172. β-Cleavage of Bis(homoallylic) Potassium Alkoxides. Two-Step Preparation of Propenyl Ketones from Carboxylic Esters. Synthesis of *ar*-Turmerone, α-Damascone, β-Damascone, and β-Damascenone

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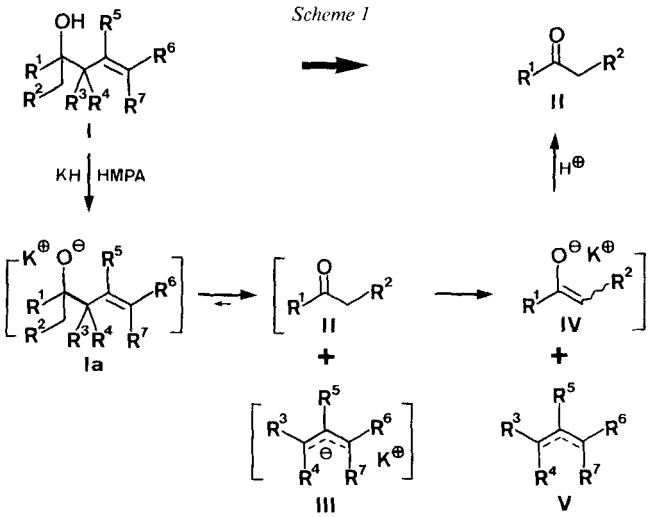
The transformation of 36 bis(homoallylic) alcohols **VII** to alkenones **IX** and **X** *via* β-cleavage of their potassium alkoxides **VIIa** in HMPA has been investigated *(cf. Scheme 2)*. These studies have established an order of β-cleavage for 2-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1,1-dimethyl-2-propenyl, and benzyl groups in alkoxides **49a**–**56a** and have allowed a comparison between the β-cleavage reaction and the oxy-*Cope* rearrangement in alkoxides **74a**–**83a**. As illustrative synthetic applications, a two-step preparation of propenyl ketones **15**–**42** from carboxylic esters is described, together with syntheses of *ar*-turmerone (**48**), α-damascone ((*E*)-**71**), β-damascone ((*E*)-**109**), and β-damascenone ((*E*)-**111**).

Introduction. – Recently, we have investigated the thermolytic β-cleavage of homoallylic tertiary potassium alkoxides **Ia** in hexamethylphosphoric triamide (HMPA) and demonstrated that this reaction is a general synthetic method for the transformation of homoallylic alcohols **I** to ketones **II** *(Scheme 1)* [1] [2]. Mechanistically, this transformation involves cleavage of the allylic C–C bond in **Ia**[1]) followed by irreversible enolate formation from the resulting ketone **II** induced by either the allylic carbanion **III** or

Scheme 1



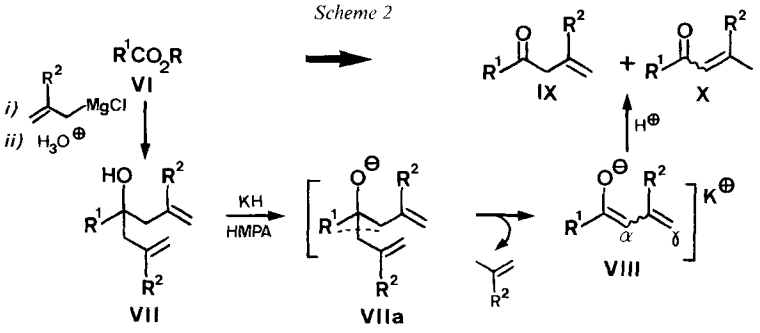
[1]) This cleavage is probably heterolytic although a mechanism involving homolytic cleavage *via* a ketyl intermediate cannot be excluded; for a mechanistic discussion, see [3–5].

Ia[2]); both processes lead to the formation of alkene **V** and the potassium enolate **IV** which subsequently affords **II** by protonation.

In continuation of this work, we now describe systematic studies of the β-cleavage of bis(homoallylic) tertiary potassium alkoxides **VIIa**. In this context, we also report a two-step preparation of propenyl ketones from carboxylic esters[3]) and syntheses of *ar*-turmerone (**48**), α-damascone ((*E*)-**71**), β-damascone ((*E*)-**109**), and β-damascenone ((*E*)-**111**), the last three compounds being members of the perfumistically valuable family of rose ketones [8].

Results and Discussion. – *Two-step Preparation of Propenyl Ketones from Carboxylic Esters: β-Cleavage of Bis(homoallylic) Potassium Alkoxides* **1a–14a**. A general method for the synthesis of a ketone from a carboxylic ester is a long-standing synthetic problem[4]). For the synthesis of propenyl ketones **IX** and **X**[5]), we envisaged that an indirect solution to this problem would involve the β-cleavage of a bis(homoallylic) potassium alkoxide **VIIa**, whose parent alcohol **VII** would be readily available from a carboxylic ester **VI** by double addition of an allylic *Grignard* reagent; protonation of the resulting potassium dienolate **VIII** would then afford the β,γ- and α,β-unsaturated ketones **IX** and **X** *(cf. Scheme 2)*. Indeed, in the cases studied, this two-step preparation of **IX** and **X** from

Scheme 2



VI (R^1 = alkyl, phenyl; R^2 = H, Me) proceeds in good overall yield *(cf. Table 1)*. Thus, treatment of the appropriate methyl carboxylate with an excess of either allylmagnesium chloride or methallylmagnesium chloride, formed *in situ* under *Barbier* conditions, in refluxing tetrahydrofuran (THF) afforded, after an aqueous workup, the bis(homoallylic) alcohols **1**–**14** in 76–87% yields. Addition of these alcohols to a slurry of KH (1.1 mol-equiv.) in HMPA[6]) at 20° afforded HMPA solutions of the corresponding potassium

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[2]) Enolatisation of **II** by **Ia** has previously been considered to be more likely [6]; however, for certain cyclic substrates, we have shown that intramolecular enolate formation is effected by **III** *via* a 1,5-H shift [1] [2].

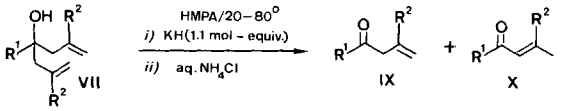
[3]) Part of this work has been the subject of preliminary communications [7].

[4]) For a discussion of this problem and an elegant solution for the direct synthesis of propenyl ketones from carboxylic esters, see [9].

[5]) For the synthesis of propenyl ketones *via* the thermal *retro*-ene reaction of bis(homoallylic) alcohols, see [10].

[6]) For all the β-cleavages described throughout this work, KH/HMPA was the base/solvent system employed; however, *t*-BuOK (1.5 mol-equiv.) in HMPA or other dipolar aprotic solvents such as dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) gives similar results.

Table 1. *β-Cleavage of Bis(homoallylic) Potassium Alkoxides* **1a–14a**



Entry	Alcohol **VII**	R^1	R^2	Yield[a] [%]	Products **IX** **X**	Yield[b] [%]
1	**1**	Bu	H	83	**15** + (*E*/*Z*)-**16**[c] (6:1)	75
2	**2**	Bu	Me	84	**17** + **18** (5:1)	79
3	**3**	i-Bu	H	84	**19** + (*E*/*Z*)-**20**[c] (5:1)	83
4	**4**	i-Bu	Me	84	**21** + **22** (4:1)	84
5	**5**	*s*-Bu	H	80	**23** + (*E*/*Z*)-**24**[c] (5:1)	79
6	**6**	*s*-Bu	Me	82	**25** + **26** (5:1)	82
7	**7**		H	76	**27** + (*E*/*Z*)-**28**[c] (7:1)	81
8	**8**		Me	84	**29** + **30** (5:1)	85
9	**9**		H	76	**31** + (*E*/*Z*)-**32**[c] (5:1)	84
10	**10**		Me	84	**33** + **34** (5:1)	83
11	**11**	*t*-Bu	H	85	**35** + (*E*/*Z*)-**36**[c] (7:1)	83
12	**12**	*t*-Bu	Me	86	**37** + **38** (3:1)	79
13	**13**	Ph	H	87	**39** + (*E*/*Z*)-**40**[c] (1.5:1)	84
14	**14**	Ph	Me	81	**41** + **42** (3:1)	82

[a]) Yield from corresponding methyl carboxylate **VI**.

[b]) Yield corresponds to the distilled mixture **IX**/**X**; analysis by GC/MS coupling and ^{1}H-NMR (360 MHz) spectroscopy *(cf. Exper. Part)*.

[c]) $(E/Z) > 5:1$.

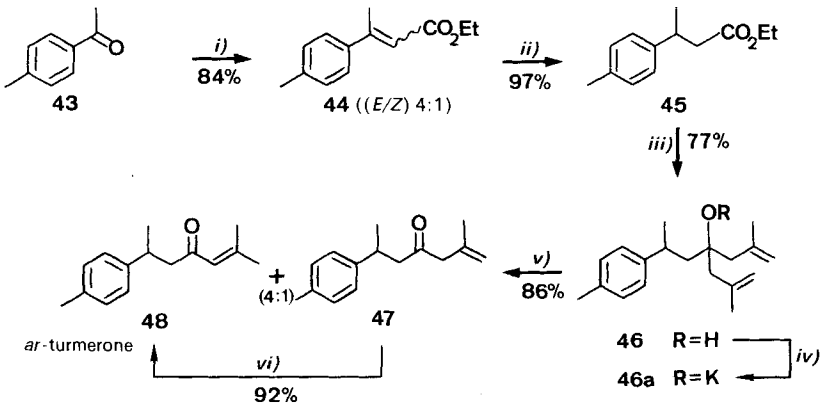
alkoxides **1a–14a** which were then heated at 80° for 2 h. Quenching of the cooled reaction mixtures with aqueous NH_4Cl solution, extractive workup, and distillation furnished mixtures of the β,γ- and α,β-unsaturated ketones **15–42** in 75–85% yield[7]). For characterisation purposes, these isomers were readily separated by chromatography on silica gel and identified from their spectral data (IR, ^{1}H-NMR and MS, *cf. Exper. Part)*. It should be noted that in all cases, the β,γ-unsaturated isomer is the major product, a result which is kinetically controlled and reflects a regioselective protonation of **VIII** at the α- rather

[7]) Each isomeric mixture **IX**/**X** can be readily equilibrated under acidic conditions (*e.g.* TsOH/THF, reflux) to afford almost exclusively (> 90%) the (*E*)-configurated α,β-unsaturated ketone **X** (R^2 = H).

than the γ-position. Additionally, when R^2 = H *(cf. Scheme 2)* (*E*)-**X** is strongly favoured with respect to (*Z*)-**X** ((*E*/*Z*) *ca.* 10:1)[8]).

Synthesis of ar-*Turmerone* (**48**, *cf. Scheme 3*). A synthetic application of the aforementioned methodology is illustrated by an efficient synthesis of racemic *ar*-turmerone (**48**), a naturally occurring sesquiterpenoid ketone isolated from the rhizomes of *Curcuma longa* [11]. The synthesis starts from *p*-methylacetophenone (**43**) which underwent a *Wadsworth-Emmons* reaction with the sodium salt of ethyl (diethoxyphosphoryl)acetate to afford the α,β-unsaturated ester **44** ((*E*/*Z*) 4:1) in 84% yield. Catalytic hydrogenation smoothly led to the ester **45** (97% yield) which was then treated with methallylmagnesium chloride to afford the bis(homoallylic) alcohol **46** in 77% yield. Treatment of **46** with KH (1.2 mol-equiv.) in HMPA at 20° resulted in the formation of the potassium alkoxide **46a** which was then heated to 40° to effect the β-cleavage and furnish, after an aqueous workup, a 4:1 mixture of **48** and its β,γ-unsaturated isomer **47** in 86% yield. Subsequent acid-catalysed equilibration of this mixture (TsOH/THF, reflux) afforded **48** in 92% yield.

Scheme 3

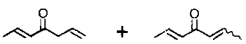
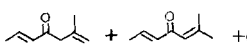
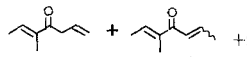
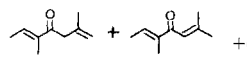
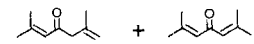
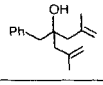


i) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF; *ii)* H_2, Pd/C, EtOH; *iii)*  Cl, Mg, Et_2O/THF, reflux, then $H_3O^{\oplus}$; *iv)* KH (1.2 mol-equiv.), HMPA, 20°; *v)* HMPA, 20–40°, then aq. NH_4Cl; *vi)* TsOH·H_2O (cat.), THF, reflux.

β-Cleavage of Tris(homoallylic) Potassium Alkoxides **49a–56a**. We next turned our attention to an investigation of the β-cleavage of tris(homoallylic) alkoxides **49a–56a** (*i.e.* **VIIa**: R^1 = allyl, benzyl; *Table 2*). The tris(homoallylic) alcohols **49–56** were readily prepared (77–86% yield) by reaction of the corresponding β,γ-unsaturated methyl carboxylate (for **49–54**) or methyl phenylacetate (for **55** and **56**) with allylmagnesium chloride or methallylmagnesium chloride in THF. Treatment of **49–56** with KH (1.1 mol-equiv.) in HMPA at 20° was followed by heating of the resulting potassium alkoxides **49a–56a** until reaction was complete. After the standard aqueous workup *(vide supra)*, the

[8]) Small amounts ($\leq$ 3%) of (*Z*)-**X** (R^2 = H) detected in the product mixtures of *Entries 1,3,5,7,9,11*, and *13 (cf. Table 1)* by ^{1}H-NMR and GC/MS analysis may be formed either directly by γ-protonation of **VIII** or, indirectly, from the dienol of **IX** *via* a thermolytic 1,5-H shift; as evidence for the latter hypothesis, distillation (105–110°/15 Torr) of a crude 1.5:1 mixture **39**/(*E*)-**40** resulted in the formation of a 5:2.5:1 mixture **39**/(*Z*)-**40**/(*E*)-**40**.

Table 2. *β-Cleavage of Tris(homoallylic) Potassium Alkoxides* **49a–56a**

Entry	Alcohol	Yield[a] [%]	Products[b]	Yield [%]
1	 **49**	77	 **57** (3.3:1) **58**[c]	76
2	 **50**	79	 **60** (4%) **61** (21%) +**62**, **63** (2:1) (57%)	82[d]
3	 **51**	82	 **64** (15%) **65**[c] (23%) +**57**, **58**[c] (2:1) (43%)	81
4	 **52**	86	 **66** (8%) **67** (4%) +**62**, **63** (2:1) (67%)	79
5	 **53**	84	**57**+**58**[c] (2:1)	82
6	 **54**	86	 **62** (3.2:1) **63**	83
7	 **55**	82	**57**+**58**[c] (2.3:1)	84
8	 **56**	85	**62**+**63** (3.3:1)	80

[a]) Yield from corresponding methyl carboxylate **VI**.

[b]) *β*-Cleavage reaction conditions: KH (1.1 mol-equiv.), HMPA, 20–40° (for *Entries 5–8*) or 80° (for *Entries 1–4*), then aq. NH_4Cl soln.; analysis by GC/MS coupling and ^{1}H-NMR (360 MHz) spectroscopy.

[c]) (*E,E*)-**58**/(*E,Z*)-**58** *ca.* 3:1.

[d]) 6-Methyl-1,5-heptadien-4-one (**59**) (*ca.* 1% yield) was also detected.

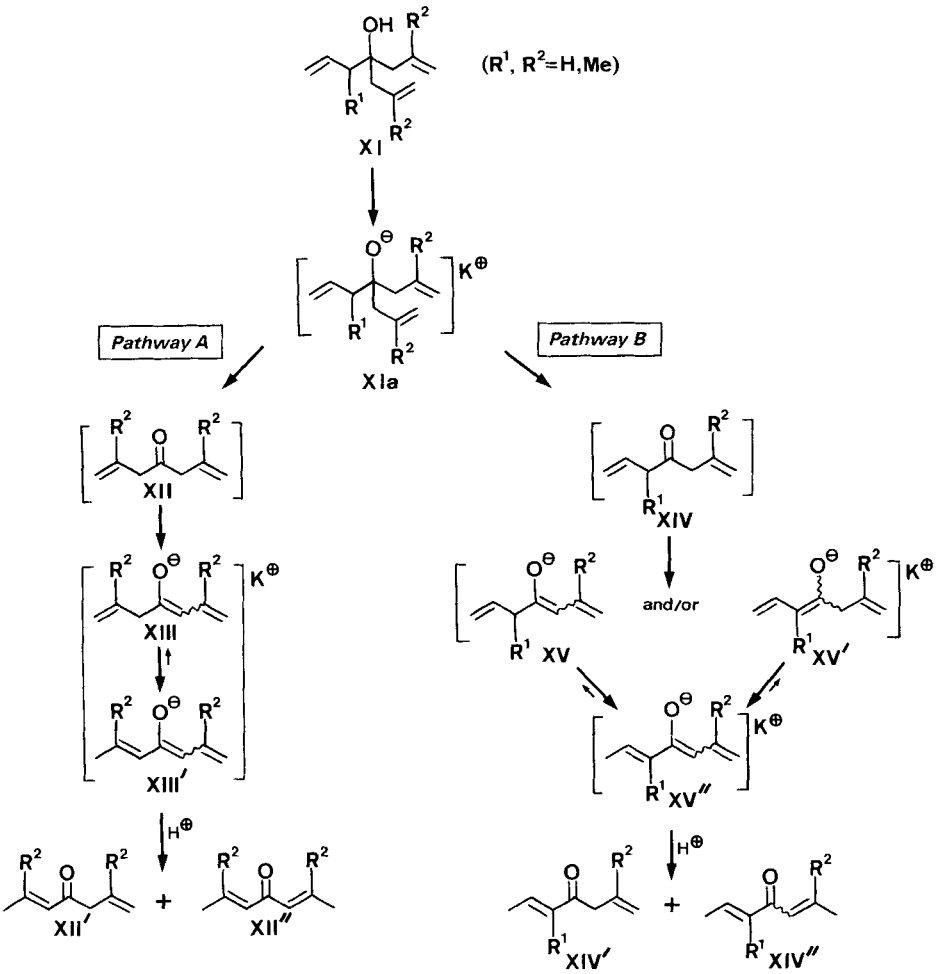
[e]) (2*E*,5*E*)-**65**/(2*E*,5*Z*)-**65** *ca.* 1:1.

dienones **57–67** derived from *β*-cleavages were isolated in 76–84% yield *(cf. Table 2)*. In each experiment, the product mixture was analysed by TLC, GC/MS coupling, and ^{1}H-NMR (360 MHz) spectroscopy, and in three cases *(cf. Entries 2–4)*, purification was effected by chromatography on silica gel to complement this analysis[9]). With **49** as substrate, each allylic group is equivalent and *β*-cleavage of its potassium alkoxide **49a** afforded a 3.3:1 mixture of dienones **57** and **58** *(cf. Entry 1)*. In contrast, alcohols **50–56** represent substrates whose potassium alkoxides **50a–56a** may undergo either one of two possible *β*-cleavages[10]). For **50a–52a** *(cf. Entries 2–4)*, these two distinct reaction pathways *(Pathways A* and *B, cf. Scheme 4)* are indeed observed and result in the formation of dienone mixtures whose compositions are indicated in *Table 2*. However, the *β*-cleavages of **53a–56a** result in exclusive cleavage of the 1,1-dimethyl-2-propenyl group and the benzyl group to afford **57**/**58** and **62**/**63** *(cf. Entries 5–8)*. The proposed reaction mecha-

[9]) Structural identification of **57–67** was effected by inspection of their ^{1}H-NMR (360 MHz), IR, and mass spectra and, when possible, by comparison with published spectral data (*cf. Exper. Part*).

[10]) It is assumed that there is no preference for the *β*-cleavage of either one of the two non-equivalent, diastereotopic 2-propenyl or 2-methyl-2-propenyl groups in **51a** and **52a**, respectively.

Scheme 4



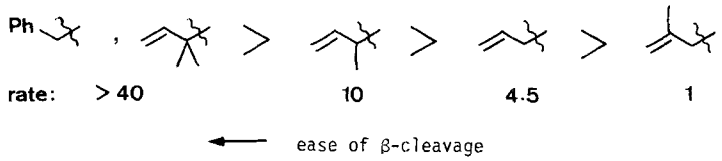
nism for the β-cleavages of **49a–52a** is outlined in *Scheme 4*[11]). Thus, the substrate alcohol **XI** is converted to its potassium alkoxide **XIa** in which β-cleavage of the allylic C–C bonds leads to either **XII** *(Pathway A)* or **XIV** *(Pathway B)*. Rapid enolate formation then gives the potassium dienolates **XIII** or **XV/XV'**, which undergo equilibration[12]) to their isomeric potassium trienolates **XIII'** or **XV''**; protonation finally affords dienones **XII'/XII''** and **XIV'/XIV''**, respectively.

Allowing for statistical factors, the product distribution of the dienone mixtures in *Entries 2–8* reflects the ease of β-cleavage for 2-propenyl, 1-methyl-2-propenyl, 2-methyl-

[11]) For substrates **53–56**, the reaction mechanism is identical to *Pathway A (cf. Scheme 4)* after β-cleavage of the allylic or benzylic C,C bond in **53a–56a**.

[12]) For evidence of potassium-enolate equilibration following an alkoxide-accelerated oxy-*Cope* rearrangement, see [12].

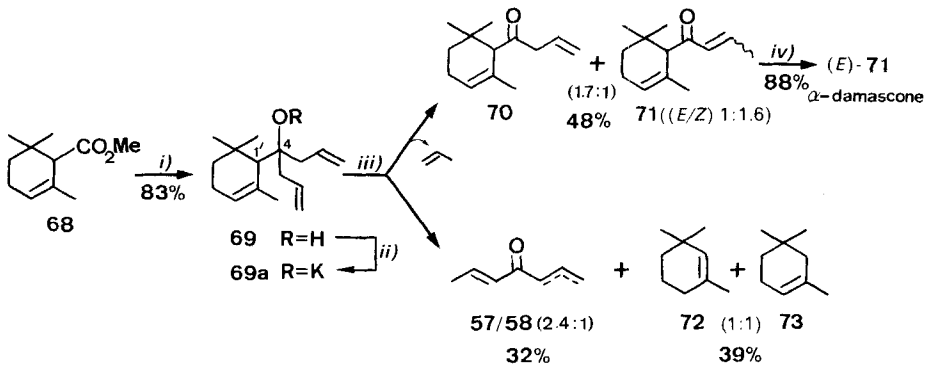
Scheme 5



2-propenyl, 1,1-dimethyl-2-propenyl, and benzyl groups in **50a–56a** and thus allows a rough quantitative estimate for their relative rates of cleavage[13]) *(cf. Scheme 5)*. A rational explanation for the observed order of β-cleavage preference for different allylic or benzylic groups probably involves a combination of two factors. Firstly, the release of non-bonding interactions in the substrate tris(homoallylic) potassium alkoxide and secondly, the thermodynamic stability of the allylic (or benzylic) carbanion resulting from the β-cleavage. This would then explain why the 1,1-dimethyl-2-propenyl and benzyl groups are cleaved more rapidly with respect to the three other allylic groups studied. In addition, the fact that the 2-propenyl group is cleaved more slowly than the 1-methyl-2-propenyl group may be a consequence of higher non-bonding interactions in the latter case; in contrast, the 2-propenyl group is cleaved faster than the 2-methyl-2-propenyl group where the relative stability of the allylic carbanion may be the decisive factor.

Synthesis of α*-Damascone* ((*E*)-**71**; *cf. Scheme 6*). The above conclusions concerning the relative ease of β-cleavage for different allylic groups in tris(homoallylic) potassium alkoxides were now tested for the potassium alkoxide **69a** whose β-cleavage of a 2-propenyl group provides a synthetic access to α-damascone ((*E*)-**71**). Thus, treatment of alcohol **69** [13], readily prepared from the reaction between methyl α-cyclogeranate (**68**) [14] and allylmagnesium chloride in THF (83% yield), with KH (1.1 mol-equiv.) in HMPA at 25–40°, followed by an aqueous workup, resulted in the isolation of a 1.7:1 mixture **70**/**71** ((*E*/*Z*)1:1.6) in 48% yield which was subsequently equilibrated (TsOH,

Scheme 6



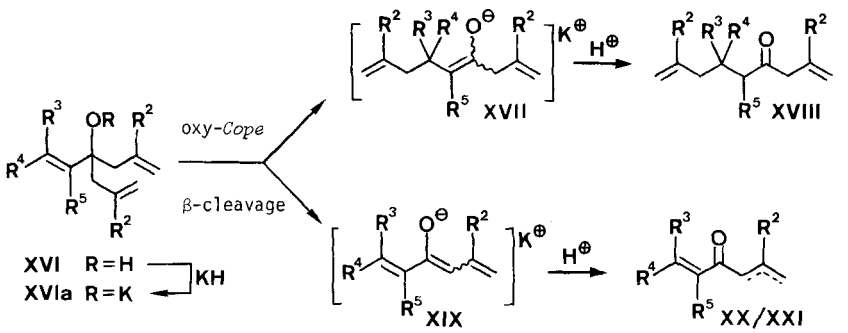
i) Cl, Mg, THF, reflux, then $H_3O^{\oplus}$; *ii)* KH (1.1 mol-equiv.), HMPA, 25°; *iii)* HMPA, 25–40°, then aq. NH_4Cl; *iv)* TsOH·H_2O (cat.), THF, reflux.

[13]) By analogy with previous work [1], it is assumed that the β-cleavage of the allylic (or benzylic) C–C bond is rate-determining.

THF, reflux) to (*E*)-**71** in 88% yield[14]). In addition, a 2.4:1 mixture **57**/**58** ((*E*/*Z*)2.8:1) and the trimethylcyclohexenes **72**/**73** (*ca.* 1:1 mixture) were isolated in 32 and 39% yields, respectively. Allowing for statistical factors, this reflects a 1.3:1 selectivity in favour of β-cleavage of the allylic C(4)–C(1′) bond *vs.* β-cleavage of either one of the two 2-propenyl groups in **69a**[15]). This result is thus in qualitative agreement with the foregoing model studies which showed that substitution of the C-atom adjacent to the alkoxide group, as exemplified by the 1-methyl-2-propenyl and 1,1-dimethyl-2-propenyl groups in **51a**–**54a**, favours β-cleavage of the allylic C–C bond.

β-Cleavage of Allylic Bis(homoallylic) Potassium Alkoxides **74a**–**83a**. In principle, allylic homoallylic potassium alkoxides can undergo either an alkoxide-accelerated oxy-*Cope* rearrangement [15] or a β-cleavage. In general, it is the former reaction which is preferred, except in cases where a quaternary centre is generated as a consequence of the *Cope* process [16]. We now decided to study the behaviour of allylic bis(homoallylic) potassium alkoxides **XVIa** (*i.e.* **VIIa**: R^1 = 1-alkenyl) which can also undergo these two reaction pathways *(cf. Scheme 7)*. Thus, an oxy-*Cope* rearrangement leads to dienone **XVIII** after protonation of the potassium enolate **XVII**, whilst a β-cleavage affords the β,γ- and α,β-unsaturated ketones **XX**/**XXI** *via* the potassium dienolate **XIX**.

Scheme 7

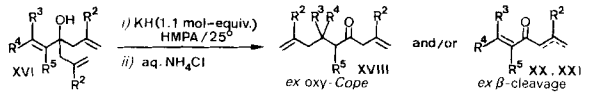


The alcohols **74**–**83** were readily prepared in 40–90% yield by reaction of the corresponding α,β-unsaturated methyl carboxylate with allylmagnesium chloride or methallylmagnesium chloride in THF *(Table 3)*. Treatment of alcohols **74**–**81** with KH (1.1 mol-equiv.) in HMPA at 25° afforded, after the standard aqueous workup and distillation, ketones **84**–**99** derived exclusively from oxy-*Cope* rearrangements of the potassium alkoxides **74a**–**81a** in 77–86% yields *(cf. Table 3, Entries 1–8)*. GC-Analysis of the crude product mixtures prior to distillation confirmed the absence of ketones resulting from putative β-cleavages. In contrast, identical preparation and treatment of potassium alkoxides **82a** and **83a** furnished a 2:1 mixture **100**/**101** ((*E*/*Z*)1:1) in 43% yield and a 2.8:1 mixture **102**/**103** in 48% yield, respectively, resulting from oxy-*Cope* rearrangements, together with the ketones **59**/**60**/**61** (3.4:1.4:1; 35% yield) and **62**/**63** (2.3:1; 38% yield), respectively, which derive from β-cleavages *(cf. Table 3, Entries 9* and *10)*. These

[14]) Treatment of **69** with *t*-BuOK (1.5 mol-equiv.) in DMF at 40° afforded (*E*)-**71** in 61% yield, after equilibration with aqueous acid [7].

[15]) In analogy with **51a** *(cf. Footnote 10)*, it is assumed that there is no preference for the β-cleavage of either one of the two diastereotopic 2-propenyl groups in **69a**.

Table 3. *Oxy*-Cope *Rearrangement/β-Cleavage of Allylic Bis(homoallylic) Potassium Alkoxides* **74a–83a**



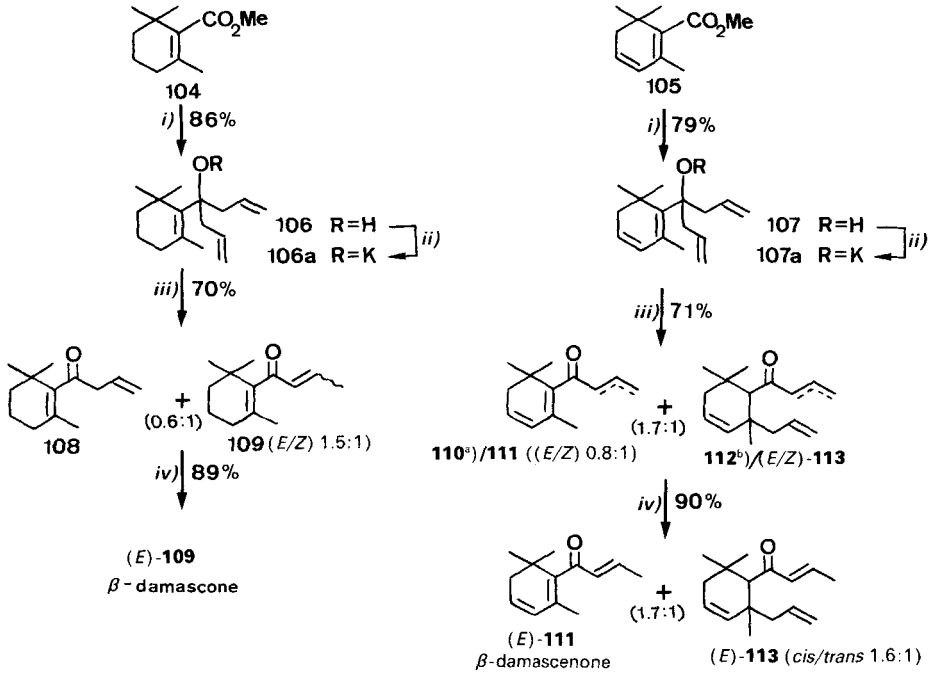
Entry	Alcohol		Yield[a]) [%]	Products[b])	Yield [%]
1		**74**	64	**84** + **85** (5:1) ((*E*/*Z*) 3:1)	81
2		**75**	40	**86** + **87** (4:1)	84
3		**76**	65	**88** + **89** (3:1) ((*E*/*Z*) 1:1)	78
4		**77**	72	**90** + **91** (3:1)	81
5		**78**	84	**92** + **93** (5:1) ((*E*/*Z*) 1:1)	83
6		**79**	81	**94** + **95** (6:1)	86
7		**80**	90	**96**[c]) + **97** (3:1) ((*E*/*Z*) 2:1)[c])	77
8		**81**	73	**98**[c]) + **99**[c]) (5:1)	82
9		**82**	83	**100**/**101**[d]) + **59**/**60**/**61**[e]) (1.2:1)	78
10		**83**	86	**102**/**103**[f]) + **62**/**63** (2.3:1)	84

[a]) Yield from corresponding methyl carboxylate **VI**.
[b]) Analysis by GC/MS coupling and ^{1}H-NMR (360 MHz) spectroscopy.
[c]) Diastereoisomeric 1:1 mixture.
[d]) **100**/**101** ((*E*/*Z*) 1:1) (2:1).
[e]) **59**/**60**/**61** 3.4:1.4:1.
[f]) **102**/**103** 2.8:1.

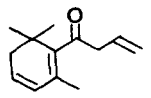
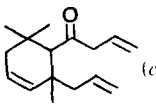
results are thus in qualitative agreement with the conclusions drawn by *Evans* [16] *(vide supra)* as **74a–83a** show a strong bias for the oxy-*Cope* rearrangement with respect to β-cleavage. Even **82a** and **83a**, despite the formation of a quaternary centre, exhibit a 1.2:1 selectivity in favour of the oxy-*Cope* process.

Synthesis of β-Damascone ((*E*)-**109**) *and β-Damascenone* ((*E*)-**111**; *cf. Scheme 8*). The allylic bis(homoallylic) alcohols **106** and **107** were prepared in 86 and 79% yields, respectively, from methyl β-cyclogeranate [14] and methyl β-safranate [17] by reaction with allylmagnesium chloride in THF [13]. Treatment of **106** with KH (1.1 mol-equiv.) in

Scheme 8



i) ⟋⟍Cl, Mg, THF, reflux, then $H_3O^{\oplus}$; *ii)* KH (1.1 mol-equiv.) HMPA, 25°; *iii)* HMPA, 25°, then aq. NH_4Cl; *iv)* TsOH · H_2O (cat.) THF, reflux.

a) **110**:  b) **112**:  (*cis*/*trans* mixture)

HMPA at 25° resulted in the exclusive formation of products resulting from the β-cleavage of **106a**, *i.e.* a 0.6:1 mixture **108**/**109** ((*E*/*Z*)1.5:1) in 70% yield. Subsequent equilibration (TsOH, THF, reflux) afforded (*E*)-**109** in 89% yield (62% from **106**). Analysis (GC and ^{1}H-NMR (360 MHz)) of the crude product mixture confirmed the absence ($\leq 5\%$) of products from a putative oxy-*Cope* rearrangement of **106a**. In contrast, subjection of **107** to identical conditions afforded a 1.7:1 mixture (71% yield) of **110**/(*E*/*Z*)-**111** (β-cleavage products) and **112**/(*E*/*Z*)-**113** (diastereoisomeric mixtures; oxy-*Cope* products). Subsequent equilibration (TsOH, THF, reflux) of this crude mixture converted the β,γ- and (*Z*)-configurated α,β-unsaturated ketones to their (*E*)-configurated α,β-unsaturated ketones whose chromatographic purification on silica gel furnished (*E*)-**111** (40% yield from **107**) and an inseparable 1.6:1 mixture (24% yield from **107**) of *cis*- and *trans*-(*E*)-**113**[16]).

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[16]) Structural assignment of *cis*- and *trans*-*(E)*-**113** was effected on the basis of their ^{1}H- and ^{13}C-NMR spectra combined with a ^{13}C,^{1}H-correlation experiment (CH–CORR). In particular, the major component *cis*-*(E)*-**113** where the pseudoaxial allyl group at C(2′) is *cis* to the pseudoequatorial but-2-enone side chain at C(1′), the ^{13}C-NMR spectrum exhibits resonances at 42.3 ppm for C(1″) and 29.1 ppm for CH_3–C(2′); in the minor component *trans*-(*E*)-**113** in which the allyl group at C(2′) is pseudoequatorial and *trans* to the pseudoequatorial but-2-enone side chain at C(1′), C(1″) resonates at 48.1 ppm and CH_3–C(2′) at 23.7 ppm.

At first sight, these results are surprising. Whereas the comparably substituted potassium alkoxides **82a** and **83a** exhibit a 1.2:1 selectivity for the oxy-*Cope* rearrangement *vs.* β-cleavage *(cf. Table 3)*, **106a** and **107a** show either a total or partial selectivity favouring the latter pathway. This difference in behaviour is possibly due to the presence of the cyclohexene and cyclohexadiene rings which may increase non-bonding interactions in the oxy-*Cope* transition states of **106a** and **107a**, thus disfavouring these processes.

Experimental Part

General. Mg turnings for the *Grignard* reactions were obtained from *Mimeta SA* (Martigny). Hexamethylphosphoric triamide (HMPA; *purum*), freshly distilled from CaH_2 before use, and KH (*pract.; ca.* 20% in oil) were obtained from *Fluka AG* (Buchs). GC: *Hewlett Packard* instrument, model *5890A;* capillary columns *Chrompack CPWax 57CB* (10 m) and *EPSiL 5CB* (10 m). TLC: silica gel *60 (Merck,* layer thickness 0.25 mm); R_f values calculated using CH_2Cl_2 as eluent. Column chromatography (CC): silica gel *60 (Merck,* 0.063–0.2 mm, 70–230 mesh, *ASTM*). Bulb-to-bulb distillation: *Büchi GKR-50* oven; b.p. correspond to the air temp. IR spectra (liquid film): *Perkin-Elmer 297* spectrometer; cm^{-1}. ^{1}H-NMR spectra ($CDCl_3$): *Bruker-WH-360* (360 MHz) or *Varian-EM360* (60 MHz) spectrometers; unless otherwise indicated, 360-MHz spectra are reported; δ (ppm) rel. to TMS as internal standard. MS: *Varian MAT 112* spectrometer (*ca.* 70 eV); intensities in % relative to the base peak (100%).

General Procedure for the Preparation of Alcohols 1–14. – A soln. of either allyl chloride or 2-methylallyl chloride (0.25 mol) and the corresponding methyl carboxylate (*vide infra*; 0.1 mol) in THF (120 ml) was added dropwise to a stirred slurry of Mg turnings (0.24 mol) in THF (20 ml) under N_2 at such a rate as to maintain a gentle reflux. After the addition (*ca.* 1 h), the mixture was refluxed until TLC indicated completion of the reaction (1–3 h). The cooled mixture was then poured into cold sat. aq. NH_4Cl soln. After separation of the two layers, the H_2O phase was extracted with Et_2O (4 × 50 ml) and the combined extract washed once with H_2O and 4 times with sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated. Fractional distillation *i.v.* afforded **1–14** as colourless oils.

4-Butyl-1,6-heptadien-4-ol (**1**) (83% yield from methyl pentanoate). R_f 0.52. B.p. 83–87°/15 Torr ([18]: 87–90°/23 Torr). IR: 3450 (br.), 3090, 1644, 1444, 1000, 920. ^{1}H-NMR (60 MHz; +D_2O): 0.90 (*t*, *J* = 7,3 H); 0.80–1.70 (6 H); 2.20 (*d*, *J* = 7,4 H); 4.85–5.25 (4 H); 5.90 (*m*, 2 H). MS: 168 (0, $M^{+\cdot}$), 127 (11), 85 (100), 69 (24), 57 (72), 41 (42).

4-Butyl-2,6-dimethyl-1,6-heptadien-4-ol (**2**) (84% yield from methyl pentanoate). R_f 0.70. B.p. 102–107°/15 Torr. IR: 3500 (br.), 3090, 1642, 1458, 1380, 1070, 894. ^{1}H-NMR (60 MHz; +D_2O): 0.90 (*t*, *J* = 7, 3 H); 0.80–1.70 (4 H); 1.81 (6 H); 2.18 (*s*, 4 H); 4.76 (2 H); 4.92 (2 H). MS: 196 (0, $M^{+\cdot}$), 141 (11), 85 (100), 57 (62), 55 (16), 41 (17).

4-(2'-Methylpropyl)-1,6-heptadien-4-ol (**3**) (83% yield from methyl 3-methylbutanoate). R_f 0.42. B.p. 83–85°/15 Torr ([18]: 78–80°/28 Torr). IR: 3480 (br.), 3090, 1640, 1000, 920, 880. ^{1}H-NMR (60 MHz; +D_2O): 0.95 (*d*, *J* = 7, 6 H); 1.38 (*d*, *J* = 7, 2 H); 1.87 (*m*, 1 H); 2.24 (*d*, *J* = 7, 4 H); 4.85–5.25 (4 H); 5.87 (*m*, 2 H). MS: 168 (0, $M^{+\cdot}$), 127 (10), 111 (3), 85 (100), 69 (30), 57 (94).

2,6-Dimethyl-4-(2'-methylpropyl)-1,6-heptadien-4-ol (**4**) (84% yield from 3-methylbutanoate). R_f 0.60. B.p. 101–102°/15 Torr. IR: 3560 (br.), 3080, 1640, 1380, 1130, 1070, 892, 780. ^{1}H-NMR (60 MHz; +D_2O): 0.95 (*d*, *J* = 7, 6 H); 1.41 (*d*, *J* = 7, 2 H); 1.83 (6 H); 1.87 (*m*, 1 H); 2.23 (*s*, 4 H); 4.77 (2 H); 4.93 (2 H). MS: 196 (0, $M^{+\cdot}$), 141 (9), 85 (100), 69 (3), 57 (92), 55 (24).

4-(1'-Methylpropyl)-1,6-heptadien-4-ol (**5**) (80% yield from methyl 2-methylbutanoate). R_f 0.47. B.p. 88–89°/15 Torr. IR: 3500 (br.), 3080, 1640, 1380, 1000, 915, 760. ^{1}H-NMR (60 MHz; +D_2O): 0.91 (*d*, *J* = 7, 3 H); 0.94 (*t*, *J* = 7, 3 H); 1.00–2.00 (3 H); 2.24 (*d*, *J* = 7, 4 H); 4.85–5.25 (4 H); 5.89 (*m*, 2 H). MS: 168 (0, $M^{+\cdot}$), 127 (7), 111 (4), 85 (49), 69 (39), 57 (100).

2,6-Dimethyl-4-(1'-methylpropyl)-1,6-heptadien-4-ol (**6**) (82% yield from methyl 2-methylbutanoate). R_f 0.60. B.p. 102–105°/15 Torr. IR: 3560 (br.), 3080, 1640, 1380, 1070, 1000, 892, 760. ^{1}H-NMR (60 MHz; +D_2O): 0.90 (*d*, *J* = 7, 3 H); 0.93 (*t*, *J* = 7, 3 H); 1.00–2.00 (3 H); 1.83 (6 H); 2.21 (4 H); 4.73 (*m*, 2 H); 4.91 (*m*, 2 H). MS: 196 (0, $M^{+\cdot}$), 141 (7), 85 (56), 57 (100), 55 (25), 41 (17).

4-Cyclopentyl-1,6-heptadien-4-ol (**7**) (76% yield from methyl cyclopentanecarboxylate). R_f 0.41. B.p. 32–37°/0.03 Torr. IR: 3480 (br.), 3060, 2940, 2860, 1638, 1440, 990, 904, 640. ^{1}H-NMR (60 MHz; +D_2O): 1.20–2.00 (9 H); 2.25 (*d*, *J* = 7, 4 H); 5.03 (*m*, 2 H); 5.07 (*m*, 2 H); 5.85 (*m*, 2 H). MS: 180 (0, $M^{+\cdot}$), 139 (4), 97 (59), 69 (100), 55 (7), 41 (12).

4-Cyclopentyl-2,6-dimethyl-1,6-heptadien-4-ol (**8**) (84% yield from methyl cyclopentanecarboxylate). R_f 0.56. B.p. 54–60°/0.05 Torr. IR: 3550 (br.), 3060, 2940, 2860, 1638, 1440, 1368, 1054, 890. ^{1}H-NMR (60 MHz; +D_2O): 1.40–1.90 (9 H); 1.84 (6 H); 2.21 (*s*, 4 H); 4.77 (2 H); 4.90 (2 H). MS: 208 (0, $M^{+\cdot}$), 153 (4), 97 (59), 83 (11), 69 (100), 55 (15).

4-Cyclohexyl-1,6-heptadien-4-ol (**9**) (76% yield from methyl cyclohexanecarboxylate). R_f 0.43. B.p. 62–63°/0.03 Torr. IR: 3460 (br.), 3060, 2910, 2850, 1636, 1440, 990, 902. ^{1}H-NMR (60 MHz; +D_2O): 0.90–2.10 (11 H); 2.20 (*d*, *J* = 7, 4 H); 5.00 (*m*, 2 H); 5.05 (*m*, 2 H); 5.83 (*m*, 2 H). MS: 194 (0, $M^{+\cdot}$), 153 (3), 111 (40), 83 (100), 69 (28), 55 (30).

4-Cyclohexyl-2,6-dimethyl-1,6-heptadien-4-ol (**10**) (84% yield from methyl cyclohexanecarboxylate). R_f 0.63. B.p. 66–68°/0.03 Torr. IR: 3550 (br.), 3060, 2910, 2850, 1638, 1440, 1366, 1045, 880. ^{1}H-NMR (60 MHz; +D_2O): 0.90–2.10 (11 H); 1.81 (6 H); 2.18 (*AB*, *J* = 14, 4 H); 4.70 (2 H); 4.89 (2 H). MS: 222 (0, $M^{+\cdot}$), 167 (3), 111 (32), 83 (100), 55 (32).

4-(1',1'-Dimethylethyl)-1,6-heptadien-4-ol (**11**) (85% yield from methyl 2,2-dimethylpropanoate). R_f 0.48. B.p. 80–83°/15 Torr ([19]: 187.5°/746 Torr). IR: 3450 (br.), 3090, 1640, 1400, 1370, 1000, 918, 860. ^{1}H-NMR (60 MHz; +D_2O): 0.98 (*s*, 9 H); 2.37 (*d*, *J* = 7, 4 H); 4.85–5.25 (4 H); 5.95 (*m*, 2 H). MS: 168 (0, $M^{+\cdot}$), 127 (10), 111 (5), 85 (32), 69 (71), 57 (100).

4-(1',1'-Dimethylethyl)-2,6-dimethyl-1,6-heptadien-4-ol (**12**) (86% yield from methyl 2,2-dimethylpropanoate). R_f 0.65. B.p. 99–101°/15 Torr. IR: 3460 (br.), 3080, 1640, 1400, 1275, 1090, 995, 892. ^{1}H-NMR (60 MHz; + D_2O): 0.98 (*s*, 9 H); 1.87 (6 H); 2.31 (4 H); 4.79 (2 H); 4.88 (2 H). MS: 196 (0, $M^{+\cdot}$), 141 (5), 97 (1), 85 (23), 69 (1), 57 (100), 55 (36), 41 (20).

4-Phenyl-1,6-heptadien-4-ol (**13**) (87% yield from methyl benzoate). R_f 0.45. B.p. 127–130°/15 Torr ([20]: 124–126°/30 Torr). IR: 3500 (br.), 3080, 2990, 1640, 1500, 1448, 1000, 920, 704. ^{1}H-NMR (60 MHz; +D_2O): 2.58 (*m*, 4 H); 4.80–6.00 (6 H); 7.35 (5 H). MS: 188 (0, $M^{+\cdot}$), 147 (18), 105 (100), 91 (1), 77 (30), 51 (6), 41 (9).

2,6-Dimethyl-4-phenyl-1,6-heptadien-4-ol (**14**) (81% yield from methyl benzoate). R_f 0.60. B.p. 73–77°/0.01 Torr. IR: 3550 (br.), 3080, 1640, 1498, 1443, 1380, 1070, 1030, 900, 730, 700. ^{1}H-NMR (60 MHz; +D_2O): 1.40 (6 H); 2.59 (*s*, 4 H); 4.68 (*m*, 2 H); 4.81 (*m*, 2 H); 7.34 (5 H). MS: 216 (0, $M^{+\cdot}$), 161 (8), 106 (6), 105 (100), 77 (24), 55 (3).

General Procedure for the β-Cleavage of Potassium Alkoxides 1a–14a: Preparation of Ketones 15–42. – A soln. of the corresponding alcohol (10 mmol) in HMPA (5 ml) was added dropwise within 15 min to a stirred slurry of KH (11 mmol) in HMPA (25 ml) at r.t. under N_2. The mixture was stirred at r.t. for a further 20 min and then heated at 80° until TLC (after quenching of an aliquot with sat. aq. NH_4Cl soln. followed by extraction with Et_2O) indicated completion of the reaction (1–2 h). The cooled mixture was then poured cautiously into cold sat. aq. NH_4Cl soln. (150 ml). Extraction with Et_2O (4 × 50 ml), washing of the combined org. phase with H_2O, sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., drying (Na_2SO_4), concentration at atmospheric pressure followed by distillation *i.v.* of the residual oil afforded **15–42** as colourless oils. In each experiment, the product mixture was analysed by TLC, GC/MS coupling, and ^{1}H-NMR (360 MHz) spectroscopy.

1-Octen-4-one (**15**) *and (E)-2-Octen-4-one* ((*E*)-**16**) (6:1 mixture, 75% yield from **1**). B.p. 56–58°/15 Torr ([18]: 60–62°/23 Torr (**15**), 81–82°/20 Torr ((*E*)-**16**)).

15: R_f 0.66. IR: 1710. ^{1}H-NMR: 0.90 (*t*, *J* = 7, 3 H); 1.31 (*m*, 2 H); 1.56 (*m*, 2 H); 2.44 (*t*, *J* = 7, 2 H); 3.17 (*d*, *J* = 7, 2 H); 5.14 (br. *d*, *J* = 18, 1 H); 5.18 (br. *d*, *J* = 11, 1 H); 5.92 (*m*, 1 H). MS: 126 (2, $M^{+\cdot}$), 85 (100), 69 (16), 57 (98), 41 (59).

16: R_f 0.50. IR: 1685. ^{1}H-NMR: 0.91 (*t*, *J* = 7, 3 H); 1.00–1.60 (4 H); 1.89 (*dd*, *J* = 7, 2, 3 H); 6.12 (br. *d*, *J* = 15, 1 H); 6.84 (*m*, 1 H). MS: 126 (1, $M^{+\cdot}$), 111 (4), 97 (3), 84 (27), 69 (100), 41 (22).

2-Methyl-1-octen-4-one (**17**) *and 2-Methyl-2-octen-4-one* (**18**) (5:1 mixture, 79% yield from **2**). B.p. 64–68°/15 Torr.

17: R_f 0.71. IR: 1705. ^{1}H-NMR: 0.90 (*t*, *J* = 7, 3 H); 1.32 (*m*, 2 H); 1.55 (*m*, 2 H); 1.74 (*s*, 3 H); 2.45 (*t*, *J* = 7, 2 H); 3.10 (*s*, 2 H); 4.81 (br. *s*, 1 H); 4.94 (br. *s*, 1 H). MS: 140 (4, $M^{+\cdot}$), 85 (92), 83 (15), 57 (100), 55 (22), 41 (28).

18: R_f 0.63. IR: 1680. ^{1}H-NMR: 0.90 (*t*, *J* = 7, 3 H); 1.32 (*m*, 2 H); 1.55 (*m*, 2 H); 1.88 (*s*, 3 H); 2.14 (*s*, 3 H); 2.40 (*t*, *J* = 7, 2 H); 6.07 (br. *s*, 1 H). MS: 140 (1, $M^{+\cdot}$), 111 (2), 98 (19), 83 (100), 55 (29).

6-Methyl-1-hepten-4-one (**19**) [21] *and (E)-6-Methyl-2-hepten-4-one* ((*E*)-**20**) (5:1 mixture, 83% yield from **3**). B.p. 53–56°/15 Torr.

19: R_f 0.69. IR: 1710. ^{1}H-NMR: 0.91 (*d*, *J* = 7, 6 H); 2.13 (*m*, 1 H); 2.32 (*d*, *J* = 7, 2 H); 3.15 (*d*, *J* = 7, 2 H); 5.13 (br. *d*, *J* = 18, 1 H); 5.18 (br. *d*, *J* = 11, 1 H); 5.92 (*dddd*, *J* = 18, 11, 7, 7, 1 H). MS: 126 (1, $M^{+\cdot}$), 85 (82), 69 (19), 57 (100), 41 (49).

(*E*)-**20**: R_f 0.55. IR: 1685. ^{1}H-NMR: 0.92 (*d*, *J* = 7, 6 H); 1.89 (*dd*, *J* = 7, 2, 3 H); 2.14 (*m*, 1 H); 2.39 (*d*, *J* = 7, 2 H); 6.12 (br. *d*, *J* = 15, 1 H); 6.83 (*dq*, *J* = 15, 7, 1H). MS: 126 (0.2, $M^{+\cdot}$), 111 (16), 84 (20), 69 (100), 41 (21).

2,6-Dimethyl-1-hepten-4-one (**21**) *and 2,6-Dimethyl-2-hepten-4-one* (**22**) (4:1 mixture, 84% yield from **4**). B.p. 60–64°/15 Torr.

21: R_f 0.72. IR: 1704. ^{1}H-NMR: 0.91 (*d*, *J* = 7, 6 H); 1.74 (*s*, 3 H); 2.14 (*m*, 1 H); 2.33 (*d*, *J* = 7, 2 H); 3.08 (*s*, 2 H); 4.81 (br. *s*, 1 H); 4.94 (br. *s*, 1 H). MS: 140 (3, M^+), 85 (78), 83 (12), 57 (100), 55 (17), 41 (26).

22: R_f 0.64. IR: 1680. ^{1}H-NMR: 0.92 (*d*, *J* = 7, 6 H); 1.88 (*s*, 3 H); 2.14 (*s*, 3 H); 2.15 (*m*, 1 H); 2.27 (*d*, *J* = 7, 2 H); 6.06 (br. *s*, 1 H). MS: 140 (2, M^+), 125 (9), 98 (5), 83 (100), 55 (27).

5-Methyl-1-hepten-4-one (**23**) *and (*E*)-5-Methyl-2-hepten-4-one* ((*E*)-**24**) (5:1 mixture, 79% yield from **5**). B.p. 52–55°/15 Torr.

23: R_f 0.68. IR: 1710. ^{1}H-NMR: 0.88 (*t*, *J* = 7, 3 H); 1.08 (*d*, *J* = 7, 3 H); 1.40 (*m*, 1 H); 1.69 (*m*, 1 H); 2.52 (*tq*, *J* = 7, 7, 1 H); 3.21 (*d*, *J* = 7, 2 H); 5.13 (br. *d*, *J* = 18, 1 H); 5.17 (br. *d*, *J* = 11, 1 H); 5.93 (*dddd*, *J* = 18, 11, 7, 7, 1 H). MS: 126 (1, M^+), 85 (48), 69 (11), 57 (100), 41 (44).

(*E*)-**24**: R_f 0.57. IR: 1686. ^{1}H-NMR: 0.91 (*t*, *J* = 7, 3 H); 1.08 (*d*, *J* = 7, 3 H); 1.40 (*m*, 1 H); 1.69 (*m*, 1 H); 1.90 (*dd*, *J* = 7, 2, 3 H); 2.65 (*tq*, *J* = 7, 7, 1 H); 6.20 (br. *d*, *J* = 15, 1 H); 6.89 (*dq*, *J* = 15, 7, 1 H). MS: 126 (0, M^+), 111 (6), 98 (9), 69 (100), 41 (22).

2,5-Dimethyl-1-hepten-4-one (**25**) *and 2,5-Dimethyl-2-hepten-4-one* (**26**) (5:1 mixture, 82% yield from **6**). B.p. 62–64°/15 Torr.

25: R_f 0.71. IR: 1705. ^{1}H-NMR: 0.88 (*t*, *J* = 7, 3 H); 1.07 (*d*, *J* = 7, 3 H); 1.38 (*m*, 1 H); 1.68 (*m*, 1 H); 1.75 (*s*, 3 H); 2.76 (*tq*, *J* = 7, 1 H); 3.15 (*s*, 2 H); 4.80 (br. *s*, 1 H); 4.94 (br. *s*, 1 H). MS: 140 (3, M^+), 85 (39), 83 (10), 57 (100), 55 (15), 41 (23).

26: R_f 0.64. IR: 1680. ^{1}H-NMR: 0.90 (*t*, *J* = 7, 3 H); 1.06 (*d*, *J* = 7, 3 H); 1.38 (*m*, 1 H); 1.68 (*m*, 1 H); 1.89 (*s*, 3 H); 2.14 (*s*, 3 H); 2.41 (*tq*, *J* = 7, 7, 1 H); 6.10 (br. *s*, 1 H). MS: 140 (7, M^+), 83 (100), 55 (25), 39 (5).

1-Cyclopentyl-3-buten-1-one (**27**) *and (*E*)-1-Cyclopentyl-2-buten-1-one* ((*E*)-**28**) (7:1 mixture, 81% yield from **7**). Bulb-to-bulb distillation: b.p. 70–80°/0.04 Torr[17]).

27: R_f 0.53. IR: 1710. ^{1}H-NMR: 1.50–1.90 (8 H); 2.93 (*dddd*, *J* = 7, 1 H); 3.23 (*d*, *J* = 7, 2 H); 5.13 (*dd*, *J* = 18, 2, 1 H); 5.17 (*dd*, *J* = 11, 2, 1 H); 5.93 (*m*, 1 H). MS: 138 (2, M^+), 123 (2), 97 (38), 69 (100), 41 (32).

(*E*)-**28**: R_f 0.43. IR: 1685. ^{1}H-NMR: 1.50–1.90 (8 H); 1.90 (*dd*, *J* = 7, 2, 3 H); 3.07 (*dddd*, *J* = 7, 1 H); 6.18 (*m*, 1 H); 6.87 (*m*, 1 H). MS: 138 (1, M^+), 123 (22), 97 (19), 69 (100), 41 (21).

1-Cyclopentyl-3-methyl-3-buten-1-one (**29**) *and 1-Cyclopentyl-3-methyl-2-buten-1-one* (**30**) (5:1 mixture, 85% yield from **8**). Bulb-to-bulb distillation: b.p. 70–90°/0.05 Torr.

29: R_f 0.54. IR: 1706. ^{1}H-NMR: 1.55–1.90 (8 H); 1.75 (*s*, 3 H); 2.97 (*dddd*, *J* = 7, 1 H); 3.17 (*s*, 2 H); 4.80 (br. *s*, 1 H); 4.94 (br. *s*, 1 H). MS: 152 (2, M^+), 97 (43), 83 (11), 69 (100), 55 (11), 41 (18).

30: R_f 0.50. IR: 1682. ^{1}H-NMR: 1.55–1.90 (8 H); 1.89 (*s*, 3 H); 2.15 (*s*, 3 H); 2.85 (*dddd*, *J* = 7, 1 H); 6.10 (br. *s*, 1 H). MS: 152 (9, M^+), 111 (3), 83 (100), 55 (21).

1-Cyclohexyl-3-buten-1-one (**31**) *and (*E*)-1-Cyclohexyl-2-buten-1-one* ((*E*)-**32**) (5:1 mixture, 84% yield from **9**). Bulb-to-bulb distillation: b.p. 70–90°/0.05 Torr[18]).

31: R_f 0.55. IR: 1710. ^{1}H-NMR: 1.10–1.90 (10 H); 2.40 (*m*, 1 H); 3.21 (*d*, *J* = 7, 2 H); 5.12 (*dd*, *J* = 18, 2, 1 H); 5.16 (*dd*, *J* = 11, 2, 1 H); 5.92 (*m*, 1 H). MS: 152 (1, M^+), 111 (28), 83 (100), 69 (15), 55 (80), 41 (23).

(*E*)-**32**: R_f 0.43. IR: 1692. ^{1}H-NMR: 1.10–1.90 (10 H); 1.89 (*dd*, *J* = 6, 2, 3 H); 2.54 (*m*, 1 H); 6.18 (*m*, 1 H); 6.88 (*m*, 1 H). MS: 152 (2, M^+), 137 (18), 97 (11), 69 (100), 55 (27), 41 (21).

1-Cyclohexyl-3-methyl-3-buten-1-one (**33**) *and 1-Cyclohexyl-3-methyl-2-buten-1-one* (**34**) (5:1 mixture, 83% yield from **10**). Bulb-to-bulb distillation: b.p. 70–90°/0.02 Torr.

33: R_f 0.55. IR: 1710. ^{1}H-NMR: 1.10–1.90 (10 H); 1.73 (*s*, 3 H); 2.44 (*m*, 1 H); 3.14 (*s*, 2 H); 4.78 (br. *s*, 1 H); 4.92 (br. *s*, 1 H). MS: 166 (2, M^+), 111 (25), 83 (100), 67 (4), 55 (59).

34: R_f 0.51. IR: 1680. ^{1}H-NMR: 1.10–1.90 (10 H); 1.88 (*s*, 3 H); 2.13 (*s*, 3 H); 2.30 (*m*, 1 H); 6.11 (br. *s*, 1 H). MS: 166 (7, M^+), 111 (2), 83 (100), 67 (2), 55 (25).

2,2-Dimethyl-5-hexen-3-one (**35**) *and (*E*)-2,2-Dimethyl-4-hexen-3-one* ((*E*)-**36**) (7:1 mixture, 83% yield from **11**). B.p. 48–50°/15 Torr ([22]: 48–50°/13 Torr ((*E*)-**36**)).

35: R_f 0.67. IR: 1710. ^{1}H-NMR: 1.16 (*s*, 9 H); 3.29 (*d*, *J* = 7, 2 H); 5.10 (br. *d*, *J* = 18, 1 H); 5.15 (br. *d*, *J* = 11, 1 H); 5.94 (*m*, 1 H). MS: 126 (1, M^+), 85 (25), 69 (7), 57 (100), 55 (6), 41 (41).

(*E*)-**36**: R_f 0.59. IR: 1685. ^{1}H-NMR: 1.15 (*s*, 9 H); 1.89 (br. *d*, *J* = 7, 3 H); 6.52 (br. *d*, *J* = 7, 1 H); 6.95 (*m*, 1 H). MS: 126 (4, M^+), 98 (5), 69 (100), 57 (31), 41 (28).

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[17]) (*Z*)-**28** ($\leq$ 2%) was also detected by ^{1}H-NMR and GC/MS analysis. ^{1}H-NMR: 2.11 (br. *d*, *J* = 6, 3 H). MS: 138 (9, M^+), 123 (5), 97 (10), 69 (100), 41 (20).

[18]) (*Z*)-**32** ($\leq$ 2%) was also detected by ^{1}H-NMR and GC/MS analysis. ^{1}H-NMR: 2.10 (br. *d*, *J* = 6, 3 H). MS: 152 (7, M^+), 137 (7), 97 (10), 69 (100), 55 (24), 41 (20).

2,2,5-Trimethyl-5-hexen-3-one (**37**) *and 2,2,5-Trimethyl-4-hexen-3-one* (**38**) (3:1 mixture, 79% yield from **12**). B.p. 60–64° Torr ([23]: 164–165°/760 Torr (**38**)).

37: R_f 0.68. IR: 1705. ^{1}H-NMR: 1.16 (*s*, 9 H); 1.74 (*s*, 3 H); 3.22 (*s*, 2 H); 4.74 (*s*, 1 H); 4.93 (*s*, 1 H). MS: 140 (2, M^+), 85 (24), 83 (5), 57 (100), 55 (14), 41 (24).

38: R_f 0.59. IR: 1680. ^{1}H-NMR: 1.14 (*s*, 9 H); 1.91 (*s*, 3 H); 2.11 (*s*, 3 H); 6.31 (*s*, 1 H). MS: 140 (3, M^+), 83 (100), 57 (10), 55 (29), 41 (7).

1-Phenyl-3-buten-1-one (**39**) *and (*E*)-1-Phenyl-2-buten-1-one* ((*E*)-**40**) (1.5:1 mixture[19]), 84% yield from **13**). B.p. 105–110°/15 Torr.

39: R_f 0.68. IR: 1690. ^{1}H-NMR: 3.76 (*d*, *J* = 7, 2 H); 5.20 (br. *d*, *J* = 11, 1 H); 5.22 (br. *d*, *J* = 18, 1 H); 6.09 (*m*, 1 H); 7.40–8.00 (5 H). MS: 146 (46, M^+), 131 (19), 105 (92), 77 (100), 69 (29), 51 (42).

(*E*)-**40**: R_f 0.55. IR: 1670. ^{1}H-NMR: 2.00 (*dd*, *J* = 7, 1.5, 3 H); 6.90 (*d*, *J* = 15, 1 H); 7.07 (*dq*, *J* = 15, 7, 1 H); 7.40–8.00 (5 H). MS: 146 (35, M^+), 131 (39), 105 (100), 77 (83), 69 (57), 51 (37).

3-Methyl-1-phenyl-3-buten-1-one (**41**) *and 3-Methyl-1-phenyl-2-buten-1-one* (**42**) (3:1 mixture, 82% yield from **14**). B.p. 115–120°/15 Torr.

41: R_f 0.77. IR: 1700. ^{1}H-NMR: 1.82 (*s*, 3 H); 3.69 (*s*, 2 H); 4.85 (br. *s*, 1 H); 4.98 (br. *s*, 1 H); 7.40–8.00 (5 H). MS: 160 (2, M^+), 105 (100), 77 (45), 51 (14).

42: R_f 0.70. IR: 1675. ^{1}H-NMR: 2.02 (*s*, 3 H); 2.21 (*s*, 3 H); 6.75 (br. *s*, 1 H); 7.40–7.95 (5 H). MS: 160 (38, M^+), 159 (24), 145 (46), 105 (55), 83 (71), 77 (100), 55 (68).

Ethyl 3-(4'-Methylphenyl)-2-butenoate (**44**) ((*E*/*Z*) 4:1). A soln. of ethyl (diethoxyphosphoryl)acetate (80 g, 0.35 mol) in THF (100 ml) was added dropwise, within 30 min to a stirred slurry of NaH (55% dispersion in oil (*Fluka*); 16.5 g, 0.38 mol) in THF (900 ml) at r.t. under N_2. During the addition, the temp. rose to 35° and after a further 30 min, a soln. of *p*-methylacetophenone (**43**; 42 g, 0.30 mol) in THF (250 ml) was added dropwise within 20 min. The mixture was then refluxed for 24 h, cooled to 5°, and sat. aq. NH_4Cl soln. (200 ml) added dropwise. The H_2O phase was extracted with Et_2O (200 ml) and the combined org. phase washed with sat. aq. NaCl soln. (3 × 250 ml), dried (Na_2SO_4), and concentrated. Fractional distillation *i.v.* afforded **44** ((*E*/*Z*) 4:1) as a colourless oil (51 g, 84%). B.p. 75–80°/0.07 Torr.

(*E*)-**44**: R_f 0.58. IR: 1700, 1620, 1440, 1360, 1340, 1260, 1150, 1032, 864, 808. ^{1}H-NMR: 1.31 (*t*, *J* = 7, 3 H); 2.36 (*s*, 3 H); 2.56 (*d*, *J* = 1.5, 3 H); 4.21 (*q*, *J* = 7, 2 H); 6.13 (*d*, *J* = 1.5, 1 H); 7.17 (*d*, *J* = 8, 2 H); 7.38 (*d*, *J* = 8, 2 H). MS: 204 (39, M^+), 175 (22), 159 (100), 132 (53), 115 (82), 91 (70), 65 (23).

(*Z*)-**44**: R_f 0.53. IR: 1700. ^{1}H-NMR: 1.11 (*t*, *J* = 7, 3 H); 2.16 (*d*, *J* = 1.5, 3 H); 2.35 (*s*, 3 H); 4.02 (*q*, *J* = 7, 2 H); 5.88 (*d*, *J* = 1.5, 1 H); 7.12 (*AB*, *J* = 8, 4 H). MS: 204 (38, M^+), 175 (22), 159 (100), 132 (51), 115 (84), 91 (70), 65 (25).

Ethyl 3-(4'-Methylphenyl)butanoate (**45**). A soln. of **44** ((*E*/*Z*) 4:1; 49 g, 0.24 mol) in EtOH (500 ml) containing 10% Pd/C (1.5 g) was hydrogenated at r.t. After 70 min (5.5 l of H_2 absorbed), the mixture was filtered, concentrated, and distilled *i.v.* to afford **45** as a colourless oil (48 g, 97%). B.p. 67–69°/0.06 Torr. R_f 0.56. IR: 1720, 1508, 1442, 1360, 1260, 1152, 1026, 812, 720. ^{1}H-NMR: 1.18 (*t*, *J* = 7, 3 H); 1.28 (*d*, *J* = 7, 3 H); 2.30 (*s*, 3 H); 2.55 (*m*, 2 H); 3.24 (*m*, 1 H); 4.07 (*q*, *J* = 7, 2 H); 7.10 (4 H). MS: 206 (9, M^+), 132 (57), 119 (100), 105 (10), 91 (22), 77 (8).

2,6-Dimethyl-4-[2'-(4''-methylphenyl)propyl]-1,6-heptadien-4-ol (**46**). A soln. of **45** (20.6 g, 0.1 mol) and 2-methylallyl chloride (28.6 g, 0.3 mol) in Et_2O (450 ml) was added dropwise to a stirred slurry of Mg (6.3 g, 0.26 mol) in Et_2O (50 ml) under N_2 at such a rate as to maintain a gentle reflux. After the addition (80 min), THF (100 ml) was added to obtain a clear soln., and the mixture was refluxed for 16 h. To the cooled mixture (*ca.* 5°) was then added cautiously and dropwise sat. aq. NH_4Cl soln. (50 ml) followed by H_2O (100 ml). The aq. phase was extracted with Et_2O (100 ml) and the combined org. phase washed with sat. aq. NaCl soln. (3 × 200 ml), dried (Na_2SO_4), and concentrated. Distillation *i.v.* afforded **46** as a colourless oil (21 g, 77%). B.p. 97–99°/0.06 Torr. R_f 0.62. IR: 3560 (br.), 1636, 1508, 1432, 1360, 1060, 880, 810, 720. ^{1}H-NMR (+D_2O): 1.24 (*d*, *J* = 7, 3 H); 1.76 (*dd*, *J* = 14, 4, 1 H); 1.78 (*s*, 6 H); 1.95 (*dd*, *J* = 14, 9, 1 H); 2.17 (*m*, 4 H); 2.30 (*s*, 3 H); 2.99 (*m*, 1 H); 4.70 (br. *s*, 2 H); 4.89 (br. *s*, 2 H); 7.11 (*AB*, *J* = 8, 4 H). MS: 272 (0, M^+), 161 (7), 119 (100), 105 (5), 91 (12), 55 (8).

2-Methyl-6-(4'-methylphenyl)-1-hepten-4-one (**47**) *and 2-Methyl-6-(4'-methylphenyl)-2-hepten-4-one* (= *ar-turmerone*; **48**). A soln. of **46** (6 g, 0.022 mol) in HMPA (20 ml) was added dropwise within 20 min to a stirred slurry of KH (0.027 mol) in HMPA (30 ml) at r.t. under N_2. After 1 h at r.t., the mixture was heated at 40° for 1 h, cooled, and cautiously poured into cold sat. aq. NH_4Cl soln. (200 ml). The mixture was extracted with Et_2O (3 × 100 ml). The combined org. phase was washed with sat. aq. NaCl soln. (3 × 100 ml), dried (Na_2SO_4), and

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[19]) (*Z*)-**40** (≤ 2%) was also detected by ^{1}H-NMR analysis. ^{1}H-NMR: 2.15 (*dd*, *J* = 7, 1.5, 3 H); 6.44 (*dq*, *J* = 11, 7, 1 H); 6.83 (*dd*, *J* = 11, 1.5, 1 H).

concentrated to afford an orange oil (8.9 g) which was purified by CC (silica gel (180 g), cyclohexane/AcOEt 97:3) to afford an inseparable 4:1 mixture **48**/**47** as a colourless oil (4.1 g, 86%). B.p. (bulb-to-bulb distillation) 130–150°/0.04 Torr.

Data of **47**: R_f 0.58. ^{1}H-NMR: 1.23 (*d*, *J* = 7, 3 H); 1.65 (*s*, 3 H); 2.32 (*s*, 3 H); 2.65 (*m*, 2 H); 2.99 (*s*, 2 H); 3.29 (*m*, 1 H); 4.74 (br. *s*, 1 H); 4.90 (br. *s*, 1 H); 7.10 (4 H). MS: 216 (15, M^+), 201 (9), 132 (14), 119 (46), 91 (13), 83 (100).

A soln. of the foregoing 4:1 mixture **48**/**47** (4 g, 0.018 mol) in THF (50 ml) containing TsOH·H_2O (0.4 g) was stirred for 24 h at r.t. and then heated at reflux for a further 22 h. The cooled mixture was diluted with Et_2O (50 ml), washed with sat. aq. NaCl soln. (3 × 100 ml), dried (Na_2SO_4), and concentrated. Distillation *i.v.* afforded a 19:1 mixture **48**/**47** as a colourless oil (3.9 g, 97%). B.p. 90–92°/0.06 Torr ([11]: 159–160°/10 Torr).

Data of **48**: R_f 0.52. IR: 1680, 1610, 1506, 1430, 1370, 1002, 808, 718, 680. ^{1}H-NMR: 1.23 (*d*, *J* = 7, 3 H); 1.85 (*s*, 3 H); 2.11 (*s*, 3 H); 2.31 (*s*, 3 H); 2.60 (*dd*, *J* = 14, 8, 1 H); 2.70 (*dd*, *J* = 14, 6, 1 H); 3.29 (*m*, 1 H); 6.02 (*s*, 1 H); 7.10 (4 H). MS: 216 (20, M^+), 201 (13), 132 (18), 119 (61), 105 (9), 83 (100), 55 (18).

Preparation of Alcohols 49–56. – Using the procedure described for the preparation of **1–14** (*vide supra*), **49–56** were prepared from the corresponding methyl carboxylates.

4-(2'-Propenyl)-1,6-heptadien-4-ol (**49**) (77% yield from methyl 3-butenoate). R_f 0.39. B.p. 76–78°/15 Torr ([24]: 189–192°/760 Torr). IR: 3450 (br.), 3080, 2990, 1640, 1440, 1000, 920, 860. ^{1}H-NMR (60 MHz; +D_2O): 2.23 (*d*, *J* = 7, 6 H); 4.85–5.25 (6 H); 5.90 (*m*, 3 H). MS: 152 (0, M^+), 111 (15), 69 (81), 55 (4), 41 (100), 39 (20).

2,6-Dimethyl-4-(2'propenyl)-1,6-heptadien-4-ol (**50**) (79% yield from methyl 3-butenoate). R_f 0.55. B.p. 94–98°/15 Torr. IR: 3550 (br.), 3080, 1642, 1440, 1380, 1080, 1000, 900, 790. ^{1}H-NMR (60 MHz; +D_2O): 1.84 (6 H); 2.21 (*s*, 4 H); 2.28 (*d*, *J* = 7, 2 H); 4.78 (2 H); 4.94 (2 H); 4.90–5.20 (2 H); 5.90 (*m*, 1 H). MS: 180 (0, M^+), 125 (19), 83 (45), 69 (86), 55 (84), 41 (100).

3-Methyl-4-(2'-propenyl)-1,6-heptadien-4-ol (**51**) (82% yield from methyl 2-methyl-3-butenoate[20]). R_f 0.54. B.p. 88–90°/15 Torr. IR: 3450 (br.), 3060, 2920, 1636, 1430, 1410, 1360, 986, 903. ^{1}H-NMR (60 MHz; +D_2O): 1.03 (*d*, *J* = 7, 3 H); 2.26 (*d*, *J* = 7, 4 H); 2.36 (*dq*, *J* = 7, 7, 1 H); 4.80–5.20 (6 H); 5.50–6.30 (3 H). MS: 166 (0, M^+), 125 (4), 111 (5), 83 (25), 69 (100), 55 (71), 41 (66).

2,6-Dimethyl-4-(1'-methyl-2'-propenyl)-1,6-heptadien-4-ol (**52**) (86% yield from methyl 2-methyl-3-butenoate[21]). R_f 0.77. B.p. 101–103°/15 Torr. IR: 3550 (br.), 3050, 2900, 1630, 1430, 1362, 1050, 1000, 880, 722. ^{1}H-NMR (60 MHz; +D_2O): 1.05 (*d*, *J* = 7, 3 H); 1.86 (6 H); 2.23 (4 H); 2.50 (*dq*, *J* = 7, 7, 1 H); 4.77 (2 H); 4.92 (2 H); 4.80–5.20 (2 H); 5.93 (*m*, 1 H). MS: 194 (0, M^+), 139 (4), 97 (5), 83 (35), 55 (100).

3,3-Dimethyl-4-(2'-propenyl)-1,6-heptadien-4-ol (**53**) (84% yield from methyl 2,2-dimethyl-3-butenoate[21]). R_f 0.63. B.p. 95–98°/15 Torr. IR: 3500 (br.), 3060, 2950, 1626, 1428, 1405, 988, 902. ^{1}H-NMR (60 MHz; +D_2O): 1.07 (*s*, 6 H); 2.37 (*d*, *J* = 7, 4 H); 4.80–5.20 (6 H); 5.60–6.30 (2 H); 6.11 (*dd*, *J* = 18, 11, 1 H). MS: 180 (0, M^+), 139 (2), 111 (5), 97 (11), 69 (100), 55 (10), 41 (29).

2,5,5-Trimethyl-4-(2'-methyl-2'-propenyl)-1,6-heptadien-4-ol (**54**) [26] (86% yield from methyl 2,2-dimethyl-3-butenoate[21]). R_f 0.78. B.p. 117–120°/15 Torr. IR: 3540 (br.), 3060, 2940, 1630, 1438, 1368, 1002, 880. ^{1}H-NMR (60 MHz; +D_2O): 1.10 (*s*, 6 H); 1.85 (6 H); 2.27 (4 H); 4.70–5.20 (6 H); 6.15 (*dd*, *J* = 18, 11, 1 H). MS: 208 (0, M^+), 153 (4), 97 (18), 83 (51), 69 (100), 55 (84), 41 (23).

4-Benzyl-1,6-heptadien-4-ol (**55**) (82% yield from methyl phenylacetate). R_f 0.41. B.p. 81–84°/0.02 Torr. IR: 3560 (br.), 3475 (br.), 3080, 3042, 2922, 1640, 1610, 1500, 1440, 1000, 920, 796, 750, 700. ^{1}H-NMR (60 MHz; +D_2O): 2.22 (*d*, *J* = 7, 4 H); 2.77 (*s*, 2 H); 4.90–5.30 (4 H); 4.95 (*m*, 2 H); 7.27 (5 H). MS: 202 (0, M^+), 161 (3), 119 (9), 111 (15), 92 (39), 91 (100), 69 (65), 41 (65).

4-Benzyl-2,6-dimethyl-1,6-heptadien-4-ol (**56**) (85% yield from methyl phenylacetate). R_f 0.60. B.p. 91–96°/0.01 Torr. IR: 3560 (br.), 3080, 3040, 1642, 1608, 1500, 1380, 1252, 900, 790, 750, 705. ^{1}H-NMR (60 MHz; +D_2O): 1.83 (6 H); 2.20 (4 H); 2.80 (*s*, 2 H); 4.77 (*m*, 1 H); 4.93 (*m*, 1 H); 7.23 (*s*, 5 H). MS: 230 (0, M^+), 180 (1), 124 (5), 91 (26), 83 (5), 63 (10), 56 (100), 55 (52).

General Procedure for the β-Cleavage of Alkoxides 49a–56a: Preparation of Ketones 57–67. – Using the procedure described for the preparation of **15–42** (*vide supra*), **49–56** were converted to **49a–56a** which were then heated at either 80° (for **49a–52a**) or 40° (for **53a–56a**) until completion of the reaction (1–2 h). Workup afforded a

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[20]) Prepared from 2-methyl-3-butenoic acid [25] by acid-catalysed esterification (MeOH/conc. H_2SO_4).

[21]) Prepared from 2,2-dimethyl-3-butenoic acid (MeOH/conc. H_2SO_4) which was readily available by the reaction of prenylmagnesium chloride with CO_2 in Et_2O using a procedure analogous to that used for 2-methylbutenoic acid [25].

product mixture whose composition was analysed by TLC, GC/MS coupling, and ^{1}H-NMR (360 MHz) spectroscopy; in 3 experiments (*cf. Table 2: Entries 2, 3,* and *4*), the mixture was purified by CC with CH_2Cl_2.

(E)-1,5-Heptadien-4-one (**57**) *and 2,5-Heptadien-4-one* (**58**; *(E,E)*/*(E,Z)* 2.8:1) (5:1 mixture, 76% yield from **49**). B.p. 70–74°/15 Torr. ([27]: 58°/23 Torr (**57**); [28]: 62°/15 Torr (**57**)).

(E)-**57**: R_f 0.50. IR: 1700, 1680. ^{1}H-NMR: 1.91 (br. *d*, *J* = 7, 3 H); 3.31 (*d*, *J* = 7, 2 H); 5.15 (br. *d*, *J* = 18, 1 H); 5.19 (br. *d*, *J* = 11, 1 H); 5.95 (*m*, 1 H); 6.18 (br. *d*, *J* = 15, 1 H); 6.89 (*m*, 1 H). MS: 110 (7, M^+), 95 (62), 77 (10), 69 (100), 67 (9), 41 (78), 39 (58).

(E,E)-**58** [29]: R_f 0.34. IR: 1670. ^{1}H-NMR: 1.91 (br. *d*, *J* = 7, 6 H); 6.15 (br. *d*, *J* = 15, 2 H); 6.86 (*m*, 2 H). MS: 110 (16, M^+), 95 (30), 69 (100), 67 (5), 41 (60), 39 (39).

(E,Z)-**58**: ^{1}H-NMR: 2.10 (br. *d*, *J* = 7, 3 H); 6.32 (br. *d*, *J* = 11, 1 H); 6.27 (*m*, 1 H). MS: 110 (6, M^+), 95 (67), 69 (100), 41 (44), 39 (32).

6-Methyl-1,5-heptadien-4-one (**59**) [27][30], *(E)-2-Methyl-1,5-heptadien-4-one* (**60**), *(E)-2-Methyl-2,5-heptadien-4-one* (**61**) [31], *2,6-Dimethyl-1,5-heptadien-4-one* (**62**) [32], *and 2,6-Dimethyl-2,5-heptadien-4-one* (= *Phorone;* **63**) (0.06:0.2:1.2:2.4:1 mixture, 83% yield from **50**). B.p. 75–85°/15 Torr.

59: R_f 0.56. ^{1}H-NMR: 1.90 (*s*, 3 H); 2.15 (*s*, 3 H); 3.17 (*d*, *J* = 7, 2 H); 5.13 (br. *d*, *J* = 18, 1 H); 5.17 (br. *d*, *J* = 11, 1 H); 5.95 (*m*, 1 H); 6.09 (br. *s*, 1 H). MS: 124 (0, M^+), 109 (2), 83 (100), 55 (31), 39 (10).

60: R_f 0.50. ^{1}H-NMR: 1.75 (*s*, 3 H); 1.90 (*dd*, *J* = 7, 1.5, 3 H); 3.23 (*s*, 2 H); 4.82 (br. *s*, 1 H); 4.94 (br. *s*, 1 H); 6.19 (br. *d*, *J* = 15, 1 H); 6.90 (*m*, 1 H). MS: 124 (2, M^+), 109 (5), 69 (100), 41 (25), 39 (13).

61: R_f 0.44. ^{1}H-NMR: 1.89 (*dd*, *J* = 7, 1.5, 3 H); 1.92 (*s*, 3 H); 2.15 (*s*, 3 H); 6.16 (*dd*, *J* = 15, 1.5, 1 H); 6.21 (br. *s*, 1 H); 6.84 (*m*, 1 H). MS: 124 (7, M^+), 109 (100), 83 (25), 69 (12), 55 (14), 39 (20).

62: R_f 0.67. ^{1}H-NMR: 1.75 (*s*, 3 H); 1.92 (*s*, 3 H); 2.17 (*s*, 3 H); 3.10 (*s*, 2 H); 4.82 (br. *s*, 1 H); 4.93 (br. *s*, 1 H); 6.14 (br. *s*, 1 H). MS: 138 (1, M^+), 123 (2), 83 (100), 55 (42), 39 (14).

63: R_f 0.58. ^{1}H-NMR: 1.89 (*s*, 6 H); 2.15 (*s*, 6 H); 6.05 (br. *s*, 2 H). MS: 138 (5, M^+), 123 (100), 108 (11), 95 (15), 83 (45), 55 (45), 39 (24).

With **51** as substrate, a 2.5:1:0.4:1.4:1.1:1 mixture of *(E)*-**57**, *(E,E)*-**58**, *(E,Z)*-**58**, *(E)-5-methyl-1,5-heptadien-4-one* (**64**), *(2E,5E)-3-methyl-2,5-heptadien-4-one* ((*E,E*)-**65**), and *(2E,5Z)-3-methyl-2,5-heptadien-4-one* ((*E,Z*)-**65**) was isolated in 81% yield. B.p. 75–87°/15 Torr.

64: R_f 0.57. ^{1}H-NMR: 3.45 (*d*, *J* = 7, 2 H); 5.11 (br. *d*, *J* = 18, 1 H); 5.15 (br. *d*, *J* = 11, 1 H); 5.97 (*m*, 1 H). MS: 124 (0.5, M^+), 83 (70), 55 (100).

(E,E)-**65**: R_f 0.47. ^{1}H-NMR: 1.97 (*dd*, *J* = 7, 1.5, 3 H). MS: 124 (12, M^+), 109 (88), 81 (32), 69 (100), 55 (59).

(E,Z)-**65**: R_f 0.56. ^{1}H-NMR: 2.10 (*d*, *J* = 7, 3 H). MS: 124 (4, M^+), 109 (100), 91 (13), 81 (22), 69 (71), 55 (53).

With **52** as substrate, a mixture of **62** (47%), **63** (20%), *(E)-2,5-dimethyl-1,5-heptadien-4-one* (**66**; 8%), and *(E)-2,5-dimethyl-2,5-heptadien-4-one* [34] (**67**; 4%) was isolated in 79% yield. B.p. 82–97°/15 Torr.

66: R_f 0.70. MS: 138 (0.5, M^+), 83 (100), 55 (42).

67: R_f 0.64. MS: 138 (1, M^+), 123 (100), 108 (13), 95 (10), 83 (69), 55 (48).

With **53** as substrate, a 2:1 mixture **57**/**58** ((*E,E*)/(*E*/*Z*) 2.8:1) was isolated in 82% yield.

With **54** as substrate, a 3.2:1 mixture **62**/**63** was isolated in 83% yield.

With **55** as substrate, a 2.3:1 mixture **57**/**58** ((*E,E*)/(*E,Z*) 2.8:1) was isolated in 84% yield[22]).

With **56** as substrate, a 3.3:1 mixture **62**/**63** was isolated in 80% yield[22]).

4-(2',6',6'-Trimethyl-2'-cyclohexenyl)-1,6-heptadien-4-ol (**69**) [13]. Using the procedure described for the preparation of **1**–**14** (*vide supra*), methyl α-cyclogeranate (**68**) [14] was converted to **69** (colourless oil, 83% yield). B.p. 76–79°/0.05 Torr. R_f 0.71. IR: 3580 (br.), 3100, 1640, 1440, 1360, 990, 910, 825. ^{1}H-NMR (+D_2O): 0.90 (*s*, 3 H); 1.19 (*s*, 3 H); 1.50 (*m*, 1 H); 1.83 (*s*, 3 H); 1.91 (*m*, 1 H); 2.00 (*s*, 1 H); 2.10 (2 H); 2.34–2.52 (4 H); 5.06–5.19 (4 H); 5.54 (br. *s*, 1 H); 5.94 (*m*, 2 H). MS: 234 (0, M^+), 123 (22), 109 (31), 81 (14), 69 (100), 55 (8), 41 (57).

1-(2',6',6'-Trimethyl-2'-cyclohexenyl)-3-buten-1-one (**70**) [8] *and 1-(2',6',6'-Trimethyl-2'-cyclohexenyl)-2-buten-1-one* (**71**; (*E*/*Z*) 1:1.6) [8]. Using the procedure described for the β-cleavage of **53a**–**56a** (*vide supra*), **69** was converted to a 1.7:1 mixture **70**/**71** ((*E*/*Z*) 1:1.6), pale-yellow oil, 48% yield. B.p. (bulb-to-bulb distillation) 100–120°/1 Torr.

70: R_f 0.53. ^{1}H-NMR: 0.91 (*s*, 3 H); 0.94 (*s*, 3 H); 1.17 (*m*, 1 H); 1.59 (*s*, 3 H); 1.71 (*m*, 1 H); 2.09 (*m*, 2 H); 2.80 (*s*, 1 H); 3.26 (*ABX*, *J* = 17, 7, 2 H); 5.11 (br. *d*, *J* = 18, 1 H); 5.17 (br. *d*, *J* = 11, 1 H); 5.60 (br. *s*, 1 H); 5.93 (*m*, 1 H). MS: 192 (2, M^+), 151 (10), 123 (100), 91 (12), 81 (45), 69 (30).

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[22]) The formation of toluene in these reactions was demonstrated by GC/MS coupling and ^{1}H-NMR analysis of the crude products.

(*E*)-**71** (α-*Damascone*): R_f 0.42. IR: 1680, 1660, 1620, 1440, 1360, 1200, 1170, 1142, 560, 820. ^{1}H-NMR: 0.86 (*s*, 3 H); 0.95 (*s*, 3 H); 1.17 (*m*, 1 H); 1.57 (*s*, 3 H); 1.70 (*m*, 1 H); 1.90 (*dd*, *J* = 7, 1.5, 3 H); 2.10 (*m*, 2 H); 2.89 (*s*, 1 H); 5.62 (br. *s*, 1 H); 6.31 (*dd*, *J* = 15, 1.5, 1 H); 6.89 (*dq*, *J* = 15, 7, 1 H). MS: 192 (12, M^+), 123 (25), 107 (11), 91 (12), 81 (28), 69 (100).

(*Z*)-**71**: R_f 0.52. ^{1}H-NMR: 0.89 (*s*, 3 H); 0.94 (*s*, 3 H); 1.17 (*m*, 1 H); 1.59 (*s*, 3 H); 1.70 (*m*, 1 H); 2.10 (*dd*, *J* = 7, 1.5, 3 H); 2.09 (*m*, 2 H); 2.69 (*s*, 1 H); 5.60 (br. *s*, 1 H); 6.17 (*dq*, *J* = 11, 7, 1 H); 6.31 (br. *d*, *J* = 11, 1 H). MS: 192 (9, M^+), 123 (31), 91 (11), 81 (34), 69 (100).

This foregoing mixture was equilibrated (TsOH·H_2O(cat.)/THF, reflux 4 h) to afford (*E*)-**71** in 88% yield.

Also isolated was a 2.4:1 mixture (32% yield from **69**) **57**/**58** ((*E*/*E*)/(*E*,*Z*) 2.8:1), together with a *ca.* 1:1 mixture (39% yield from **69**) of *1,3,3-trimethyl-1-cyclohexene* (**72**) [38] *and 1,5,5-trimethyl-1-cyclohexene* (**73**) [35].

72: ^{1}H-NMR: 0.93 (*s*, 6 H); 1.35 (*m*, 2 H); 1.60 (*m*, 2 H); 1.62 (*s*, 3 H); 1.83 (br. *t*, *J* = 7, 2 H); 5.11 (br. *s*, 1 H). MS: 124 (19, M^+), 109 (100), 81 (14), 67 (21).

73: ^{1}H-NMR: 0.89 (*s*, 6 H); 1.27 (*t*, *J* = 7, 2 H); 1.62 (*s*, 3 H); 1.68 (br. *s*, 2 H), 1.99 (*m*, 2 H); 5.34 (*m*, 1 H). MS: 124 (64, M^+), 109 (100), 82 (17), 68 (98).

Preparation of Alcohols 74–83. – Using the procedure described for the preparation of **1**–**14** (*vide supra*), **74**–**83** were prepared from the corresponding methyl carboxylates.

4-Ethenyl-1,6-heptadien-4-ol (**74**) (64% yield from methyl acrylate). R_f 0.45. B.p. 62–68°/15 Torr ([36]: 57.5–58.5°/11 Torr; [37]: 167°/777 Torr; 50°/6 Torr) IR: 3425 (br.), 3060, 2900, 1638, 980, 910. ^{1}H-NMR (60 MHz; + D_2O): 2.30 (*d*, *J* = 7, 4 H); 4.85–5.35 (6 H); 5.50–6.20 (2 H); 5.91 (*dd*, *J* = 18, 11, 1 H). MS: 138 (0, M^+), 105 (3), 97 (31), 91 (6), 77 (7), 55 (100).

4-Ethenyl-2,6-dimethyl-1,6-heptadien-4-ol (**75**) (40% yield from methyl acrylate). R_f 0.86. B.p. 85–90°/15 Torr. IR: 3530, 3060, 2920, 1638, 1438, 990, 890, 724. ^{1}H-NMR (60 MHz; +D_2O): 1.77 (6 H); 2.28 (*s*, 4 H); 4.70–5.40 (6 H); 5.89 (*dd*, *J* = 18, 11, 1 H). MS: 166 (0, M^+), 133, (11), 125 (10), 105 (40), 91 (45), 83 (100), 79 (19), 55 (26).

4-(1'-Methylethenyl)-1,6-heptadien-4-ol (**76**) (65% yield from methyl 2-methylpropenoate). R_f 0.41. B.p. 67–69°/15 Torr. IR: 3500 (br.), 3060, 1636, 1430, 1330, 982, 900, 750, 718, 672. ^{1}H-NMR (60 MHz; +D_2O): 1.73 (3 H); 2.36 (*m*, 4 H); 4.48–5.25 (6 H); 5.80 (*m*, 2 H). MS: 152 (0, M^+), 111, (22), 91 (8), 69 (100), 41 (40).

2,6-Dimethyl-(1'-methylethenyl)-1,6-heptadien-4-ol (**77**) (72% yield from methyl 2-methylpropenoate). R_f 0.56. B.p. 90–91°/15 Torr. IR: 3530 (br.), 3060, 1636, 1432, 1368, 1322, 1256, 902, 762, 736, 636, 610. ^{1}H-NMR (60 MHz; +D_2O): 1.76 (9 H); 2.34 (4 H); 4.75 (2 H); 4.87 (3 H); 5.06 (1 H). MS: 180 (0, M^+), 125 (18), 105 (3), 91 (4), 69 (100), 55 (10), 41 (32).

(E)-4-(2'-Propenyl)-1,5-heptadien-4-ol (**78**) (84% yield from methyl (*E*)-2-butenoate). R_f 0.39. B.p. 75–76°/15 Torr ([38]: 93.5°/35 Torr). IR: 3460 (br.), 3090, 1640, 1440, 1000, 972, 920, 810. ^{1}H-NMR (60 MHz; +D_2O): 1.70 (*d*, *J* = 6, 3 H); 2.28 (*d*, *J* = 7, 4 H); 4.85–5.25 (4 H); 5.53 (*m*, 2 H); 5.83 (*m*, 2 H). MS: 152 (0, M^+), 111 (11), 91 (2), 69 (100), 55 (3), 41 (30), 39 (12).

(E)-2-Methyl-4-(2'-methyl-2'-propenyl)-1,5-heptadien-4-ol (**79**) (81% yield from methyl (*E*)-2-butenoate). R_f 0.59. B.p. 90–91°/15 Torr ([38]: 89°/12 Torr). IR: 3560 (br.), 3080, 1642, 1380, 1340, 975, 900, 810. ^{1}H-NMR (60 MHz; +D_2O): 1.70 (*d*, *J* = 6, 3 H); 1.75 (6 H); 2.25 (*s*, 4 H); 4.75 (2 H); 4.88 (2 H); 5.51 (*m*, 2 H). MS: 180 (0, M^+), 125 (15), 91 (1), 69 (100), 55 (5), 41 (18), 39 (6).

(E)-5-Methyl-4-(2'-propenyl)-1,5-heptadien-4-ol (**80**) (90% yield from methyl (*E*)-2-methyl-2-butenoate). R_f 0.43. B.p. 84–86°/15 Torr ([38]: 81–82°/11 Torr). IR: 3450 (br.), 3060, 1636, 1430, 990, 902, 830, 716. ^{1}H-NMR (60 MHz; +D_2O): 1.50–1.80 (6 H); 2.35 (*m*, 4 H); 4.85–5.05 (4 H); 5.60 (*m*, 1 H); 5.77 (2 H). MS: 166 (0, M^+), 125 (21), 105 (8), 91 (12), 83 (100), 55 (57), 41 (14).

(E)-2,5-Dimethyl-4-(2'-methyl-2'-propenyl)-1,5-heptadien-4-ol (**81**) (73% yield from methyl (*E*)-2-methyl-2-butenoate). R_f 0.59. B.p. 93–94°/15 Torr ([38]: 105°/15 Torr). IR: 3530 (br.), 3060, 1636, 1432, 1364, 1326, 1250, 880, 740, 720, 640. ^{1}H-NMR (60 MHz; +D_2O): 1.58 (br. *d*, *J* = 7, 3 H); 1.60 (*s*, 3 H); 1.70 (6 H); 2.33 (*AB*, *J* = 13, 4 H); 4.71 (2 H); 4.83 (2 H); 5.60 (*m*, 1 H). MS: 194 (0, M^+), 139 (8), 105 (2), 83 (100), 55 (42).

6-Methyl-4-(2'-propenyl)-1,5-heptadien-4-ol (**82**) (83% yield from methyl 3-methyl-2-butenoate[23]). R_f 0.54. B.p. 85–88°/15 Torr. IR: 3450 (br.), 3050, 2900, 1638, 1430, 1370, 990, 902, 818. ^{1}H-NMR (60 MHz; +D_2O): 1.71 (3 H); 1.85 (3 H); 2.25 (*d*, *J* = 7, 4 H); 4.90–5.25 (4 H); 5.50–6.30 (3 H). MS: 166 (0, M^+), 133 (10), 125 (9), 105 (40), 91 (44), 83 (100), 55 (26).

2,6-Dimethyl-4-(2'-methyl-2'-propenyl)-1,5-heptadien-4-ol (**83**) (86% yield from methyl 3-methyl-2-butenoate[23]). R_f 0.68. B.p. 100–101°/15 Torr. IR: 3530 (br.), 3060, 2900, 1636, 1432, 1368, 1020, 884, 838, 722. ^{1}H-NMR (60 MHz; +D_2O): 1.70 (3 H); 1.81 (*s*, 3 H); 1.85 (3 H); 2.33 (*s*, 3 H); 4.78 (2 H); 4.90 (2 H); 5.20 (1 H). MS: 194 (0, M^+), 161 (4), 119 (8), 105 (11), 83 (100), 55 (29).

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[23]) Prepared from 3-methyl-2-butenoic acid by acid-catalysed esterification (MeOH/conc. H_2SO_4).

General Procedure for the oxy-*Cope* Rearrangement and/or *β*-Cleavage of Alkoxides 74a–83a: Preparation of Ketones 84–103. – A soln. of the corresponding alcohol (10 mmol) in HMPA (5 ml) was added dropwise within 15 min to a stirred slurry of KH (11 mmol) in HMPA (25 ml) at r.t. under N_2. The mixture was stirred at r.t. until TLC indicated completion of the reaction (30 min–2 h). The mixture was then submitted to the same workup procedure described for the preparation of **15–42** (*vide supra*) to afford a product mixture whose composition was analysed by TLC, GC/MS coupling, and ^{1}H-NMR (360 MHz) spectroscopy; purification was effected by CC with CH_2Cl_2.

1,8-Nonadien-4-one (**84**) [37] *and 2,8-Nonadien-4-one* (**85**; (*E*/*Z*) 3:1) (5:1 mixture, 81% yield from **74**). B.p. 72–78°/15 Torr.

84: R_f 0.74. IR: 2920, 1710, 1638, 985, 910. ^{1}H-NMR: 1.68 (*tt*, *J* = 7, 7, 2 H); 2.06 (*dt*, *J* = 7, 7, 2 H); 2.45 (*t*, *J* = 7, 2 H); 3.16 (*d*, *J* = 7, 2 H); 4.98 (br. *d*, *J* = 11, 1 H); 5.01 (*dd*, *J* = 18, 1.5, 1 H); 5.13 (*dd*, *J* = 18, 1.5, 1 H); 5.18 (*dd*, *J* = 11, 1.5, 1 H); 5.76 (*m*, 1 H); 5.92 (*m*, 1 H). MS: 138 (0, M^+), 97 (98), 69 (100), 55 (55), 41 (81).

(*E*)-**85** [39]: R_f 0.55. IR: 1685. ^{1}H-NMR: 1.90 (*dd*, *J* = 7, 1.5, 3 H); 2.53 (*t*, *J* = 7, 2 H); 6.11 (br. *d*, *J* = 15, 1 H); 6.84 (*m*, 1 H). MS: 138 (0.5, M^+), 123 (7), 109 (2), 84 (38), 69 (100), 41 (18).

(*Z*)-**85** [40]: R_f 0.73. ^{1}H-NMR: 2.11 (*d*, *J* = 7, 3 H). MS: 138 (1, M^+), 123 (3), 109 (6), 84 (29), 69 (100), 41 (20).

2,8-Dimethyl-1,8-nonadien-4-one (**86**) *and 2,8-Dimethyl-2,8-nonadien-4-one* (**87**) (3.7:1 mixture, 84% yield from **75**). B.p. 85–92°/15 Torr.

86: R_f 0.75. IR: 2910, 1705, 1640, 882. ^{1}H-NMR: 1.70 (*s*, 3 H); 1.70 (*m*, 2 H); 1.75 (*s*, 3 H); 2.01 (*t*, *J* = 7, 2 H); 2.45 (*t*, *J* = 7, 2 H); 3.10 (*s*, 2 H); 4.67 (br. *s*, 1 H); 4.72 (br. *s*, 1 H); 4.81 (br. *s*, 1 H); 4.94 (br. *s*, 1 H). MS: 166 (0, M^+), 111 (27), 83 (19), 69 (17), 55 (100), 141 (10).

87: R_f 0.66. IR: 1680. ^{1}H-NMR: 1.72 (*s*, 3 H); 1.88 (*s*, 3 H); 2.14 (*s*, 3 H); 2.40 (*t*, *J* = 7, 2 H); 6.07 (br. *s*, 1 H). MS: 166 (0, M^+), 111 (3), 98 (13), 83 (100), 55 (23).

5-Methyl-1,8-nonadien-4-one (**88**) *and 5-Methyl-2,8-nonadien-4-one* (**89**; (*E*/*Z*) 1:1) (2.6:1 mixture, 78% yield from **76**). B.p. 80–84°/15 Torr.

88: R_f 0.61. IR: 3060, 2910, 1710, 1642, 1440, 985, 910. ^{1}H-NMR: 1.09 (*d*, *J* = 7, 3 H); 1.41 (*m*, 1 H); 1.79 (*m*, 1 H); 2.03 (br. *q*, *J* = 7, 2 H); 2.61 (*m*, 1 H); 3.22 (br. *d*, *J* = 7, 2 H); 4.97 (br. *d*, *J* = 11, 1 H); 5.01 (br. *d*, *J* = 18, 1 H); 5.13 (br. *d*, *J* = 18, 1 H); 5.18 (br. *d*, *J* = 11, 1 H); 5.76 (*m*, 1 H); 5.92 (*m*, 1 H). MS: 152 (0, M^+), 111 (29), 83 (35), 55 (100), 41 (41).

(*E*)-**89**: R_f 0.45. IR: 1685. ^{1}H-NMR: 1.90 (br. *d*, *J* = 7, 3 H); 6.18 (br. *d*, *J* = 15, 1 H); 6.89 (*dq*, *J* = 15, 7, 1 H). MS: 152 (1, M^+), 137 (3), 98 (40), 83 (11), 69 (100), 55 (10), 41 (19).

(*Z*)-**89**: R_f 0.60. ^{1}H-NMR: 2.11 (*d*, *J* = 6, 3 H). MS: 152 (1, M^+), 137 (2), 98 (40), 83 (5), 69 (100), 55 (10), 41 (27).

2,5,8-Trimethyl-1,8-nonadien-4-one (**90**) *and 2,5,8-Trimethyl-2,8-nonadien-4-one* (**91**) (3.3:1 mixture, 81% yield from **77**). B.p. 98–104°/15 Torr.

90: R_f 0.63. IR: 3060, 2900, 1705, 1642, 1624, 1440, 1368, 880. ^{1}H-NMR: 1.10 (*d*, *J* = 7, 3 H); 1.44 (*m*, 1 H); 1.71 (*s*, 3 H); 1.75 (*s*, 3 H); 1.83 (*m*, 1 H); 1.98 (br. *t*, *J* = 7, 2 H); 2.64 (*m*, 1 H); 3.16 (*s*, 2 H); 4.67 (br. *s*, 1 H); 4.72 (br. *s*, 1 H); 4.80 (br. *s*, 1 H); 4.95 (br. *s*, 1 H). MS: 180 (0, M^+), 125 (19), 97 (21), 83 (18), 69 (18), 55 (100).

91: R_f 0.54. IR: 1680. ^{1}H-NMR: 1.08 (*d*, *J* = 7, 3 H); 1.45 (*m*, 1 H); 1.71 (*s*, 3 H); 2.65 (*m*, 1 H); 1.90 (*s*, 3 H); 1.98 (2 H); 2.15 (*s*, 3 H); 2.49 (*m*, 1 H); 4.67 (br. *s*, 1 H); 4.72 (br. *s*, 1 H); 6.10 (br. *s*, 1 H). MS: 180 (1, M^+), 112 (20), 83 (100), 55 (23).

6-Methyl-1,8-nonadien-4-one (**92**) *and 6-Methyl-2,8-nonadien-4-one* (**93**; (*E*/*Z*) 1:1) (5:1 mixture, 83% yield from **78**). B.p. 80–86°/15 Torr.

92: R_f 0.61. IR: 3100, 2975, 1710, 1644, 1372, 1000, 920. ^{1}H-NMR: 0.91 (*d*, *J* = 7, 3 H); 1.85–2.20 (3 H); 2.23 (*dd*, *J* = 16, 8, 1 H); 2.46 (*dd*, *J* = 16, 5, 1 H); 3.15 (*d*, *J* = 7, 2 H); 5.01 (br. *d*, *J* = 18, 1 H); 5.02 (br. *d*, *J* = 11, 1 H); 5.14 (br. *d*, *J* = 18, 1 H); 5.18 (br. *d*, *J* = 11, 1 H); 5.74 (*m*, 1 H); 5.91 (*m*, 1 H). MS: 152 (0.5, M^+), 111 (58), 83 (22), 69 (75), 55 (100), 41 (68).

(*E*)-**93**: R_f 0.49. IR: 1685. ^{1}H-NMR: 1.89 (*dd*, *J* = 7, 1.5, 3 H); 6.12 (br. *d*, *J* = 15, 1 H); 6.84 (*m*, 1 H). MS: 152 (1, M^+), 137 (12), 84 (52), 69 (100), 41 (22).

(*Z*)-**93**: R_f 0.60. ^{1}H-NMR: 2.11 (*d*, *J* = 7, 3 H). MS: 152 (1, M^+), 137 (6), 109 (4), 84 (36), 69 (100), 41 (24).

2,6,8-Trimethyl-1,8-nonadien-4-one (**94**) *and 2,6,8-Trimethyl-2,8-nonadien-4-one* (**95**) (6:1 mixture, 86% yield from **79**). B.p. 104–108°/15 Torr. **94**: R_f 0.68. IR: 3060, 2900, 1706, 1640, 1370, 890. ^{1}H-NMR: 0.88 (*d*, *J* = 7, 3 H); 1.70 (*s*, 3 H); 1.74 (*s*, 3 H); 1.80–2.50 (5 H); 3.09 (*s*, 2 H); 4.65 (br. *s*, 1 H); 4.75 (br. *s*, 1 H); 4.81 (br. *s*, 1 H); 4.94 (br. *s*, 1 H). MS: 180 (0, M^+), 165 (2), 125 (33), 83 (80), 69 (87), 55 (100), 41 (16).

95: R_f 0.58. IR: 1682. ^{1}H-NMR: 0.88 (*d*, *J* = 7, 3 H); 1.70 (*s*, 3 H); 1.80–2.50 (5 H); 1.88 (*s*, 3 H); 2.14 (*s*, 3 H); 4.65 (br. *s*, 1 H); 4.75 (br. *s*, 1 H); 6.05 (br. *s*, 1 H). MS: 180 (1, M^+), 165 (2), 125 (4), 98 (15), 83 (100), 55 (15).

5,6-Dimethyl-1,8-nonadien-4-one (**96**) *and 5,6-Dimethyl-2,8-nonadien-4-one* (**97**; (*E*/*Z*) 2:1): both are diastereoisomeric 1:1 mixtures; **96**/**97** 3:1, 77% yield from **80**. B.p. 86–89°/15 Torr.

96: R_f 0.61. IR: 3060, 2930, 1710, 1636, 1440, 1376, 984, 904. ^{1}H-NMR: 0.82, 0.89, 0.99, 1.06 (4*d*, *J* = 7, 12 H); 1.60–2.80 (8 H); 3.21 (*d*, *J* = 7, 4 H); 5.01, 5.04 (2 br. *s*, 4 H); 5.13 (br. *d*, *J* = 18, 2 H); 5.18 (br. *d*, *J* = 11, 2 H); 5.75 (*m*, 2 H); 5.93 (*m*, 2 H). MS (isomer **A**): 166 (0, M^+), 125 (17), 97 (20), 69 (28), 55 (100), 41 (25). MS (isomer **B**): 166 (0, M^+), 125 (17), 97 (21), 69 (18), 55 (100), 41 (23).

(*E*)-**97**: R_f 0.48. IR: 1685. ^{1}H-NMR: 0.81, 0.88, 0.99, 1.06 (4*d*, *J* = 7, 12 H); 1.90 (br. *d*, *J* = 7, 6 H); 1.60–2.80 (8 H); 5.00–5.10 (4 H); 5.76 (*m*, 2 H); 6.19 (br. *d*, *J* = 15, 2 H); 6.88 (*m*, 2 H). MS (isomer **A**): 166 (0, M^+), 151 (6), 98 (52), 83 (11), 69 (100), 55 (19), 41 (17). MS (isomer **B**): 166 (0, M^+), 151 (4), 98 (40), 83 (14), 69 (100), 55 (16), 41 (15).

(*Z*)-**97**: R_f 0.60. ^{1}H-NMR: 2.11 (*d*, *J* = 7, 6 H).

2,5,6,8-Tetramethyl-1,8-nonadien-4-one (**98**) *and 2,5,6,8-Tetramethyl-2,8-nonadien-4-one* (**99**): both are diastereoisomeric 1:1 mixtures; **98**/**99** 5:1, 82% yield from **81**. B.p. 106–109°/15 Torr.

98: R_f 0.65. IR: 3060, 2920, 1705, 1642, 1622, 1440, 1370, 885. ^{1}H-NMR: 0.78, 0.85, 0.98, 1.06 (4*d*, *J* = 7, 12 H); 1.68, 1.72, 1.75, 1.76 (4*s*, 12 H); 1.80–2.20 (6 H); 2.55 (*m*, 2 H); 3.16 (2 H); 3.17 (br. *s*, 2 H); 4.67, 4.69, 4.79, 4.94 (4 br. *s*, 8 H). MS (isomer **A**): 194 (0, M^+), 139 (17), 97 (21), 83 (21), 69 (100), 55 (67). MS (isomer **B**): 194 (0, M^+), 139 (13), 97 (17), 83 (20), 69 (100), 55 (57).

99: R_f 0.57. IR: 1680. ^{1}H-NMR: 0.76, 0.84, 0.98, 1.04 (4*d*, *J* = 7, 12 H); 1.65–2.20 (24 H); 2.40 (*m*, 2 H); 4.67, 4.75 (2 br. *s*, 4 H); 6.09, 6.11 (2 br. *s*, 2 H). MS (isomer **A**): 194 (0.5, M^+), 112 (20), 83 (100), 55 (20). MS (isomer **B**): 194 (0.5, M^+), 112 (20), 83 (100), 55 (16).

6,6-Dimethyl-1,8-nonadien-4-one (**100**) *and 6,6-Dimethyl-2,8-nonadien-4-one* (**101**; (*E*/*Z*) 1:1) (2:1 mixture, 43% yield from **82**). B.p. 86–89°/15 Torr.

100: R_f 0.68. IR: 3060, 2900, 1710, 1640, 1350, 1045, 990, 910. ^{1}H-NMR: 1.00 (*s*, 6 H); 2.09 (*d*, *J* = 7, 2 H); 2.32 (*s*, 2 H); 3.13 (*d*, *J* = 7, 2 H); 5.02 (br. *d*, *J* = 18, 1 H); 5.07 (br. *d*, *J* = 11, 1 H); 5.11 (br. *d*, *J* = 18, 1 H); 5.17 (br. *d*, *J* = 11, 1 H); 5.79 (*m*, 1 H); 5.90 (*m*, 1 H). MS: 166 (0, M^+), 125 (20), 83 (29), 69 (100), 55 (65), 41 (48).

(*E*)-**101**: R_f 0.55. IR: 1685. ^{1}H-NMR: 0.99 (*s*, 6 H); 1.88 (br. *d*, *J* = 7, 3 H); 2.10 (*d*, *J* = 7, 2 H); 2.39 (*s*, 2 H); 5.02 (br. *d*, *J* = 18, 1 H); 5.05 (br. *d*, *J* = 11, 1 H); 5.82 (*m*, 1 H); 6.12 (br. *d*, *J* = 15, 1 H); 6.79 (*dq*, *J* = 15, 7, 1 H). MS: 166 (0, M^+), 151 (1), 82 (15), 69 (100), 55 (9), 40 (22).

(*Z*)-**101**: R_f 0.68. ^{1}H-NMR: 2.10 (*d*, *J* = 7, 3 H). MS: 166 (0, M^+), 151 (4), 125 (4), 82 (29), 69 (100), 55 (14), 41 (23).

Also isolated was a 3.4:1.4:1 mixture **59**/**60**/**61** (35% yield from **82**).

2,6,6,8-Tetramethyl-1,8-nonadien-4-one (**102**) *and 2,6,6,8-Tetramethyl-2,8-nonadien-4-one* (**103**) (2.8:1 mixture, 46% yield from **83**). B.p. 107–110°/15 Torr.

102: R_f 0.74. IR: 3060, 2900, 1702, 1640, 1436, 1370, 890. ^{1}H-NMR: 1.03 (*s*, 6 H); 1.74 (*s*, 3 H); 1.77 (*s*, 3 H); 2.11 (*s*, 2 H); 2.38 (2 H); 3.07 (*s*, 2 H); 4.65 (br. *s*, 1 H); 4.79 (br. *s*, 1 H); 4.87 (br. *s*, 1 H); 4.93 (br. *s*, 1 H). MS: 194 (0, M^+), 139 (23), 97 (23), 83 (80), 55 (100).

103: R_f 0.62. IR: 1680. ^{1}H-NMR: 1.03 (*s*, 6 H); 1.77 (*s*, 3 H); 1.87 (*s*, 3 H); 2.08 (*s*, 2 H); 2.13 (*s*, 3 H); 2.32 (*s*, 2 H); 4.66 (br. *s*, 1 H); 4.87 (br. *s*, 1 H); 6.05 (br. *s*, 1 H). MS: 194 (0, M^+), 179 (5), 96 (11), 83 (100), 55 (20).

Also isolated was a 2.3:1 mixture **62**/**63** (38% yield from **83**).

4-(2',6',6'-Trimethyl-1'-cyclohexenyl)-1,6-heptadien-4-ol (**106**) [13]. Using the procedure described for the preparation of **1**–**14** *(vide supra)*, methyl β-cyclogeranate (**104**) [14] was converted to **106** (colourless oil, 85% yield). B.p. 74–76°/0.04 Torr. R_f 0.80. IR: 3580 (br.), 3090, 1640, 1360, 1000, 918, 722. ^{1}H-NMR (+D_2O): 1.24 (*s*, 6 H); 1.39 (*m*, 2 H); 1.49 (*m*, 2 H); 1.72 (*s*, 3 H); 1.95 (*dd*, *J* = 6, 6, 2 H); 2.34 (*dd*, *J* = 14, 8, 2 H); 2.81 (*dd*, *J* = 14, 7, 2 H); 5.09 (*d*, *J* = 18, 2 H); 5.12 (*d*, *J* = 10, 2 H); 5.87 (*m*, 2 H). MS: 234 (0, M^+), 193 (15), 151 (100), 123 (45), 81 (32), 69 (15), 55 (12), 41 (53).

4-(2',6',6'-Trimethyl-1',3'-cyclohexadienyl)-1,6-heptadien-4-ol (**107**) [13]. Using the procedure described for the preparation of **1**–**14** *(vide supra)*, methyl β-safranate (**105**) [17] was converted to **107** (colourless oil, 83% yield). B.p. 89–90°/0.09 Torr. R_f 0.80. IR: 3580 (br.), 3090, 1640, 1360, 1000, 918, 750, 721. ^{1}H-NMR (+D_2O): 1.19 (*s*, 6 H); 1.85 (*s*, 3 H); 2.02 (2 H); 2.34 (*dd*, *J* = 14, 8, 2 H), 2.86 (*dd*, *J* = 14, 6.5, 2 H); 5.12 (*d*, *J* = 10, 2 H); 5.13 (*d*, *J* = 18, 2 H); 5.67 (2 H); 5.88 (*m*, 2 H). MS: 232 (0, M^+), 191 (21), 149 (100), 121 (13), 105 (19), 91 (24), 41 (55).

1-(2',6',6'-Trimethyl-1'-cyclohexenyl)-3-buten-1-one (**108**) [8] *and 1-(2',6',6'-Trimethyl-1'-cyclohexenyl)-2-buten-1-one* (**109**; (*E*/*Z*) 1.5:1) [8]. Using the procedure described for the oxy-*Cope* rearrangement and/or β-cleavage of **74a**–**83a** *(vide supra)*, **106** was converted to a 0.6:1 mixture **108**/**109** ((*E*/*Z*) 1.5:1). Pale-yellow oil, 70% yield, b.p. (bulb-to-bulb distillation) 100–130°/0.1 Torr.

108: R_f 0.44. ^{1}H-NMR: 1.07 (*s*, 6 H); 1.57 (*s*, 3 H); 5.11 (br. *d*, *J* = 18, 1 H); 5.18 (br. *d*, *J* = 11, 1 H); 6.01 (*m*, 1 H). MS: 192 (4, M^+), 177 (15), 151 (100), 120 (40), 81 (41).

(*E*)-**109** *(β-Damascone):* R_f 0.35. IR: 1670, 1640, 1620, 1440, 1370, 1360, 1280, 1230, 1160, 970, 928. ^{1}H-NMR: 1.02 (*s*, 6 H); 1.46 (*m*, 2 H); 1.51 (*s*, 3 H); 1.69 (*m*, 2 H); 1.92 (*dd*, *J* = 7, 1.5, 3 H); 1.99 (*dd*, *J* = 6, 6, 2 H); 6.16 (br. *d*, *J* = 15, 1 H); 6.73 (*dq*, *J* = 15, 7, 1 H). MS: 192 (30, M^+), 177 (100), 135 (20), 123 (50), 107 (32), 81 (24), 69 (34).

(*Z*)-**109**: R_f 0.44. ^{1}H-NMR: 1.07 (*s*, 6 H); 1.57 (*s*, 3 H); 2.14 (*d*, *J* = 6, 3 H). MS: 192 (31, M^+), 177 (100), 135 (20), 123 (53), 107 (35), 81 (29), 69 (34).

This foregoing mixture was equilibrated (TsOH·H_2O(cat.), THF, reflux 16 h) to afford (*E*)-**109** in 89% yield (62% yield from **106**).

1-(2',6',6'-Trimethyl-1',3'-cyclohexadienyl)-3-buten-1-one (**110**) [13] *and 1-(2',6',6'-Trimethyl-1',3'-cyclohexadienyl)-2-buten-1-one* (**111**; (*E*/*Z*) 0.8:1) [8]. Using the aforementioned procedure *(vide supra)*, **107** was converted to a 1:1.7 mixture **110**/**111** ((*E*/*Z*) 0.8:1). Pale-yellow oil, 45% yield, b.p. (bulb-to-bulb distillation) 120–150°/0.1 Torr.

110: R_f 0.50. ^{1}H-NMR: 1.10 (*s*, 6 H); 1.73 (*s*, 3 H); 2.10 (*d*, *J* = 3, 2 H); 3.34 (*d*, *J* = 7, 2 H); 5.14 (br. *d*, *J* = 18, 1 H); 5.19 (br. *d*, *J* = 11, 1 H); 5.83 (2 H); 5.99 (*m*, 1 H). MS: 190 (2, M^+), 149 (100), 121 (18), 105 (26), 91 (15), 79 (11).

(*E*)-**111** *(β-Damascenone):* R_f 0.32. IR: 1660, 1630, 1610, 1440, 1396, 1374, 1356, 1282, 1246, 1220, 962, 924, 698. ^{1}H-NMR: 1.05 (*s*, 6 H); 1.64 (*s*, 3 H); 1.94 (*dd*, *J* = 7, 1.5, 3 H); 2.12 (*d*, *J* = 3, 2 H); 5.83 (2 H); 6.19 (br. *d*, *J* = 15, 1 H); 6.84 (*dq*, *J* = 15, 7, 1 H). MS: 190 (15, M^+), 175 (6), 121 (67), 105 (20), 91 (10), 69 (100), 41 (22).

(*Z*)-**111**: R_f 0.43. ^{1}H-NMR: 1.08 (*s*, 6 H); 1.71 (*s*, 3 H); 2.12 (*d*, *J* = 3, 2 H); 2.15 (*d*, *J* = 6, 3 H); 5.83 (2 H); 6.23 (2 H). MS: 190 (19, M^+), 175 (7), 121 (81), 105 (23), 91 (12), 69 (100), 41 (26).

Also detected (TLC and GC analysis) was a complex mixture **112**/*(E/Z)*-**113** (diastereoisomeric mixtures): *ca.* 26% yield.

The crude mixture **110**–**113** was treated with a catalytic amount of TsOH·H_2O in refluxing THF for 16 h to afford a 1.7:1 mixture of (*E*)-**111** and *(E)-1-[2'-(2"-propenyl)-2',6',6'-trimethyl-3'-cyclohexenyl]-2-buten-1-one* ((*E*)-**113**; *cis*/*trans* 1.6:1) which, after a standard aq. workup, was purified by CC with CH_2Cl_2 to afford (*E*)-**111** (40% yield from **107**) and (*E*)-**113** (*cis*/*trans* 1.6:1): colourless oil, 24% yield from **107.**

cis-(*E*)-**113**: R_f 0.50. ^{1}H-NMR: 0.94 (*s*, 3 H); 1.08 (*s*, 3 H); 1.16 (*s*, 3 H); 1.70–2.10 (6 H); 2.54 (*dd*, *J* = 14, 8, 1 H); 2.82 (*s*, 1 H); 4.97 (br. *d*, *J* = 18, 1 H); 5.01 (br. *d*, *J* = 11, 1 H); 5.48 (br. *d*, *J* = 10.5, 1 H); 5.59 (*ddd*, *J* = 10.5, 4, 4, 1 H); 5.79 (*m*, 1 H); 6.21 (br. *d*, *J* = 15, 1 H); 6.81 (*m*, 1 H). ^{13}C-NMR: 203.0 (*s*); 141.4 (*d*); 135.8 (*d*); 135.4 (*d*); 134.1 (*d*); 123.4 (*d*); 117.5 (*t*); 62.2 (*d*); 42.3 (*t*); 40.4 (*t*); 37.8 (*s*); 33.4 (*s*); 30.9 (*q*); 29.1 (*q*); 24.8 (*q*); 18.2 (*q*). MS: 232 (0, M^+), 191 (5), 135 (25), 125 (22), 107 (19), 91 (24), 69 (100), 41 (53).

trans-(*E*)-**113:** R_f 0.50. ^{1}H-NMR: 0.90 (*s*, 3 H); 1.04 (*s*, 3 H); 1.16 (*s*, 3 H); 1.70–2.10 (7 H); 2.90 (*s*, 1 H); 5.03 (br. *d*, *J* = 18, 1 H); 5.11 (br. *d*, *J* = 11, 1 H); 5.35 (br. *d*, *J* = 10.5, 1 H); 5.62 (*m*, 1 H); 5.79 (*m*, 1 H); 6.17 (br. *d*, *J* = 15, 1 H); 6.81 (*m*, 1 H). ^{13}C-NMR: 202.9 (*s*); 141.3 (*d*); 135.6 (*d*); 135.5 (*d*); 135.3 (*d*); 124.0 (*d*); 117.8 (*t*); 57.9 (*d*); 48.1 (*t*); 41.2 (*t*); 39.1 (*t*); 33.5 (*s*); 30.6 (*q*); 24.1 (*q*); 23.7 (*q*); 18.1 (*q*). MS: 232 (0, M^+), 191 (7), 135 (27), 107 (18), 91 (28), 69 (100), 41 (42).

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