of  $\psi$ -*exo* and  $\psi$ -*endo* stereoisomers, in latter case).<sup>10</sup> For such dienols, the formation of the very stable  $\eta^4$  complexes is preferred over the hydride migration. Several other types of polyunsaturated systems have been studied, however, without success. In the cases of 1,4 dienols **43** and **44**, propargylic alcohol **45**, as well as enyne **46**, only starting material was recovered. Using higher catalyst loading (until 25% M) gave similar results with only minor quantities of unidentified degradation products. These results indicate that, using iron carbonyls as catalysts, the isomerization process has clear limitations with regard to the number of unsaturations in the starting allylic alcohols. Finally, another limitation has been encountered in the case of trifluoromethylated alcohols **47a** and **47b**: no reaction was observed and only the starting material was recovered, even using higher catalyst loading. This is probably due to the strong electron withdrawing effect of the CF<sub>3</sub> group, inhibiting hydride migration leading to the  $\pi$ -allyl iron intermediate, which is a key step in this reaction (Scheme 1).

In conclusion, we have shown that Fe(CO)<sub>5</sub> is an inexpensive and versatile catalyst for the isomerization of allylic alcohols to saturated carbonyl compounds. Its scope appears relatively broad for alkenes bearing alkyl, aryl or electron withdrawing substituents, though competitive processes may occur in some cases. However, severe limitations exist for polyunsaturated derivatives. Finally, we have reported a new and efficient preparation of two perfume components using, as a key step, this isomerization reaction.

## 1. Experimental

### 1.1. General

Except for **21**, all the starting allylic alcohols are already known in the literature. They were prepared by standard procedures:

addition of Grignard or organolithium derivatives on the corresponding aldehyde for **1**, **3**, **5**, **7**, **9**, **11**, **15**, **17**, **19**, **21**, **41**, **43**, **45**, **46**;

reduction by  $\text{LiAlH}_4$  of the corresponding propargylic alcohol for **13**;

for the primary alcohols, Dibal-H reduction of the corresponding esters for **29a**, **29b** while **23**, **25** and **39** are commercially available;

a Baylis–Hilman reaction for **33**;

Wittig reactions, starting from 2-hydroxy hexanal,<sup>11</sup> for **31**, **35**, **37**; in latter case, the (7:3) mixture of *E* (**37a**) and *Z* (**37b**) isomers could be separated by flash chromatography on silica gel;

reaction of Ruppert's reagent ( $\text{Me}_3\text{SiCF}_3 + \text{F}^-$ ) on corresponding aldehydes for **47**

**1.1.1. Allylic alcohol 21.** From  $\alpha$ -methylcinnamaldehyde (3 g, 20.5 mmol) and using 1.5 equiv. of  $n\text{-C}_5\text{H}_{11}\text{MgBr}$  in THF at  $-50^\circ\text{C}$ , allylic alcohol **21** was isolated after flash chromatography on silica gel using a 1:4 mixture of ether (E) and low boiling ( $<60^\circ\text{C}$ ) petroleum ether (Ep) as eluent. **21**: 3.7 g, 79% yield. TLC:  $R_f=0.31$  (E/Ep: 30:70).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.19–7.34 (m, 5H arom); 6.47 (s, 1H,  $\text{H}_1$ ); 4.16 (dt,  $J=6.9$ , 1.3 Hz, 1H,  $\text{H}_3$ ); 1.85 (d,  $J=1.3$  Hz, 3H,  $\text{CH}_3$ ); 1.72 (broad s, 1H, OH); 1.60–1.65 (m, 2H,  $\text{CH}_2$ ); 1.24–1.45 (m, 6H,  $\text{CH}_2$ ); 89 (t,  $J=7.1$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  140.37, 137.55, 128.92, 128.05, 128.05, 126.35, 125.70 ( $\text{C}_{\text{Ph}}$  and  $\text{C}=\text{C}$ ); 77.90 ( $\text{C}_3$ ); 34.98, 31.75, 25.46, 22.59 ( $\text{CH}_2$ ); 14.03, 13.05 ( $\text{CH}_3$ ). HRMS (EI): for  $\text{C}_{15}\text{H}_{22}\text{O}$ ,  $[\text{M}]^+$ : calcd: 218.1671; found: 218.1675. Anal. calcd for  $\text{C}_{15}\text{H}_{22}\text{O}$ : C, 82.51; H, 10.15. Found: C, 81.98; H, 10.17.

### 1.2. Representative procedure: preparation of foliaver

**1.2.1. Ester 28b.** A solution of aldehyde **27b** (1.9 g, 8.93 mmol) and  $\alpha$ -methyl carbethoxymethylenetriphenylphosphorane (3.88 g, 10.7 mmol) in  $\text{CH}_3\text{CN}$  (60 ml) was heated under reflux for 45 min. After distillation of solvent under vacuo, the ester was isolated by flash chromatography on silica gel using a 3:7 mixture of ether and low boiling petroleum ether as eluent. **28b**: 2.58 g, 97% yield. TLC:  $R_f=0.60$  (E/Ep: 50:50).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.68 [broad s, 1H,  $-\text{CH}=\text{C}(\text{CH}_3)$ ]; 7.38–7.51 (m, 4H arom); 5.51 [s, 1H,  $-\text{CH}(\text{OEt})_2$ ]; 4.27 (q,  $J=7.1$  Hz, 2H,  $-\text{CO}_2\text{CH}_2$ ); 3.64 (q,  $J=7.1$  Hz, 1H,  $\text{OCH}_2\text{CH}_3$ ); 3.62 (q,  $J=7.1$  Hz, 1H,  $\text{OCH}_2\text{CH}_3$ ); 3.56 (q,  $J=7.1$  Hz, 1H,  $\text{OCH}_2\text{CH}_3$ ); 3.54 (q,  $J=7.1$  Hz, 1H,  $\text{OCH}_2\text{CH}_3$ ); 2.11 [d,  $J=1.2$  Hz, 3H,  $-\text{CH}=\text{C}(\text{CH}_3)$ ]; 1.35 (t,  $J=7.1$  Hz, 3H,  $-\text{CO}_2\text{CH}_2\text{CH}_3$ ); 1.24 [t,  $J=7.1$  Hz, 6H,  $\text{CH}(\text{OCH}_2\text{CH}_3)_2$ ].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  168.56 ( $\text{CO}_2\text{Et}$ ), 139.07, 138.23, 135.85, 129.44, 128.68, 126.57 ( $\text{C}_{\text{Ph}}$  and  $\text{C}=\text{C}$ ); 101.02 [ $\text{CH}(\text{OEt})_2$ ]; 61.02, 60.79 ( $\text{OCH}_2$ ); 15.11

[( $\text{OCH}_2\text{CH}_3$ )<sub>2</sub>]; 14.24, 14.00 [( $\text{OCH}_2\text{CH}_3$ ) and ( $\text{C}=\text{CCH}_3$ )]. HRMS (EI): for  $\text{C}_{17}\text{H}_{24}\text{O}_4$ ,  $[\text{M}]^+$ : calcd: 292.1676; found: 292.1673. Anal. calcd for  $\text{C}_{17}\text{H}_{24}\text{O}_4$ : C, 69.83; H, 8.27. Found: C, 69.91; H, 8.22.

**1.2.2. Allylic alcohol 29b.** To a solution of ester **28b** (4 g, 13.7 mmol) in anhydrous ether (100 ml) was added dropwise under nitrogen at  $-35^\circ\text{C}$ , a 1 M solution of Dibal-H in hexanes (27.4 ml, 27.4 mmol). After 15 min stirring at this temperature, water (100 ml) was added and the reaction mixture was allowed to come back to room temperature. After addition of NaOH (2.4 g), the allylic alcohol was extracted with ether (3 $\times$ 50 ml). The organic phases were washed with brine, water, dried ( $\text{MgSO}_4$ ) and concentrated in vacuo. The alcohol was purified by flash chromatography using 1:1 mixture of ether and low boiling petroleum ether as eluent. **29b**: 2.95 g, 86% yield. TLC:  $R_f=0.25$  (E/Ep: 50:50).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.42–7.44 (d,  $J=8.1$  Hz, 2H arom); 7.26–7.28 (d,  $J=8.1$  Hz, 2H arom); 6.51 [broad s, 1H,  $-\text{CH}=\text{C}(\text{CH}_3)$ ]; 5.50 (s, 1H,  $-\text{CH}(\text{OEt})_2$ ); 5.50 [s, 1H,  $-\text{CH}(\text{OCH}_2\text{CH}_3)_2$ ]; 4.15 (m, 2H,  $-\text{CH}_2\text{OH}$ ); 3.58 [dq,  $J=7.12$ , 14.2 Hz, 4H,  $-\text{CH}(\text{OCH}_2\text{CH}_3)_2$ ]; 2.22 (s, 1H, OH); 1.88 (s, 3H,  $\text{CH}_3$ ); 1.24 [t,  $J=6.8$  Hz,  $-(\text{OCH}_2\text{CH}_3)_2$ ].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  137.87, 137.55, 136.95, 128.61, 126.32, 124.42 ( $\text{C}_{\text{Ph}}$  and  $\text{C}=\text{C}$ ); 101.38 [ $-\text{CH}(\text{OEt})_2$ ]; 68.67 ( $-\text{CH}_2\text{OH}$ ); 60.99 [ $-(\text{OCH}_2\text{CH}_3)_2$ ]; 15.22 ( $-\text{CH}=\text{CCH}_3$ ); 15.09 [ $-(\text{OCH}_2\text{CH}_3)_2$ ]. HRMS (EI): for  $\text{C}_{15}\text{H}_{22}\text{O}_3$ ,  $[\text{M}]^+$ : calcd: 250.1569; found: 250.1557. Anal. calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3$ : C, 71.96; H, 8.85. Found: C, 71.49; H, 8.88.

### 1.3. Representative procedure for isomerization: preparation of foliaver

**1.3.1. Monoacetal 30b.** Caution:  $\text{Fe}(\text{CO})_5$  is known to be toxic, therefore all reactions involving this reagent should be carried out under a ventilated fume hood.

Argon was bubbled (15 min) through a pentane solution (20 ml) of alcohol **29b** (1.26 g, 5 mmol) in a 50 ml pyrex flask. Then  $\text{Fe}(\text{CO})_5$  (33  $\mu\text{l}$ , 5% molar) was added via a syringe. The reaction mixture was irradiated, under magnetic stirring, by an external UV lamp (Phillips HPK 125W) until the disappearance of allylic alcohol (TLC monitoring): after 1 h, the reaction was complete. The reaction mixture was filtered on a short  $\text{SiO}_2$  plug and the solvent evaporated. The carbonyl derivative **30b** was purified by flash chromatography on silica gel using a 5:95 mixture of ether and low boiling petroleum ether as eluent. **30b**: 1.14 g, 90% yield. TLC:  $R_f=0.52$  (E/Ep: 50:50).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.71 (s, 1H, CHO); 7.40 (d,  $J=7.9$  Hz, 2H arom); 7.16 (d,  $J=8.1$  Hz, 2H arom); 5.48 [s, 1H,  $-\text{CH}(\text{OEt})_2$ ]; 3.55 (m, 4H,  $(\text{OCH}_2\text{CH}_3)_2$ ); 3.08 (dd,  $J=5.6$  Hz, 1H,  $-\text{CH}_a\text{H}_b\text{Ph}$ ); 2.65 (m, 1H,  $-\text{CHCH}_3$ ); 2.59 (dd, 1H,  $-\text{CH}_a\text{H}_b\text{Ph}$ ); 1.23 [t,  $J=7.1$  Hz, 6H,  $-\text{CH}(\text{CH}_3)_2$ ]; 1.075 (d,  $J=6.8$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  204.24 ( $-\text{CHO}$ ), 138.82, 137.18, 128.74, 126.72 ( $\text{C}_{\text{Ph}}$ ); 101.33 [ $-\text{CH}(\text{OEt})_2$ ]; 60.94 [ $-\text{CH}(\text{OCH}_2\text{CH}_3)_2$ ]; 47.90 ( $-\text{CCHO}$ ); 36.22 ( $-\text{CH}_2$ ); 15.09 [ $-\text{CH}(\text{OCH}_2\text{CH}_3)_2$ ]; 13.08 ( $-\text{CH}_3$ ). HRMS (EI):  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , the intensity of the molecular ion was too low to be measured. For:  $[\text{M}^-\text{OCH}_2\text{CH}_3]^+$  ( $\text{C}_{13}\text{H}_{17}\text{O}_2$ ): calcd:

205.1228; found: 205.1234. Anal. calcd for C<sub>15</sub>H<sub>22</sub>O: C, 71.96; H, 8.85. Found C, 71.68; H, 8.44.

**1.3.2. Foliaver 30'b.** A solution of acetal **30b** (0.5 g, 2 mmol) in pure formic acid (1 ml) was heated to 60°C during 45 min. After addition of a saturated Na<sub>2</sub>CO<sub>3</sub> solution and extraction with ether (3×30 ml), the organic phases were washed with brine and dried (MgSO<sub>4</sub>). Foliaver was purified by flash chromatography on SiO<sub>2</sub> using a 1:1 mixture of ether and low boiling petroleum ether as eluent. **30'b**: 0.3 g, 86% yield. TLC: R<sub>f</sub>=0.27 (E/Ep: 50:50). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.97 (s, 1H, -CHO); 9.71 (d, J=1.0 Hz, 1H, -CHCHO); 7.81 (d, J=8.1 Hz, 2H arom); 7.34 (d, J=8.1 Hz, 2H arom); 3.17 (dd, J=12.7 Hz, 1H, -CH<sub>a</sub>H<sub>b</sub>Ph); 2.65–2.77 (m, 1H, -CHCH<sub>3</sub>); 2.66 (dd, 1H, -CH<sub>a</sub>H<sub>b</sub>Ph); 1.11 (d, J=6.8 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 203.45 (-CHCHO), 191.87 (-PhCHO); 146.33, 134.88, 130.01, 129.70 (C<sub>Ph</sub>); 47.68 (-CCHO); 36.55 (-CH<sub>2</sub>); 13.26 (-CH<sub>3</sub>).

Except **22**, all carbonyl compounds obtained via this procedure are already known in the literature (from Beilstein data base). They have spectroscopical data (IR, <sup>1</sup>H and <sup>13</sup>C NMR) in good agreement with the indicated structures and with literature data.

**1.3.3. Ketone 22.** TLC: R<sub>f</sub>=0.60 (E/Ep: 30:70). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.14–7.26 (m, 5H arom); 2.96 (dd, J=7.1, 13.4 Hz, 1H, -PhCH<sub>a</sub>H<sub>b</sub>); 2.82 (m, 1H, -CH<sub>a</sub>H<sub>b</sub>CH); 2.54 (dd, 1H, -PhCH<sub>a</sub>H<sub>b</sub>); 2.38 (dt, J=7.3, 14.7 Hz, 1H, -COCH<sub>d</sub>H<sub>e</sub>); 1.14 (dt, 1H, -COCH<sub>d</sub>H<sub>e</sub>); 1.44–1.51 (m, 2H, -COCH<sub>d</sub>H<sub>e</sub>CH<sub>2</sub>); 1.12–1.30 [m, 4H, -(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>]; 1.07 (d, J=6.8 Hz, 3H, -CHCH<sub>3</sub>); 0.85 (d, J=7.1 Hz, 3H, -CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 214.38 (-CO), 139.79, 128.89, 128.30, 126.10 (C<sub>Ph</sub>); 48.02 (-CHCH<sub>3</sub>), 41.95, 30.07, 31.27, 23.09, 22.38 (-CH<sub>2</sub>); 16.85 (-CHCH<sub>3</sub>); 13.85 (-CH<sub>3</sub>). HRMS (EI) for C<sub>15</sub>H<sub>22</sub>O, [M]<sup>+</sup>: calcd: 218.1671; found: 218.1675. Anal. calcd for C<sub>15</sub>H<sub>22</sub>O: C, 82.51; H, 10.15. Found: C, 82.43; H, 10.07.

### Acknowledgements

We thank Dr I. Storet (Rhodia) for useful suggestions dealing with the perfume components, Dr M. Bartberger for very fruitful discussions and M. Prakesch for his help during the preparation of the manuscript.

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