Diastereoselectivity in the Addition of Crotylmagnesium Bromide to Unsymmetrical Ketones

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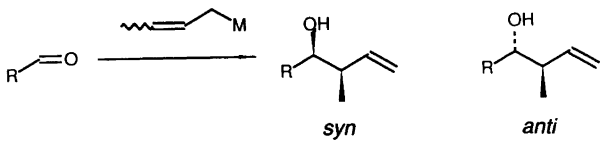
Reactions of the Grignard reagent prepared from 1-bromo-2-butene (crotylmagnesium bromide, $CH_3CH{=}CHCH_2MgBr$) with 19 unsymmetrical ketones (R'RC=O; R'≠R; R=Me and R'=Et, *i*-Pr, *c*-Hex or *t*-Bu; R=Me, Et, *i*-Pr, *c*-Hex or *t*-Bu and R'=2-Fur, 2-Th or Ph) have been performed in order to study the diastereoselectivity of the reaction. All ketones gave two diastereomers of tertiary homoallyl alcohols formed by addition of an α-methylallyl group. With dialkyl ketones the major isomer had the *anti* configuration. With alkyl aryl(heteroaryl) ketones the *syn* isomer predominated. The diastereoselectivities were quite low, except with *t*-Bu ketones which gave a maximum de of 84. Possible transition states are discussed and a mechanism is proposed based on our observations.

Stereoselectivity in the reactions between allylic organometallic reagents and conformationally flexible carbonyl compounds has gained much attention recently, from a synthetic as well as a mechanistic viewpoint.[1a–e] The reactions of crotylmetal reagents with aldehydes have been extensively studied and in many cases excellent diastereoselectivities, and with enantiomeric reagents even enantioselectivities, have been achieved in the formation of secondary β-methylhomoallyl alcohols, important intermediates in the synthesis of numerous macrolide and polyether antibiotics (Scheme 1).[2,3]



syn *anti*

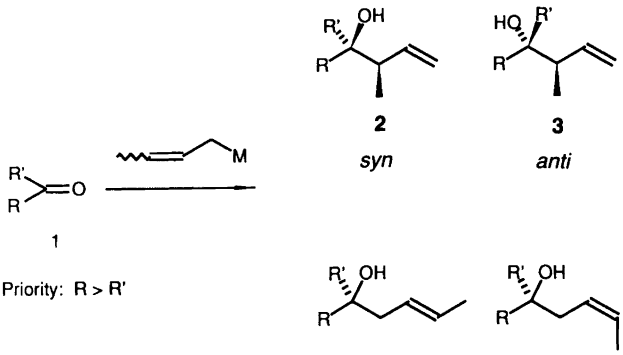
M = Li, Na, K, MgX, B...

R = Alkyl, Ar

Scheme 1.[a]

[a] However, well aware of the ambiguous character of the prefixes *syn, anti,* not to mention *erythro, threo,* when compounds of the present type are concerned, we decided to use the *syn, anti* prefixes, defined as they appear in Schemes 1 and 2, the R group having higher priority than R' according to the sequence rule. A nomenclature for the description of the relative configurations of diastereomers has been suggested which designates the diastereomer with the configurations at the two asymmetric centra being reflections of each other, as to the priority order of the substituents, as *pref* (priority reflective) and the other diastereomer as *parf* (priority antireflective).[7] The descriptors are unambiguous and easy to use with compounds containing two asymmetric carbons. The *syn* and *anti* configurations above thus correspond to *pref* and *parf,* respectively.

Much less attention has been paid to the reactions of ketones. One of the reasons for this may be that tertiary alcohols are less important than secondary ones as synthetic intermediates. Another reason is certainly that lower stereoselectivities are expected with ketones than with aldehydes due to the smaller difference in size between the substituents on the carbonyl group of ketones. Ketones (**1**, Scheme 2), especially those with sterically bulky substituents on the carbonyl group, are also known to give crotyl addition products (**4,5**) besides α-methylallyl products (**2,3**) as shown in Scheme 2.[4] Moreover, the assignment of the stereochemical structures of the diastereomeric reaction products, a prerequisite for drawing conclusions about the reaction mechanisms, is not as straightforward with tertiary as with secondary alcohols.



2 **3**

syn *anti*

1

Priority: R > R'

4 **5**

E- *Z-*

Scheme 2.

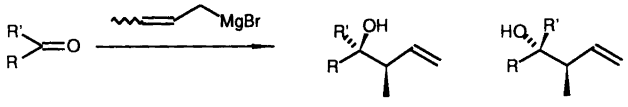
High diastereoselectivities in the addition of crotyltitanium reagents to ketones[2b,5] as well as in the addition of crotylmagnesium reagents to chromium complexes of ketones (in the presence of triethylborane or triethylalumi-

nium)[6] have been reported. With Ti reagents the major isomer had an *anti* configuration when the alkyl group in alkyl phenyl ketones was Me, Et or *i*-Pr and a *syn* configuration when the alkyl group was *t*-Bu.[5] Moreover, the selectivity decreased in the order *t*-Bu > Me > Et > *i*-Pr. The chromium complexes gave mainly *anti* products when triethylaluminium was present but gave *syn* products when triethylborane was used.[6a] A six-membered chair-like transition state has been suggested for these reactions.[5,6]

Although Benkeser and co-workers observed diastereoselectivity in their studies of the reversibility of the Grignard allylation of sterically hindered ketones,[4] no detailed studies of the diastereoselectivity of the uncatalysed addition of crotylmagnesium reagents to unsymmetrical ketones have yet been published and it seems to be generally believed that crotyl Grignard reagents display no diastereoselectivity in their reactions with acyclic unsymmetrical ketones.[1b,2b] However, in our studies of crotylmagnesium bromide additions to ketones, we observed that with some ketones the selectivities were even higher than in the corresponding reactions with aldehydes. Thus we considered it relevant to perform a study of the reactions of unsymmetrical ketones with crotylmagnesium bromide, in order to obtain information regarding the diastereoselectivity and the factors affecting it. Based on our results, the reaction mechanisms are discussed.

Results and discussion

The reactions between the ketones and crotylmagnesium bromide were performed by fast (ca. 5 min) addition of the ketone in THF to a THF solution of the Grignard reagent, at room temperature. The conversion of starting material was complete within 0.5 h. ^{1}H NMR spectra and GLC–MS of the reaction mixtures, after evaporation of the solvents, showed that the products consisted of two diastereomers of tertiary alcohols containing the α-methylallyl group (Scheme 3). Only when R=Me and R′=*t*-Bu were traces of crotyl products detected. The results are shown in Table 1.



6 **7–10**

syn *anti*

7. R′ = Me **a.** R = Et **b.** R = i-Pr **c.** R = c-Hex **d.** R = t-Bu

8. R = Fur **9.** R = Th **10.** R = Ph

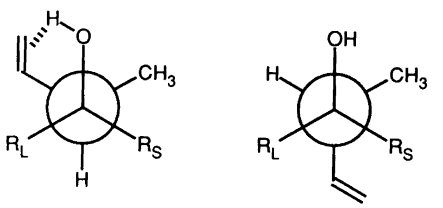
a. R′ = Me **b.** R′ = Et **c.** R′ = i-Pr **d.** R′ = c-Hex **e.** R′ = t-Bu

Scheme 3.

The chemical yields (90–100 %) and the isomer ratios were determined by GLC. After work-up of the reaction and evaporation of the solvent, ^{1}H NMR spectra of the reaction mixtures were taken. Most of the NMR signals of the isomers were well separated in the spectra of the mixtures, which allowed extraction of the spectral data of both isomers and assignment of the signals. The relative configurations of the isomers of **7b**, **7c**, **7d**, **10a**, **10b** and **10e** were assigned by comparison of their ^{1}H NMR spectra with spectra of compounds with known relative configurations.[5,6b,8] Based on this and the assumption that all ketones react analogously, the *syn* configuration was assigned to the major isomers of compounds **8–10** and the *anti* configuration to the major isomers of compounds **7** (the latter configuration is called *threo* by Gambaro *et al.*[8]). The assignments of the relative configurations of the isomers are also justified on the basis of their relative GLC retention times and ^{1}H NMR data as rationalized below. The preferred equilibrium conformations of the two isomers are mainly determined by interactions of sterically bulky groups in the molecules. The vicinal interactions between R_L and the allylic methyl group in the two isomers are minimised in the conformations shown in Scheme 4.

Table 1. Products and isomer ratios (cf. Scheme 3) in the reactions of crotylmagnesium bromide, $CH_3CH{=}CHCH_2MgBr$ with unsymmetrical ketones, R′RC=O. The total yields (by GLC) ranged between 90 and 100 %. Fur = 2-furyl, Th = 2-thienyl.

Compound	R	R′	Product ratio *syn*:*anti*
7a	Me	Et	45:55
7b	Me	*i*-Pr	41:59
7c	Me	*c*-Hex	41:59
7d	Me	*t*-Bu	10:90
8a	Me	Fur	60:40
8b	Et	Fur	59:41
8c	*i*-Pr	Fur	67:33
8d	*c*-Hex	Fur	65:35
8e	*t*-Bu	Fur	78:22
9a	Me	Th	56:44
9b	Et	Th	62:38
9c	*i*-Pr	Th	59:41
9d	*c*-Hex	Th	55:45
9e	*t*-Bu	Th	92:8
10a	Me	Ph	62:38
10b	Et	Ph	62:38
10c	*i*-Pr	Ph	64:36
10d	*c*-Hex	Ph	59:41
10e	*t*-Bu	Ph	89:11

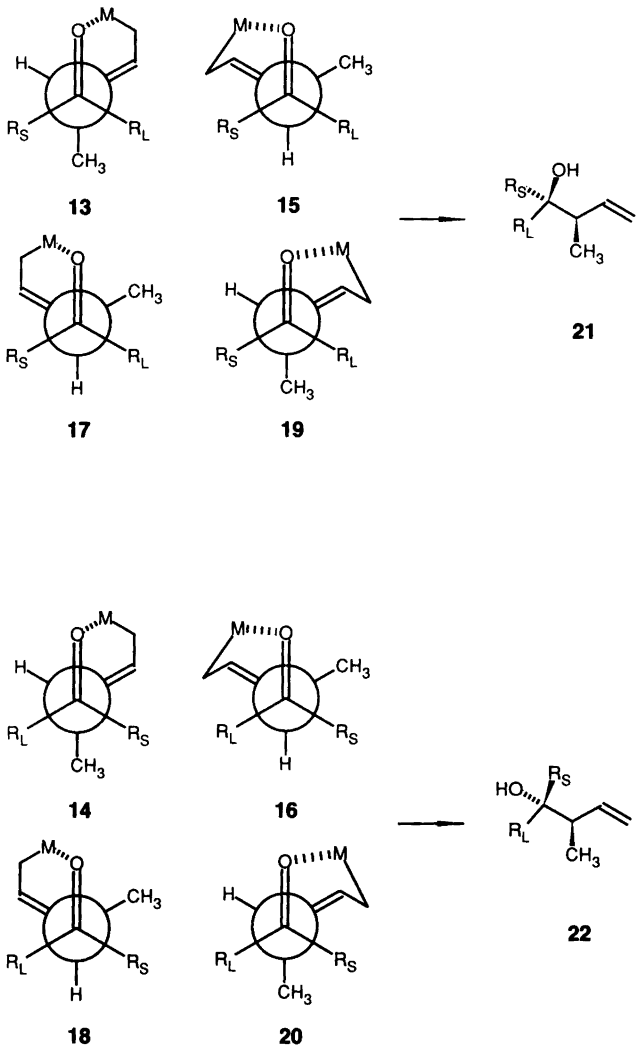


11 **12**

Scheme 4.

In compounds **7** the methyl group is classified as a small group (R_S) and the other alkyl groups as large (R_L). In compounds **8–10**, however, the phenyl, furyl and thienyl groups are classified as small groups (R_S) and all alkyl groups as large (R_L) groups, in accordance with results from studies of similar systems.[9a–d] The conformation **11** can be stabilized by a hydrogen bond between the π-system of the vinyl group and the hydrogen atom of the hydroxy group.[10,11] Thus the isomer which adopts the conformation – and has the configuration – **11** should have the shorter GC retention time.[12,13] For compounds **7** the *anti* configuration and for compounds **8–10** the *syn* configuration correspond to compound **11**. In all the present cases the major isomer had the shorter retention time. In the ^{1}H NMR spectra the shift of the hydroxy proton signal (if detected) of the major isomer was always downfield from that of the minor isomer in accordance with the presence of an intramolecular hydrogen bond in the former. Moreover, inspection of molecular models suggested that in compounds **8–10** the methyl group at the allylic carbon should be more shielded in the *syn* isomers than in the *anti* isomers by the ring-current effect. In the ^{1}H NMR spectra (except in those of **8a** and **9a**) the methyl group resonance of the major isomer is at higher field than that of the minor isomer. These observations support the suggested configurations of the major and minor isomers.

The diastereoselectivities of the reactions were moderate and of the same order of magnitude for all ketones except the *t*-Bu ketones, which gave a maximum excess of the major isomer of 84. Thus, no clear trend of increasing selectivity with increasing size of the groups R or R′ was observed. This and the trend of decreasing selectivity with increasing size of the alkyl group observed by Seebach *et al.*[5] with crotyltitanium reagents, can be explained assuming a cyclic transition state in which the Mg-atom is coordinated to the carbonyl oxygen, as shown in Scheme 5.



Scheme 5.

The possible transition states are those in which the carbonyl group and the allylic double bond are synclinal, states **13**, **15**, **17** and **19** leading to *syn* products with the dialkyl ketones and *anti* products with the alkyl aryl(heteroaryl) ketones (**21**, Scheme 5). Transition states **14**, **16**, **18** and **20** then give *anti* products with the dialkyl ketones and *syn* products with the alkyl aryl(heteroaryl) ketones (**22**, Scheme 5).

Crotyl Grignard reagents exist as equilibrium mixtures of *Z*- and *E*-isomers[14] and both configurations can exist in the transition states. In **15–18** the hydrogen atom and the carbonyl group are antiperiplanar and these states are favoured on steric grounds.[15] The possibility of several transition states should accelerate the Grignard reaction and result in the low selectivity found for Me, Et, *i*-Pr and *c*-Hex ketones. However, due to the steric bulk of the *t*-Bu group, *t*-Bu ketones would react more slowly and mainly *via* the transition states **16** and **18** where the Me–*t*-Bu *gauche* interaction is minimised. The fact that the Grignard reaction gives mainly *anti* products with dialkyl ketones and *syn* products with alkyl aryl(heteroaryl) ketones is in agreement with the reasoning above and with the suggestion that an aryl(heteroaryl) group is sterically less bulky than an alkyl group.[9a–d]

In the reaction of crotyltitanium compounds with alkyl phenyl ketones Seebach suggested a transition state corresponding to **13** (Scheme 5, R_S = Phenyl and R_L = Alkyl). This would mean that a sterically unfavourable transition state giving *anti* products is preferred. An increase of the size of the alkyl group would make **13** still more unfavourable until, finally, the main reaction is *via* **16** and **18** with the *t*-Bu ketone. This would explain Seebach's results of decreasing *anti* selectivity with increased size of the alkyl group until, finally, the selectivity is reversed and almost 100 % *syn* selectivity is obtained with the *t*-Bu ketone.

In conclusion, the reactions between crotylmagnesium bromide and acyclic unsymmetrical ketones display moderate diastereoselectivities except when one of the groups on the carbonyl group is *t*-Bu. The fact that only α-methylallyl and no crotyl adducts were formed suggests that cyclic transition states are involved. We suggest that several tran-

sition states are possible and that the main reaction path is determined by the steric bulk of the groups R and R'. The results also support the suggestion made by Nishio *et al.*[9] that 'a methyl group is effectively bulkier than a phenyl group with regard to the interaction with vicinal alkyl groups.' Thus, when estimating the relative probabilities of the suggested transition states in the present reaction, it is justified to consider the phenyl group the smaller in alkyl phenyl ketones.

Experimental

Materials. The ketones (**1**) were either commercial preparations and used without further purification or were prepared in this laboratory by standard methods. The crotyl bromide used was a product of Fluka AG (pract. grade) containing 85 % (*E*) 1-bromo-2-butene and 15 % 3-bromo-1-butene. Mg-turnings by Merck (*zur Synthese*) were used to prepare the Grignard reagents. THF was distilled under argon from a solution of sodium diphenylketyl before use. All other chemicals were commercial products and used as received.

General methods. Gas chromatographic analyses were performed with a gas chromatograph (Varian 3300) equipped with 30 m × 0.53 mm DB-1 (methylpolysiloxane) capillary column. 1-Phenylcyclohexanol was used as an internal standard in the quantitative analyses. Mass spectra were obtained on a combined GC-MS instrument (VG 7070) and ^{1}H NMR spectra on a FT NMR spectrometer operating at 400 MHz (JEOL JNM-GX-400).

The Grignard reactions. All reactions were carried out in flame-dried glassware under argon. In a typical procedure, 5 mmol of the ketone dissolved in 50 ml THF were added to a stirred, ca. 0.5 M solution of the Grignard reagent in THF at room temperature. A slight excess (1 : 1.3) of the Grignard reagent was used. Stirring was continued for 1 h. The reaction mixture was treated with a saturated NH_4Cl solution and three 50 ml portions of ether. The combined ether extracts were dried with anhydrous Na_2SO_4 and the solvents evaporated. The reaction products were not further purified prior to the analyses. The total yields and the isomer ratios were determined by gas chromatography and ^{1}H NMR and mass spectra were recorded.

Spectral data. $CDCl_3$, with TMS as an internal standard, was used as solvent in the NMR analyses. As the yields were almost quantitative and therefore no by-products were detected, NMR data on both isomers could be obtained from the spectra of the isomer mixtures. As the chemical shifts are reported to only two decimal places, in some cases the same chemical shifts are given for some of the protons in both isomers. In fact, in most cases, the shifts differ by ≥0.002 ppm and are sufficiently well separated for unambiguous assignments to be made. The vinyl protons of the compounds formed an ABX system, the AB subspectra of which overlapped severely in the spectra of the mixtures. Thus, only shift ranges are given for the AB protons. However, the AB couplings and couplings between the AB and X protons and the allylic proton could be measured and are given below. The signals of the *c*-hexyl groups (δ 0.70–2.00 ppm) and the phenyl groups (δ 7.20–7.45 ppm) gave complicated patterns which were not analysed in detail. The EI mass spectra were recorded at 70 eV ionizing energy. The spectra are presented as *m/z* (% rel.int.). Most of the mass spectra displayed no peak from the molecular ion and for most of the compounds the fragment of the highest *m/z* was that from $M^+ - H_2O$. Only the eight most abundant fragments, besides M^+ and $M^+ - H_2O$, are given below. Fragments below *m/z* 55 are reported only for the non-aromatic compounds **7a–7d**. As said before, the *anti* configuration was assigned to the major isomers of compounds **7** and the *syn* configuration to the major isomers of compounds **8–10**. However, at least some of the assignments must be considered tentative and the designations major and minor are used below for the two isomers.

3,4-Dimethyl-5-hexen-3-ol (**7a**, *major isomer*). ^{1}H NMR: δ 0.92 (t, 3 H, *J* 7.5 Hz, 1-H), 1.01 (d, 3 H, *J* 7.0 Hz, 4-Me), 1.08 (s, 3 H, 3-Me), 1.52 (q, 2 H, *J* 7.5 Hz, 2-H), 2.26 (m, 1 H, *J* 8.6, 7.0 and 0.8 Hz, 4-H), 5.04–5.12 (AB part of ABX, 2 H, *J* 2.0 and 0.8 Hz, 6-H), 5.85 (X part of ABX, 1 H, *J* 8.6 Hz, 5-H). MS: 128 (0, M^+), 110 (<1), 99 (6), 74 (7), 73 (100), 57 (21), 55 (58), 53 (4), 45 (12), 43 (93).

3,4-Dimethyl-5-hexen-3-ol (**7a**, *minor isomer*). ^{1}H NMR: δ 0.91 (t, 3 H, *J* 7.5 Hz, 1-H), 1.03 (d, 3 H, *J* 7.0 Hz, 4-Me), 1.11 (s, 3 H, 3-Me), 1.46 and 1.51 (AB system split into quartets, 2 H, *J* 14.3 and 7.5 Hz, 2-H), 2.27 (m, 1 H, *J* 8.6, 7.0 and 1.1 Hz, 4-H), 5.04–5.12 (AB part of ABX, 2 H, *J* 2.0 and 1.1 Hz, 6-H), 5.80 (X part of ABX, 1 H, *J* 8.6 Hz, 5-H). MS: 128 (0, M^+), 110 (<1), 99 (8), 74 (5), 73 (100), 57 (12), 55 (31), 53 (3), 45 (5), 43 (30).

2,3,4-Trimethyl-5-hexen-3-ol (**7b**, *major isomer*). ^{1}H NMR: δ 0.91 (d, 3 H, *J* 6.9 Hz, 1-H), 0.93 (d, 3 H, *J* 6.9 Hz, 2-Me), 1.01 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.03 (s, 3 H, 3-Me), 1.78 (sept, 1 H, *J* 6.9 Hz, 2-H), 2.40 (m, 1 H, *J* 8.5, 6.9 and 0.8 Hz, 4-H), 5.02–5.12 (AB part of ABX, 2 H, *J* 2.0 and 0.8 Hz, 6-H), 5.91 (X part of ABX, 1 H, *J* 8.5 Hz, 5-H). MS: 142 (0, M^+), 124 (<1), 99 (9), 88 (4), 87 (61), 71 (7), 69 (27), 55 (9), 45 (20), 43 (100).

2,3,4-Trimethyl-5-hexen-3-ol (**7b**, *minor isomer*). ^{1}H NMR: δ 0.88 (d, 3 H, *J* 6.9 Hz, 1-H), 0.94 (d, 3 H, *J* 6.9 Hz, 2-Me), 1.02 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.02 (s, 3 H, 3-Me), 1.84 (sept, 1 H, *J* 6.9 Hz, 2-H), 2.38 (m, *J* 8.5, 6.9 and 1.0 Hz, 4-H), 5.02–5.12 (AB part of ABX, 2 H, *J* 2.0 and 1.0 Hz, 6-H), 5.84 (X part of ABX, 1 H, *J* 8.5 Hz, 5-H). MS: 142 (0, M^+), 124 (<1), 99 (10), 88 (5), 87 (73), 71 (7), 69 (29), 55 (9), 45 (21), 43 (100).

2-Cyclohexyl-3-methyl-4-penten-2-ol (**7c**, *major isomer*). ^{1}H NMR: δ 1.00 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.03 (s, 3 H, 1-H), 2.42 (m, 1 H, *J* 8.6, 6.9 and 0.6 Hz, 3-H), 4.99–5.11 (AB part of ABX, 2 H, *J* 2.1 and 0.6 Hz, 5-H), 5.90 (X part of ABX, 1 H, *J* 8.6 Hz, 4-H). MS: 182 (0, M^+), 164 (<1), 127 (53), 109 (31), 99 (22), 83 (40), 67 (23), 55 (31), 45 (28), 43 (100).

2-Cyclohexyl-3-methyl-4-penten-2-ol (**7c**, *minor isomer*). ^{1}H NMR: δ 1.01 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.03 (s, 3 H, 1-H), 2.37 (m, 1 H, *J* 8.6, 6.9 and 0.9 Hz, 3-H), 4.99–5.11 (AB part of ABX, 2 H, *J* 2.1 and 0.9 Hz, 5-H), 5.86 (X part of ABX, 1 H, *J* 8.6 Hz, 4-H). MS: 182 (0, M^+), 164 (<1), 127 (100), 109 (52), 99 (25), 83 (54), 67 (27), 55 (32), 45 (27), 43 (83).

2,2,3,4-Tetramethyl-5-hexen-3-ol (**7d**, *major isomer*). ^{1}H NMR: δ 1.00 (s, 9 H, 1-H and 2-Me), 1.08 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.09 (s, 3 H, 3-Me), 2.59 (m, 1 H, *J* 9.0, 6.9 and 0.5 Hz, 4-H), 4.90–5.10 (AB part of ABX, 2 H, *J* 2.0 and 0.5 Hz, 6-H), 5.88 (X part of ABX, 1 H, *J* 9.0 Hz, 5-H). MS: 156 (0, M^+), 138 (0), 102 (4), 101 (57), 99 (15), 83 (30), 59 (7), 57 (16), 55 (25), 43 (100).

2,2,3,4-Tetramethyl-5-hexen-3-ol (**7d**, *minor isomer*). ^{1}H NMR: δ 0.98 (s, 9 H, 1-H and 2-Me), 1.06 (d, 3 H, *J* 6.9 Hz, 4-Me), not found (s, 3 H, 3-Me), 2.61 (m, 1 H, *J* 9.0, 6.9 and 0.8 Hz, 4-H), 4.90–5.10 (AB part of ABX, 2 H, *J* 2.0 and 0.8 Hz, 6-H), 5.80 (X part of ABX, 1 H, *J* 9.0 Hz, 5-H). MS: 156 (0, M^+), 138 (0), 102 (4), 101 (55), 99 (14), 83 (30), 59 (10), 57 (16), 55 (25), 43 (100).

2-(2-Furyl)-3-methyl-4-penten-2-ol (**8a**, *major isomer*). ^{1}H NMR: δ 1.00 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.50 (s, 3 H, 1-H), 2.61 (m, 1 H, *J* 8.6, 6.9, 1.1 and 0.8 Hz, 3-H), 5.05–5.18 (AB part of ABX, 2 H, *J* 1.8, 1.1 and 0.8 Hz, 5-H), 5.69 (X part of ABX, 1 H, *J* 8.6 Hz, 4-H), 6.17 (dd, 1 H, *J* 3.3 and 0.9 Hz, 3-H-Fur), 6.31 (dd, 1 H, *J* 3.3 and 1.8 Hz, 4-H-Fur), 7.35 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 166 (<1, M^+), 148 (1), 133 (1), 112 (7), 111 (100), 95 (7), 93 (2), 77 (2), 65 (3), 55 (3).

2-(2-Furyl)-3-methyl-4-penten-2-ol (**8a**, *minor isomer*). ^{1}H NMR: δ 0.93 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.47 (s, 3 H, 1-H), 2.76 (m, 1 H, *J* 7.8, 6.9, 1.2 and 0.9 Hz, 3-H), 5.05–5.18 (AB part of ABX, 2 H, *J* 1.8, 1.2 and 0.9 Hz, 5-H), 5.83 (X part of ABX, 1 H, *J* 7.8 Hz, 4-H), 6.21 (dd, 1 H, *J* 3.3 and 0.9 Hz, 3-H-Fur), 6.31 (dd, 1 H, *J* 3.3 and 1.8 Hz, 4-H-Fur), 7.36 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 166 (<1, M^+), 148 (1), 133 (2), 112 (7), 111 (100), 95 (8), 93 (2), 77 (2), 65 (3), 55 (4).

3-(2-Furyl)-4-methyl-5-hexen-3-ol (**8b**, *major isomer*). ^{1}H NMR: δ 0.80 (t, 3 H, *J* 7.3 Hz, 1-H), 0.93 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.79 and 1.90 (AB system split into quartets, 2 H, *J* 14.0 and 7.3 Hz, 2-H), 2.56 (m, 1 H, *J* 8.9, 6.9, 0.9 and 0.6 Hz, 4-H), 5.03–5.15 (AB part of ABX, 2 H, *J* 2.0, 0.9 and 0.6 Hz, 6-H), 5.73 (X part of ABX, 1 H, *J* 8.9 Hz, 5-H), 6.19 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.32 (dd, 1 H, *J* 3.2 and 1.8 Hz, 4-H-Fur), 7.35 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 180 (<1, M^+), 162 (1), 147 (1), 133 (1), 126 (9), 125 (100), 95 (16), 83 (7), 57 (22), 55 (5).

3-(2-Furyl)-4-methyl-5-hexen-3-ol (**8b**, *minor isomer*). ^{1}H NMR: δ 0.81 (t, 3 H, *J* 7.3 Hz, 1-H), 1.01 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.77 and 1.90 (AB system split into quartets, 2 H, *J* 14.0 and 7.3 Hz, 2-H), 2.68 (m, 1 H, *J* 7.8, 6.9, 1.2 and 0.9 Hz, 4-H), 5.03–5.15 (AB part of ABX, 2 H, *J* 2.0, 1.2 and 0.9 Hz, 6-H), 5.72 (X part of ABX, 1 H, *J* 7.8 Hz, 5-H), 6.19 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.32 (dd, 1 H, *J* 3.2 and 1.8 Hz, 4-H-Fur), 7.35 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 180 (0, M^+), 162 (1), 147 (1), 133 (1), 126 (9), 125 (100), 95 (16), 83 (8), 57 (22), 55 (5).

3-(2-Furyl)-2,4-dimethyl-5-hexen-3-ol (**8c**, *major isomer*). ^{1}H NMR: δ 0.82 (d, 3 H, *J* 6.9 Hz, 1-H), 0.92 (d, 3 H, *J* 6.9 Hz, 2-Me), 0.95 (d, 3 H, *J* 6.9 Hz, 4-Me), 2.20 (sept., 1 H, *J* 6.9 Hz, 2-H), 2.75 (m, *J* 9.0, 6.9, 0.8 and 0.5 Hz, 4-H), 5.02–5.17 (AB part of ABX, 2 H, *J* 1.8, 0.8 and 0.5 Hz, 6-H), 5.64 (X part of ABX, 1 H, *J* 9.0 Hz, 5-H), 6.17 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.33 (dd, 1 H, *J* 3.2 and 1.8 Hz, 4-H-Fur), 7.35 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 194 (<1, M^+), 176 (1), 151 (8), 140 (9), 139 (100), 97 (57), 96 (5), 95 (72), 77 (4), 55 (8).

3-(2-Furyl)-2,4-dimethyl-5-hexen-3-ol (**8c**, *minor isomer*). ^{1}H NMR: δ 0.82 (d, 3 H, *J* 6.9 Hz, 1-H), 0.89 (d, 3 H, *J* 6.9 Hz, 2-Me), 1.00 (d, 3 H, *J* 6.9 Hz, 4-Me), 2.18 (sept., 1 H, *J* 6.9 Hz, 2-H), 2.91 (m, 1 H, *J* 7.5, 6.9, 1.3 and 0.9 Hz, 4-H), 5.02–5.17 (AB part of ABX, 2 H, *J* 1.8, 1.3 and 0.9 Hz, 6-H), 5.70 (X part of ABX, 1 H, *J* 7.5 Hz, 5-H), 6.19 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.33 (dd, 1 H, *J* 3.2 and 1.8 Hz, 4-H-Fur), 7.36 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 194 (<1, M^+), 176 (1), 151 (6), 140 (9), 139 (100), 97 (59), 96 (4), 95 (65), 77 (4), 55 (9).

1-(2-Furyl)-1-cyclohexyl-2-methyl-3-buten-1-ol (**8d**, *major isomer*). ^{1}H NMR: δ 0.94 (d, 3 H, *J* 6.9 Hz, 2-Me), 2.77 (m, 1 H, *J* 8.9, 6.9, 1.2 and 0.9 Hz, 2-H), 5.03–5.15 (AB part of ABX, 2 H, *J* 2.0, 1.2 and 0.9 Hz, 4-H), 5.64 (X part of ABX, 1 H, *J* 8.9 Hz, 3-H), 6.15 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.32 (dd, 1 H, *J* 3.2 and 1.9 Hz, 4-H-Fur), 7.35 (dd, 1 H, *J* 1.9 and 0.9 Hz, 5-H-Fur). MS: 234 (<1, M^+), 216 (1), 180 (13), 179 (100), 151 (9), 97 (50), 95 (52), 81 (29), 67 (8), 55 (20).

1-(2-Furyl)-1-cyclohexyl-2-methyl-3-buten-1-ol (**8d**, *minor isomer*). ^{1}H NMR: δ 0.99 (d, 3 H, *J* 6.9 Hz, 2-Me), 2.93 (m, 1 H, *J* 7.3, 6.9, 0.8 and 0.5 Hz, 2-H), 5.03–5.15 (AB part of ABX, 2 H, *J* 2.0, 0.8 and 0.5 Hz, 4-H), 5.67 (X part of ABX, 1 H, *J* 7.3 Hz, 3-H), 6.16 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.32 (dd, 1 H, *J* 3.2 and 1.9 Hz,

4-H-Fur), 7.35 (dd, 1 H, *J* 1.9 and 0.9 Hz, 5-H-Fur). MS: 234 (0, M^+), 216 (1), 180 (13), 179 (100), 151 (8), 97 (50), 95 (47), 81 (29), 67 (8), 55 (20).

3-(2-Furyl)-2,2,4-trimethyl-5-hexen-3-ol (**8e**, *major isomer*). ^{1}H NMR: δ 0.86 (d, 3 H, *J* 6.9 Hz, 4-Me), 0.99 (s, 9 H, 1-H and 2-Me), 2.93 (m, 1 H, *J* 9.5, 6.9, 0.8 and 0.3 Hz, 4-H), 4.93–5.11 (AB part of ABX, 2 H, *J* 2.0, 0.8 and 0.3 Hz, 6-H), 5.90 (X part of ABX, 1 H, *J* 9.5 Hz, 5-H), 6.19 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.32 (dd, 1 H, *J* 3.2 and 1.8 Hz, 4-H-Fur), 7.34 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 208 (1, M^+), 190 (0), 153 (23), 151 (21), 111 (17), 109 (7), 96 (6), 95 (100), 57 (21), 55 (16).

3-(2-Furyl)-2,2,4-trimethyl-5-hexen-3-ol (**8e**, *minor isomer*). ^{1}H NMR: δ 1.01 (s, 9 H, 1-H and 2-Me), 1.01 (d, 3 H, *J* 6.9 Hz, 4-Me), 2.76 (m, 1 H, *J* 8.9, 6.9, 1.0 and 0.6 Hz, 4-H), 4.93–5.11 (AB part of ABX, 2 H, *J* 2.0, 1.0 and 0.6 Hz, 6-H), 6.05 (X part of ABX, 1 H, *J* 8.9 Hz, 5-H), 6.19 (dd, 1 H, *J* 3.2 and 0.9 Hz, 3-H-Fur), 6.32 (dd, 1 H, *J* 3.2 and 1.8 Hz, 4-H-Fur), 7.35 (dd, 1 H, *J* 1.8 and 0.9 Hz, 5-H-Fur). MS: 208 (1, M^+), 190 (0), 153 (27), 151 (17), 111 (21), 109 (8), 96 (7), 95 (100), 57 (15), 55 (11).

2-(2-Thienyl)-3-methyl-4-penten-2-ol (**9a**, *major isomer*). ^{1}H NMR: δ 1.03 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.59 (s, 3 H, 1-H), 2.54 (m, 1 H, *J* 8.3, 6.9, 1.0 and 0.7 Hz, 3-H), 5.08–5.20 (AB part of ABX, 2 H, *J* 1.8, 1.0 and 0.7 Hz, 5-H), 5.75 (X part of ABX, 1 H, *J* 8.3 Hz, 4-H), 6.87 (dd, 1 H, *J* 3.6 and 1.2 Hz, 3-H-Th), 6.95 (dd, 1 H, *J* 5.1 and 3.6 Hz, 4-H-Th), 7.19 (dd, 1 H, *J* 5.1 and 1.2 Hz, 5-H-Th). MS: 182 (0, M^+), 164 (0), 133 (1), 112 (7), 111 (100), 95 (7), 93 (2), 77 (1), 65 (2), 55 (3).

2-(2-Thienyl)-3-methyl-4-penten-2-ol (**9a**, *minor isomer*). ^{1}H NMR: δ 0.99 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.57 (s, 3 H, 1-H), 2.61 (m, 1 H, *J* 7.8, 6.9, 1.2 and 0.8 Hz, 3-H), 5.08–5.20 (AB part of ABX, 2 H, *J* 1.8, 1.2 and 0.8 Hz, 5-H), 5.84 (X part of ABX, 1 H, *J* 7.8 Hz, 4-H), 6.90 (dd, 1 H, *J* 3.6 and 1.2 Hz, 3-H-Th), 6.95 (dd, 1 H, *J* 5.1 and 3.6 Hz, 4-H-Th), 7.21 (dd, 1 H, *J* 5.1 and 1.2 Hz, 5-H-Th). MS: 182 (0, M^+), 164 (0), 133 (1), 112 (8), 111 (100), 95 (7), 93 (2), 77 (2), 65 (2), 55 (5).

3-(2-Thienyl)-4-methyl-5-hexen-3-ol (**9b**, *major isomer*). ^{1}H NMR: δ 0.85 (t, 3 H, *J* 7.5 Hz, 1-H), 0.98 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.86 (q, 2 H, *J* 7.5 Hz, 2-H), 2.54 (m, 1 H, *J* 8.9, 6.9, 0.8 and 0.7 Hz, 4-H), 5.09–5.16 (AB part of ABX, 2 H, *J* 1.9, 0.8 and 0.7 Hz, H-6), 5.77 (X part of ABX, 1 H, *J* 8.9 Hz, 5-H), 6.82 (dd, 1 H, *J* 2.8 and 1.4 Hz, 3-H-Th), 6.97 (dd, 1 H, *J* 5.2 and 2.8 Hz, 4-H-Th), 7.19 (dd, 1 H, *J* 5.2 and 1.4 Hz, 5-H-Th). MS: 196 (0, M^+), 178 (1), 143 (5), 142 (9), 141 (100), 123 (3), 111 (20), 97 (3), 57 (58), 55 (5).

3-(2-Thienyl)-4-methyl-5-hexen-3-ol (**9b**, *minor isomer*). ^{1}H NMR: δ 0.85 (t, 3 H, *J* 7.5 Hz, 1-H), 1.04 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.83 and 1.91 (AB system split into quartets, 2 H, *J* 14.0 and 7.5 Hz, 2-H), 2.63 (m, 1 H, *J* 7.5, 6.9, 1.1 and 0.9 Hz, 4-H), 5.09–5.16 (AB part of ABX, 2 H, *J* 1.9, 1.1 and 0.9 Hz, H-6), 5.78 (X part of ABX, 1 H, *J* 7.5 Hz, 5-H), 6.83 (dd, 1 H, *J* 2.8 and 1.4 Hz, 3-H-Th), 6.96 (dd, 1 H, *J* 5.2 and 2.8 Hz, 4-H-Th), 7.19 (dd, 1 H, *J* 5.2 and 1.4 Hz, 5-H-Th). MS: 196 (0, M^+), 178 (1), 143 (5), 142 (9), 141 (100), 123 (3), 111 (18), 97 (3), 57 (57), 55 (5).

3-(2-Thienyl)-2,4-dimethyl-5-hexen-3-ol (**9c**, *major isomer*). ^{1}H NMR: δ 0.86 (d, 3 H, *J* 6.8 Hz, 1-H), 0.93 (d, 3 H, *J* 6.6 Hz, 2-Me), 1.00 (d, 3 H, *J* 6.8 Hz, 4-Me), 2.15 (sept, 1 H, *J* 6.7 Hz, 2-H), 2.72 (m, 1 H, *J* 8.8, 6.8, 0.7 and 0.5 Hz, 4-H), 5.09–5.18 (AB part of ABX, 2 H, *J* 1.9, 0.7 and 0.5 Hz, 6-H), 5.66 (X part of ABX, 1 H, *J* 8.8 Hz, 5-H), 6.81 (dd, 1 H, *J* 3.6 and 1.2 Hz, 3-H-Th), 6.99 (dd, 1 H, *J* 5.1 and 3.6 Hz, 4-H-Th), 7.19 (dd, 1 H, *J* 5.1 and 1.2 Hz, 5-H-Th). MS: 210 (<1, M^+), 192 (1), 167 (7), 156 (10), 155 (100), 113 (56), 111 (80), 97 (5), 85 (9), 55 (8).

3-(2-Thienyl)-2,4-dimethyl-5-hexen-3-ol (**9c**, *minor isomer*). ^{1}H NMR: δ 0.87 (d, 3 H, *J* 6.8 Hz, 1-H), 0.90 (d, 3 H, *J* 6.6 Hz, 2-Me), 1.03 (d, 3 H, *J* 6.8 Hz, 4-Me), 2.18 (sept, 1 H, *J* 6.7 Hz, 2-H), 2.86 (m, 1 H, *J* 6.9, 6.8, 0.8 and 0.6 Hz, 4-H), 5.09–5.18 (AB part of ABX, 2 H, *J* 1.9, 0.8 and 0.6 Hz, 6-H), 5.78 (X part of ABX, 1 H, *J* 6.9 Hz, 5-H), 6.83 (dd, 1 H, *J* 3.6 and 1.2 Hz, 3-H-Th), 6.98 (dd, 1 H, *J* 5.1 and 3.6 Hz, 4-H-Th), 7.19 (dd, 1 H, *J* 5.1 and 1.2 Hz, 5-H-Th). MS: 210 (<1, M^+), 192 (1), 167 (5), 156 (10), 155 (100), 113 (55), 111 (70), 97 (5), 85 (9), 55 (8).

1-(2-Thienyl)-1-cyclohexyl-2-methyl-3-buten-1-ol (**9d**, *major isomer*). ^{1}H NMR: δ 0.99 (d, 3 H, *J* 6.9 Hz, 2-Me), 2.75 (m, 1 H, *J* 8.7, 6.9 and 0.8 Hz, 2-H), 5.08–5.17 (AB part of ABX, 2 H, *J* 1.8 and 0.8 Hz, 4-H), 5.66 (X part of ABX, 1 H, *J* 8.7 Hz, 3-H), 6.80 (dd, 1 H, *J* 3.5 and 1.1 Hz, 3-H-Th), 6.99 (dd, 1 H, *J* 5.0 and 3.5 Hz, 4-H-Th), 7.18 (dd, 1 H, *J* 5.0 and 1.1 Hz, 5-H-Th). MS: 250 (0, M^+), 232 (1), 196 (14), 195 (100), 167 (9), 113 (36), 111 (59), 97 (27), 85 (9), 55 (19).

1-(2-Thienyl)-1-cyclohexyl-2-methyl-3-buten-1-ol (**9d**, *minor isomer*). ^{1}H NMR: δ 1.03 (d, 3 H, *J* 6.9 Hz, 2-Me), 2.89 (m, 1 H, *J* 6.7, 6.9 and 1.7 Hz, 2-H), 5.08–5.17 (AB part of ABX, 2 H, *J* 1.8 and 1.7 Hz, 4-H), 5.76 (X part of ABX, 1 H, *J* 6.7 Hz, 3-H), 6.81 (dd, 1 H, *J* 3.5 and 1.1 Hz, 3-H-Th), 6.98 (dd, 1 H, *J* 5.0 and 3.5 Hz, 4-H-Th), 7.18 (dd, 1 H, *J* 5.0 and 1.1 Hz, 5-H-Th). MS: 250 (0, M^+), 232 (1), 196 (14), 195 (100), 167 (8), 113 (38), 111 (58), 97 (27), 85 (9), 55 (18).

3-(2-Thienyl)-2,2,4-trimethyl-5-hexen-3-ol (**9e**, *major isomer*). ^{1}H NMR: δ 0.93 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.03 (s, 9 H, 1-H and 2-Me), 2.88 (m, 1 H, *J* 9.5, 6.9, 0.8 and 0.3 Hz, 4-H), 5.02–5.14 (AB part of ABX, 2 H, *J* 1.8, 0.8 and 0.3 Hz, 6-H), 5.90 (X part of ABX, 1 H, *J* 9.5 Hz, 5-H), 6.89 (dd, 1 H, *J* 3.5 and 1.2 Hz, 3-H-Th), 6.97 (dd, 1 H, *J* 5.0 and 3.5 Hz, 4-H-Th), 7.17 (dd, 1 H, *J* 5.0 and 1.3 Hz, 5-H-Th). MS: 224 (<1, M^+), 206 (<1), 169 (20), 167 (18), 127 (22), 113 (5), 111 (100), 85 (8), 57 (13), 55 (9).

3-(2-Thienyl)-2,2,4-trimethyl-5-hexen-3-ol (**9e**, *minor isomer*). ^{1}H NMR: δ 1.07 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.05 (s, 9 H, 1-H and 2-Me), 2.94 (m, 1 H, *J* 7.8, 6.9 and 0.8 Hz, 4-H), 5.02–5.14 (AB part of ABX, 2 H, *J* 1.8 and 0.8 Hz, 6-H), 5.88 (X part of ABX, 1 H, *J* 7.8 Hz, 5-H), 6.89 (dd, 1 H, *J* 3.5 and 1.2 Hz, 3-H-Th), 6.97 (dd, 1 H, *J* 5.0 and 3.5 Hz, 4-H-Th), 7.17 (dd, 1 H, *J* 5.0 and 1.2 Hz, 5-H-Th). MS: 224 (<1, M^+), 206 (<1), 169 (23), 167 (15), 127 (26), 113 (5), 111 (100), 85 (10), 57 (15), 55 (9).

2-Phenyl-3-methyl-4-penten-2-ol (**10a**, *major isomer*). ^{1}H NMR: δ 0.87 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.54 (s, 3 H, 1-H), 2.55 (m, 1 H, *J* 8.2, 6.9, 0.9 and 0.6 Hz, 3-H), 5 08–5.14 (AB part of ABX, 2 H, *J* 1.8, 0.9 and 0.6 Hz, 5-H), 5.83 (X part of ABX, 1 H, *J* 8.2 Hz, 4-H). MS: 176 (0, M^+), 158 (1), 140 (17), 127 (8), 122 (17), 121 (100), 115 (2), 105 (19), 91 (6), 77 (29).

2-Phenyl-3-methyl-4-penten-2-ol (**10a**, *minor isomer*). ^{1}H NMR: δ 0.97 (d, 3 H, *J* 6.9 Hz, 3-Me), 1.54 (s, 3 H, 1-H), 2.61 (m, 1 H, *J* 7.5, 6.9, 1.1 and 0.8 Hz, 3-H), 5.08–5.14 (AB part of ABX, 2 H, *J* 1.8, 1.1 and 0.8 Hz, 5-H), 5.72 (X part of ABX, 1 H, *J* 7.5 Hz, 4-H). MS: 176 (0, M^+), 158 (1), 140 (18), 127 (8), 122 (35), 121 (100), 115 (5), 105 (36), 91 (10), 77 (53).

3-Phenyl-4-methyl-5-hexen-3-ol (**10b**, *major isomer*). ^{1}H NMR: δ 0.68 (t, 3 H, *J* 7.5 Hz, 1-H), 0.81 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.86 and 1.89 (AB system split into quartets, 2 H, *J* 14.1 and 7.5 Hz, 2-H), 2.57 (m, 1 H, *J* 8.6, 6.9, 0.9 and 0.6 Hz, 4-H), 5.01–5.16 (AB part of ABX, 2 H, *J* 2.0, 0.9 and 0.6 Hz, 6-H), 5.85 (X part of ABX, 1 H, *J* 8.6 Hz, 5-H). MS: 190 (0, M^+), 172 (<1), 136 (25), 135 (100), 117 (10), 115 (8), 105 (59), 91 (13), 77 (48), 57 (99).

3-Phenyl-4-methyl-5-hexen-3-ol (**10b**, *minor isomer*). ^{1}H NMR: δ 0.73 (t, 3 H, *J* 7.5 Hz, 1-H), 1.02 (d, 3 H, *J* 6.9 Hz, 4-Me), 1.84 and 1.96 (AB system split into quartets, 2 H, *J* 14.1 and 7.5 Hz, 2-H), 2.65 (m, 1 H, *J* 7.3, 6.9, 1.4 and 0.9 Hz, 4-H), 5.01–5.16 (AB part of ABX, 2 H, *J* 2.0, 1.4 and 0.9 Hz, 6-H), 5.63 (X part of ABX, 1 H, *J* 7.3 Hz, 5-H). MS: 190 (0, M^+), 172 (1), 136 (45), 135 (100), 117 (18), 115 (13), 105 (94), 91 (23), 77 (76), 57 (99).

3-Phenyl-2,4-dimethyl-5-hexen-3-ol (**10c**, *major isomer*). ^{1}H NMR: δ 0.78 (d, 3 H, *J* 6.9 Hz, 1-H), 0.86 (d, 3 H, *J* 6.7 Hz, 2-Me), 0.89 (d, 3 H, *J* 6.8 Hz, 4-Me), 2.24 (sept., 1 H, *J* 6.8 Hz, 2-H), 2.87 (m, 1 H, *J* 8.7, 6.8, 0.9 and 0.5 Hz, 4-H), 5.03–5.18 (AB part of ABX, 2 H, *J* 2.0, 0.9 and 0.5 Hz, 6-H), 5.65 (X part of ABX, 1 H, *J* 8.7 Hz, 5-H). MS: 204 (0, M^+), 186 (<1), 161 (12), 150 (11), 149 (100), 131 (8), 105 (95), 91 (9), 77 (24), 71 (19).

3-Phenyl-2,4-dimethyl-5-hexen-3-ol (**10c**, *minor isomer*). ^{1}H NMR: δ 0.78 (d, 3 H, *J* 6.9 Hz, 1-H), 0.86 (d, 3 H, *J* 6.7 Hz, 2-Me), 0.98 (d, 3 H, *J* 6.8 Hz, 4-Me), 2.25 (sept., 1 H, *J* 6.8 Hz, 2-H), 2.98 (m, 1 H, *J* 6.9, 6.9, 1.5 and 1.3 Hz, 4-H), 5.03–5.18 (AB part of ABX, 2 H, *J* 2.0, 1.5 and 1.3 Hz, 6-H), 5.65 (X part of ABX, 1 H, *J* 6.9 Hz, 5-H). MS: 204 (0, M^+), 186 (<1), 161 (10), 150 (12), 149 (100), 131 (8), 105 (81), 91 (9), 77 (25), 71 (21).

1-Phenyl-1-cyclohexyl-2-methyl-3-buten-1-ol (**10d**, *major isomer*). ^{1}H NMR: δ 0.87 (d, 3 H, *J* 6.8 Hz, 2-Me), 2.92 (m, 1 H, *J* 8.7, 6.8, 0.9 and 0.5 Hz, 2-H), 5.02–5.17 (AB part of ABX, 2 H, *J* 2.0, 0.9 and 0.5 Hz, 4-H), 5.70 (X part of ABX, 1 H, *J* 8.7 Hz, 3-H). MS: 244 (0, M^+), 226 (<1), 190 (13), 189 (84), 161 (22), 107 (58), 105 (100), 91 (21), 77 (20), 55 (16).

1-Phenyl-1-cyclohexyl-2-methyl-3-buten-1-ol (**10d**, *minor isomer*). ^{1}H NMR: δ 1.00 (d, 3 H, *J* 6.8 Hz, 2-Me), 3.04 (m, 1 H, *J* 6.8, 6.6, 1.7 and 1.2 Hz, 2-H), 5.02–5.17 (AB part of ABX, 2 H, *J* 2.0, 1.7 and 1.2 Hz, 4-H), 5.63 (X part of ABX, 1 H, *J* 6.6 Hz, 3-H). MS: 244 (0, M^+), 226 (<1), 190 (14), 189 (94), 161 (20), 107 (76), 105 (100), 91 (27), 77 (22), 55 (20).

3-Phenyl-2,2,4-trimethyl-5-hexen-3-ol (**10e**, *major isomer*). ^{1}H NMR: δ 0.72 (d, 3 H, *J* 6.9 Hz, 4-Me), 0.93 (s, 9 H, 1-H and 2-Me), 3.15 (m, 1 H, *J* 9.2, 6.9 and 0.8 Hz, 4-H), 4.94–5.15 (AB part of ABX, 2 H, *J* 1.8 and 0.8 Hz, 6-H), 6.16 (X part of ABX, 1 H, *J* 9.2 Hz, 5-H). MS: 218 (0, M^+), 200 (0), 164 (3), 163 (18), 161 (10), 106 (8), 105 (100), 85 (19), 77 (22), 57 (42).

3-Phenyl-2,2,4-trimethyl-5-hexen-3-ol (**10e**, *minor isomer*). ^{1}H NMR: δ 0.98 (s, 9 H, 1-H and 2-Me), 1.21 (d, 3 H, *J* 6.9 Hz, 4-Me), 3.20 (m, 1 H, *J* 6.9, 6.7, 1.5 and 1.1 Hz, 4-H), 4.94–5.15 (AB part of ABX, 2 H, *J* 1.8, 1.5 and 1.1 Hz, 6-H), 5.66 (X part of ABX, 1 H, *J* 6.7 Hz, 5-H). MS: 218 (0, M^+), 200 (0), 164 (9), 163 (75), 161 (64), 106 (7), 105 (100), 85 (15), 77 (15), 57 (22).

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