Ultrasound-Mediated Synthesis and Mass Spectrometric Fragmentation of Dimethyl-Substituted 1,2-Diphenylethanols, Convenient Dimethylstilbene Precursors

Ivan C. Burkow, Leiv K. Sydnes* and Danielle C. N. Ubeda

Department of Chemistry, University of Tromsø, P.O. Box 953, N-9001 Tromsø, Norway

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1,2-Diarylethanols were obtained in high yields by ultrasonic irradiation of mixtures of lithium sand, benzylic chlorides, and arenecarbaldehydes or aryl methyl ketones. The mass spectra of the alcohols contained dominant peaks for species formed by dehydration, α-cleavage processes and rearrangement involving hydrogen transfer. Acid-catalyzed dehydration of the alcohols gave the corresponding stilbenes in quantitative yields.

In order to obtain dimethylated phenanthrenes for geochemical purposes[1,2] we needed relatively large amounts of dimethyl-substituted stilbenes; the latter furnish the tricyclic aromatic hydrocarbons in good to excellent yields when photolyzed in the presence of iodine and oxygen.[3–5] Stilbenes can be prepared by a number of synthetic routes.[6–13] A most attractive method from a practical point of view affords such olefins by magnesium-mediated condensation of a benzylic halide with an arenecarbaldehyde or a methyl aryl ketone, followed by acid-catalyzed dehydration of the resulting 1,2-diarylethanol. However, whereas the dehydration in most cases proceeds smoothly,[14–16] the Grignard reaction is generally hampered by side reactions such as enolization, condensation, and Wurtz coupling.[17] When the carbonyl compound is an aldehyde, substantial amounts of the starting material may also be lost due to formation of diol from two molecules of aldehyde and one molecule of Grignard reagent.[18,19] As a result, the simplest method often gives stilbenes in mediocre yields.

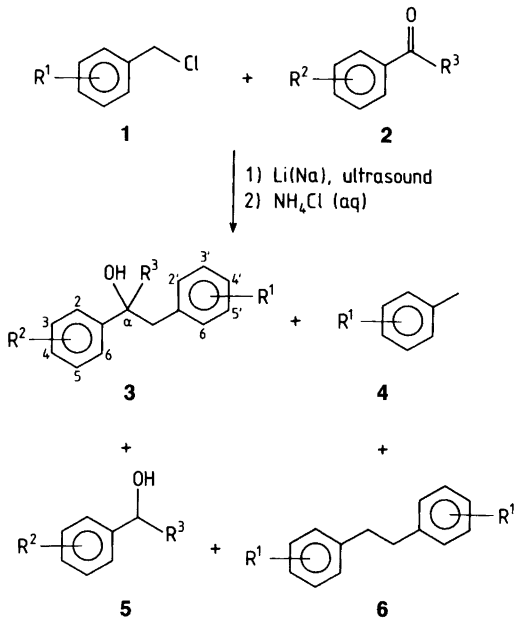
To improve the yield of stilbene using this method, the condensation step has to be made more efficient. A number of modifications have been tried, but they appeared to be useless in reactions involving benzylic halides.[20,21] However, in recent years several reports have shown that heterogeneous reactions can be facilitated dramatically by employing ultrasonic irradiation during the reaction.[22–26] This also seemed to be the case with the Barbier reaction involving benzylic halides when lithium is used instead of magnesium.[27] We therefore adopted this method for the synthesis of 1,2-diarylethanols, which were obtained in good to excellent yields under optimum conditions.

Most of the 1,2-diarylethanols synthesized were new compounds and they were consequently thoroughly characterized by physical methods. Interestingly, the mass spectra showed several systematic and significant features, and a mass fragmentation study of the alcohols was therefore also carried out.

Results and discussion

Synthesis. In order to find the best starting point for the ultrasound experiments, a number of exploratory condensation reactions were carried out employing traditional stirring, lithium in different forms, and a variety of benzylic halides (**1**) and carbonyl compounds (**2**). Two conclusions emerged from these experiments: Firstly, the yield of 1,2-diarylethanol (**3**) was generally

*To whom correspondence should be addressed.



Scheme 1.

higher, in some cases by as much as 15 %, when benzylic chlorides were used instead of the corresponding bromides and secondly, the reaction was considerably more efficient when lithium sand containing 2 % sodium was used in place of Li wire of varying purity. Typically, alcohol **3** from 4-methylbenzaldehyde and 2-methylbenzyl chloride was formed in 61 % yield when lithium sand with 2 % Na was used (Table 1, entry 1) but in <10 % yield when Li wire was employed. We therefore decided to use benzylic chlorides and lithium sand in all the ultrasound experiments.

The ultrasound-mediated reactions were carried out using a flask immersed in the water bath of an ultrasound laboratory cleaner (120 W, 35 kHz), The flask contained Li sand and a solution which was 0.5–0.7 M in both **1** and **2**. The progress of the reaction was monitored by GLC. To find the optimum conditions for alcohol formation a large number of experiments were performed, varying the reaction parameters which are known to influence Barbier- and Grignard-type reactions. The results obtained with 2-methylbenzyl chloride and 4-methylbenzaldehyde (Table 1) are representative. They clearly show that the best results are obtained when the reagents in the theoretical molar ratio are exposed to ultrasound irradiation in diethyl ether at 0 °C. When lithium was used in considerable excess, as advised by Luche and Damiano,[27] the yield of 1,2-diarylethanol (**3**) did not increase.

The reactions of a number of benzylic chlorides with a variety of methyl-substituted benzaldehydes were subsequently performed under the optimum conditions outlined above. The corresponding 1,2-diarylethanols were formed efficiently and were isolated pure by chromatography in better than 70 % yield (Table 2).

The synthesis of the dimethyl-substituted stilbenes was completed by azeotropic dehydration of the alcohols in refluxing benzene containing some *p*-toluenesulfonic acid. The reaction proceeded smoothly and gave the corresponding stilbenes (**7**) in quantitative yields. All the stilbenes were formed as mixtures of *Z* and *E* isomers

Table 1. The amounts of the main products from Barbier condensation of 2-methylbenzyl chloride (**1**-2′) with 4-methylbenzaldehyde (**2**-4) under various reaction conditions.[a]

Entry	Mixing mode	Temp./°C	Solvent	Molar ratio	Product distribution/%[b]					Other prods.
				Li : **1**–2′ : **2**–4	**2**–4	**3**–4,2′	**4**[c]	**5**[c]	**6**[c]	
1	Stirring	30	THF	2.0 : 1.0 : 0.85	4	61	3	4	26	2
2	Ultrasound	30	THF	2.0 : 1.0 : 1.0	1	67	4	6	15	7
3	Ultrasound	0	THF	2.0 : 1.0 : 1.0	0	77	6	7	9	1
4	Ultrasound	0	THF	2.0 : 1.0 : 0.70	0	67	3	4	24	2
5	Ultrasound	0	Ether[d]	2.0 : 1.0 : 0.85	2	81	4	1	8	4
6	Ultrasound	0	Ether[d]	2.0 : 1.0 : 1.0	1	92	3	1	1	2
7	Stirring	0	Ether[d]	2.0 : 1.0 : 1.0	6	79	4	2	6	3

[a]The reactions were run until **1**–2′ was consumed (45 min). [b]In percentage of the crude reaction mixture as determined by gas chromatography. [c]See Scheme 1. [d]Diethyl ether.

Table 2. Preparation of diarylalkanols **3** by ultrasound-promoted Barbier reaction.

Notation[a]	Subst. (position)[a]		R^3	Isolated yield/%	m.p./°C
	R^1	R^2			
3-2,2′	Me (2′)	Me (2)	H	71	53
3-2,3′	Me (3′)	Me (2)	H	74	59
3-2,4′	Me (4′)	Me (2)	H	76	76
3-3,2′	Me (2′)	Me (3)	H	70	[b]
3-3,3′	Me (3′)	Me (3)	H	72	[b]
3-3,4′	Me (4′)	Me (3)	H	73	[b]
3-4,2′	Me (2′)	Me (4)	H	75	51
3-4,3′	Me (3′)	Me (4)	H	70	[b]
3-4,4′	Me (4′)	Me (4)	H	76	77
3-α,2	H	Me (2)	Me	75	47
3-α,3	H	Me (3)	Me	76	[b]
3-α,4	H	Me (4)	Me	72	[b]
3-α,2′	Me (2′)	H	Me	72	[b]
3-α,3′	Me (3′)	H	Me	71	[b]
3-α,4′	Me (4′)	H	Me	74	57

[a]In the notation **3**-*x*, *y*, *x* and *y* denote the positions of the methyl groups. For the numbering of *x* and *y*, see Scheme 1. [b]The compound was an oil.

(Table 3). Due to steric interactions, the *E* isomers are less predominant when the olefinic bond is trisubstituted, i.e. when there is a methyl group attached to C−α, than when it is disubstituted.

Mass spectral studies. The electron-impact (EI) mass spectra of **3** contain a number of dominant peaks. From MS studies employing *B*/*E* and B^2/E linked scan and deuterium labelling it became apparent that the corresponding peaks in all the spectra are due to fragments resulting from the same processes (Table 4). The fragmentation processes are, therefore, discussed mainly for one compound, viz. 1,2-bis(4-methylphenyl)ethanol (**3**–4,4′).

Table 3. The isomeric composition of the stilbenes (**7**) obtained by dehydration of **3**.

Compound[a]	Isomeric composition[b]		m.p./°C
	E	*Z*	
7–2,2′	94	6	82
7–2,3′	93	7	45–47
7–2,4′	95	5	49–51
7–3,3′	97	3	54–55
7–3,4′	98	2	97
7–4,4′	98	2	181–182
7–α,2	70	30	[c]
7–α,3	84	16	47–48
7–α,4	83	17	60–60.5
7–α,2′	85	15	[c]
7–α,3′	82	18	[c]
7–α,4′	87	13	[c]

[a]For notation, see Table 2. [b]Determined by GLC measurements. [c]The compound was an oil.

The molecular ion of **3**–4,4′ (*m*/*z* 226) appeared with low intensity, and no metastable transition was observed for this ion. The primary transformations of $M^{+\cdot}$, giving rise to peaks at *m*/*z* 208, 121, 106 and 105, must therefore be very favourable. This was borne out by the mass spectrum obtained at 12 eV, which contained essentially three peaks, viz. *m*/*z* 208, 121 and 106. The peak at 208 (the base peak in the spectrum) resulted from loss of water, which is a general process for alcohols.[28] This process is particularly efficient for alcohol **3** owing to the presence of the aryl groups which facilitate the formation of dimethylstilbene radical cations (Fig. 1) and, subsequently, a number of secondary fragments *(vide infra)*. The aryl groups also render cleavage of the C_1-C_2 ethanol bond a very favourable process, since only radicals and cations that are benzylic in nature are formed;[28] thus, the mass spec-

Table 4. Selected mass spectrometric fragments of **3** ($ArCR(OH)CH_2Ar'$) in % of the base peak.

Compound	$M^{+\cdot}-H_2O$	$M^{+\cdot}-Ar'CH_2^{\cdot}$	$M^{+\cdot}-ArCOR$	$M^{+\cdot}-ArC(OH)R^{\cdot}$	$M^{+\cdot}-ArC(OH)R^{\cdot}-H_2$
3–2,2′	100	16	19	6	11
3–2,3′	100	9	13	4	10
3–2,4′	67	50	100	18	9
3–3,2′	100	46	81	17	12
3–3,3′	85	52	100	25	12
3–3,4′	100	5	8	5	9
3–4,2′	83	100	77	18	11
3–4,3′	100	24	21	10	9
3–4,4′	100	38	52	13	10
3–α,2	61	61	12	64	20
3–α,3	100	53	10	50	21
3–α,4	16	100	27	100	20
3–α,2′	67	100	57	27	43
3–α,3′	86	58	37	28	52
3–α,4′	95	53	70	43	60

trum of **3**–4,4′ contains significant peaks at *m/z* 121 and 105. Interestingly, the former peak is the more prominent [38% as compared to 13% (Table 4)] when the ionization energy is 70 eV and is the only peak due to α cleavage when the energy is 12 eV. This reflects the stabilizing capability of a hydroxy group attached to a positively charged carbon atom.

The fourth fragment resulting from a primary process appeared in the mass spectrum of **3**–4,4′ at *m/z* 106 (composition C_8H_{10}) and in the spectrum of the corresponding deuterated alochol ROD at *m/z* 107 (composition C_8H_9D). Transfer of the hydrogen atom from the hydroxy group to the benzyl group is therefore involved in the formation of this fragment. Conceivably, the transfer can take place prior to or after the ionization has occurred. In the former case, the process is a thermal retro-ene reaction which is known to take place smoothly for analogous compounds at 170 °C.[29,30] A number of experiments were therefore carried out to test the thermal stability of **3**. However, low-temperature mass-spectra of several of the alcohols were unchanged in appearance, and gas-phase thermolysis of the same compounds at temperatures as high as 350 °C resulted only in dehydration and stilbene formation. Consequently, the fragment giving rise to *m/z* 106 is formed by rearrangement of the molecular ion. Two pathways, depicted in Scheme 2, can be envisaged for this rearrangement: pathway (a) which involves a four-membered cyclic intermediate (**8**), and pathway (b) which proceeds through a six-membered cyclic transition state (**9**). Although **9**, if formed, is energetically much more favourable than **8**, pathway (b) is much

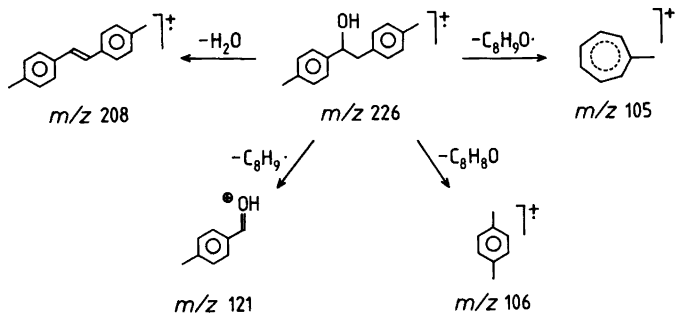
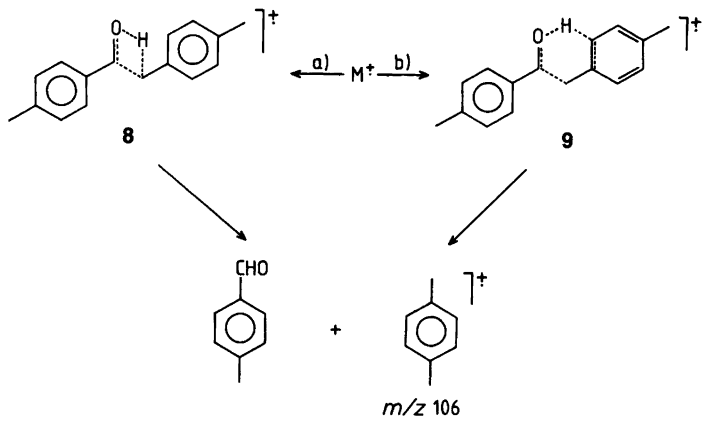


Fig. 1. Primary fragmentation of the molecular ion of **3**–4,4′.



Scheme 2.

more sensitive to steric interactions and conformational relationships than pathway (a). By analogy with alkyl-substituted benzenes containing γ-hydrogen atoms,[28,31] the rearrangement should, therefore, be much less favourable if there is a methyl group in the 2′ position and almost negligible if there are methyl groups in positions 2′ and 6′, provided pathway (b) is involved. The mass spectra of **3**–2,2′, **3**–3,2′, **3**–4,2′ and **3**–α,2′ showed intense peaks at *m/z* 106 (Table 4), and in the mass spectrum of 2-(2,6-dimethylphenyl)-1-(4-methylphenyl)ethanol, the fragment formed by expulsion of 4-methylbenzaldehyde gave rise to the base peak (*m/z* 120, see Experimental). We therefore believe that a four-centered mechanism [pathway (a), Scheme 2] is involved in the hydrogen transfer. This conclusion is supported by the cleavage reactions observed when 1,2-diarylethanols are treated with cerium (IV).[32]

m/z	Fragment ion	Metastable transitions
208	$[M-H_2O]^{+\cdot}$	
193	$[M-H_2O-CH_3\cdot]^+$	
179	$[M-H_2O-C_2H_5\cdot]^+$	
178	$[M-H_2O-CH_3\cdot-CH_3\cdot]^+$	
165	$[M-H_2O-CH_3\cdot-C_2H_4]^+$	
152	$[M-H_2O-CH_3\cdot-CH_3\cdot-C_2H_2]^{+\cdot}$	
121	$[M-C_8H_9\cdot]^+$	
119	$[M-C_8H_9\cdot-H_2]^+$	
115	$[C_9H_7]^+$	
106	$[M-C_8H_8O]^{+\cdot}$	
105	$[M-C_8H_9O\cdot]^+$	
103	$[M-C_8H_9O\cdot-H_2]^+$	
93	$[C_7H_9]^+$	
91	$[C_7H_7]^+$	
89	$[C_7H_5]^+$	
79	$[C_6H_7]^+$	
77	$[C_6H_5]^+$	

Fig. 2. The metastable fragmentation processes of **3**–4,4′.

The secondary fragmentation pattern was uncovered by B^2/E linked scan and the results are summarized in Fig. 2. All the processes observed are among those normally associated with aromatic compounds.[28,31] The most dominant fragments originate from the dehydrated molecular ions, whose structure is similar to that of the corresponding dimethylstilbene radical cations. It is, therefore, not surprising that a number of the fragmentation processes involve expulsion of methyl radicals and acetylene[33] and, furthermore, that several of the secondary fragments are among those generated by EI ionization of the stilbenes (**7**) (see Experimental). A noteworthy feature is the successive loss of two methyl radicals from the ion with *m/z* 208. When the first radical is expelled, an even-electron fragment (*m/z* 193) is formed. Subsequent loss of another methyl group yields an odd-electron fragment of *m/z* 178. This process is, therefore, a violation of the even-electron rule. However, exceptions to this rule seem to occur rather frequently among various aromatic species.[34]

The metastable transitions compiled in Fig. 2 are generally observed when **3** has one methyl group attached to each of the phenyl groups. However, when one of the methyl groups is bonded to C_α, rupture of the C_1-C_2 ethanol bond yields a protonated acetophenone derivative which is unable to undergo CO expulsion. Conse-

quently, the mass spectra of the 1,2-diaryl-2-propanols lack peaks resulting from metastable transitions corresponding to the *m/z* 121 → 93 transition in Fig. 2.

Experimental

General. IR spectra of CCl_4 solutions were recorded on a Shimadzu IR-435 spectrophotometer. ^1H NMR spectra were measured at 89.55 MHz at 33 °C on a Jeol FX9OQ FT spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in ppm downfield from TMS. EI mass spectra were obtained with a VG Micromass 7070H double-focusing spectrometer. The compounds were introduced into the ion-source either through a direct inlet system or through a Hewlett-Packard 5710 gas chromatograph equipped with a Chrompack CP Sil 8 CB fused silica capillary column (25 m, ID 0.32 mm). Helium was used as carrier gas. The ion-source temperature was generally 220 °C, but low-temperature spectra were recorded at 150 °C. The ionization energy was 70 eV unless stated otherwise. The mass spectra are reported as *m/z* (relative intensity); the most intense peak with *m/z* above 70 is set to 100 %. Metastable transitions were identified by *B/E* and B^2/E linked scan using a VG linked-scan unit. Deuterium labelling of hydroxy groups was carried out by repeated introduction of D_2O into the inlet system before introducing the alcohols. HRGC analysis was performed on a Carlo Erba Fractovap 4160 instrument equipped with FID and the capillary column mentioned above. Helium was used as carrier gas. Integration was carried out with an LDC 301 computing integrator. The ultrasound experiments were performed in a Bandelin Sonorex RK 102 laboratory cleaner. Gravity-flow circular thin-layer chromatography (GFC/TLC) was performed using a Harrison Research Chromatotron model 7924T with a Fluid Metering RP-G150 laboratory pump. The rotor was coated with a 2 mm layer of silica gel PF 254 with $CaSO_4 \cdot 0.5\ H_2O$ (Merck). Melting points are uncorrected and were determined using an Electrothermal melting point apparatus.

Chemicals. 2,6-Dimethylbenzyl chloride[35] was synthesized in 55 % yield by heating a 10 % solution of 2,6-dimethylbenzyl alcohol[36] in $SOCl_2$ under reflux for 2 h; b.p. 95–96 °C/3 mmHg (lit.[37] 65 °C/0.8 mmHg). All other chemicals were purchased from Fluka.

Condensation of **1** *and* **2** *under ultrasound irradiation; general procedure.* Lithium sand containing 2 % sodium (0.28 g, 0.040 mol) was mixed under nitrogen with a solution containing **1** (0.020 mol), **2** (0.020 mol) and dry diethyl ether (60 ml) in a flask which was immersed in a mixture of ice and water in an ultrasound bath. The mixture was irradiated with ultrasound for 30 min. During the irradiation, ice was added to keep the bath temperature at 0 °C. The reaction mixture was filtered and poured into cold saturated ammonium chloride solution (100 ml). The product was extracted with ether (2 × 50 ml) and the combined extracts were dried ($MgSO_4$). Removal of the drying agent and evaporation of the solvent left a residue from which alcohol **3** was isolated by gravity-flow circular TLC using ethyl acetate and hexane as eluents. If **3** crystallized it was recrystallized from hexane.

Fifteen dimethylated diarylethanols were synthesized according to the general procedure. The yields and melting points are compiled in Table 2.

1,2-Bis(2-methylphenyl)ethanol (**3**–2,2′), from 2-methylbenzyl chloride and 2-methylbenzaldehyde.[38]

1-(2-Methylphenyl)-2-(3-methylphenyl)ethanol (**3**–2,3′), from 3-methylbenzyl chloride and 2-methylbenzaldehyde. IR: 3640, 3600–3200, 1120 cm^{-1}; ^1H NMR: δ 2.02 (br s, 1H, OH), 2.28 (s, 3H), 2.32 (s, 3H), 2.84–2.92 (m, 2H), 5.01–5.15 (m, 1H), 7.04–7.56 (m, 8H); MS: 226 (<1, M^+), 208 (100), 193 (83), 179 (16), 178 (72), 165 (12), 152 (5), 121 (9), 119 (6), 117 (6), 116 (29), 115 (32), 106 (13), 105 (4), 103 (10), 93 (6), 92 (2), 91 (21), 89 (16), 77 (9); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.135.

1-(2-Methylphenyl)-2-(4-methylphenyl)ethanol (**3**–2,4′), from 4-methylbenzyl chloride and 2-methylbenzaldehyde. IR: 3630, 3600–3200, 1110 cm^{-1}; ^1H NMR: δ 1.91 (br s, 1H, OH), 2.27 (s, 3H), 2.31 (s, 3H), 2.84–2.94 (m, 2H), 4.98–5.13 (m, 1H), 7.02–7.54 (m, 8H); MS: 226 (<1, M^+), 208 (67), 193 (54), 179 (10), 178 (51), 165 (8), 152 (4), 121 (50), 119 (5), 117 (5), 116 (19), 115 (22), 106 (100), 105 (18), 103 (9), 93 (37), 92

(5), 91 (47), 89 (12), 77 (25); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.135.

1-(3-Methylphenyl)-2-(2-methylphenyl)ethanol (**3**–3,2′), from 2-methylbenzyl chloride and 3-methylbenzaldehyde. IR: 3630, 3600–3200, 1090 cm^{-1}; ^1H NMR: δ 2.02 (br s, 1H, OH), 2.24 (s, 3H), 2.27 (s, 3H), 2.96 (br d, 2H, *J* 6.7 Hz), 4.78 (br t, 1H, *J* 6.7 Hz), 7.00–7.21 (m, 8H); MS: 226 (<1, M^+), 208 (100), 193 (82), 179 (16), 178 (71), 165 (12), 152 (5), 121 (46), 119 (7), 117 (6), 116 (29), 115 (33), 106 (81), 105 (17), 103 (12), 93 (39), 92 (5), 91 (46), 89 (16), 77 (25); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.136.

1,2-Bis(3-methylphenyl)ethanol (**3**–3,3′), from 3-methylbenzyl chloride and 3-methylbenzaldehyde.[38]

1-(3-Methylphenyl)-2-(4-methylphenyl)ethanol (**3**–3,4′), from 4-methylbenzyl chloride and 3-methylbenzaldehyde. IR: 3620, 3600–3200, 1110 cm^{-1}; ^1H NMR: δ 2.01 (br s, 1H, OH), 2.31 (s, 3H), 2.33 (s, 3H), 2.87–2.96 (m, 2H), 4.71–4.86 (m, 1H), 7.04–7.26 (m, 8H); MS: 226 (<1, M^+), 208 (100), 193 (81), 179 (17), 178 (81), 165 (14), 152 (7), 121 (5), 119 (11), 116 (6), 115 (22), 106 (8), 105 (5), 103 (9), 93 (5), 92 (4), 91 (21), 89 (15), 77 (10); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.136.

1-(4-Methylphenyl)-2-(2-methylphenyl)ethanol (**3**–4,2′), from 2-methylbenzyl chloride and 4-methylbenzaldehyde. IR: 3630, 3600–3200, 1105 cm^{-1}; ^1H NMR: δ 1.99 (br s, 1H, OH), 2.28 (s, 3H), 2.35 (s, 3H), 3.00 (br d, 2H, *J* 6.6 Hz), 4.83 (br t, 1H, *J* 6.6 Hz), 7.08–7.29 (m, 8H); MS: 226 (<1, M^+), 208 (83), 193 (65), 179 (13), 178 (60), 165 (9), 152 (5), 121 (100), 119 (6), 117 (6), 116 (23), 115 (26), 106 (77), 105 (18), 103 (11), 93 (44), 92 (5), 91 (49), 89 (14), 77 (29); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.136.

1-(4-Methylphenyl)-2-(3-methylphenyl)ethanol (**3**–4,3′), from 3-methylbenzyl chloride and 4-methylbenzaldehyde. IR: 3625, 3600–3200, 1095 cm^{-1}; ^1H NMR: δ 2.02 (br s, 1H, OH), 2.31 (s, 3H), 2.33 (s, 3H), 2.86–2.95 (m, 2H), 4.71–4.86 (m, 1H), 7.01–7.28 (m, 8H); MS: 226 (<1, M^+), 208 (100), 193 (79), 179 (13), 178 (68), 165 (10), 152 (5), 121 (24), 119 (4), 116 (4), 115 (15), 106 (21), 105 (10), 103 (9), 93 (11), 91 (19), 89 (14), 77 (11); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.133.

1,2-Bis(4-methylphenyl)ethanol (**3**–4,4′), from 4-methylbenzyl chloride and 4-methylbenzaldehyde.[38]

2-(2-Methylphenyl)-1-phenyl-2-propanol (**3**–α,2), from benzyl chloride and 2-methylacetophenone. IR: 3610, 3600–3200, 1155 cm^{-1}; ^1H NMR: δ 1.58 (s, 3H), 1.84 (s, 1H, OH), 2.60 (s, 3H), 3.07 (d, 1H, *J* 13.3 Hz), 3.22 (d, 1H, *J* 13.3 Hz), 6.97–7.34 (m, 9H); MS: 226 (<1, M^+), 208 (61), 193 (96), 179 (17), 178 (48), 165 (9), 152 (4), 135 (61), 130 (9), 119 (7), 117 (100), 116 (43), 115 (93), 105 (3), 103 (8), 92 (12), 91 (64), 89 (20), 77 (11); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.134.

2-(3-Methylphenyl)-1-phenyl-2-propanol (**3**–α,3), from benzyl chloride and 3-methylacetophenone. IR: 3620, 3600–3200, 1155 cm^{-1}; ^1H NMR: δ 1.51 (s, 3H), 1.88 (s, 1H, OH), 2.33 (s, 3H), 2.99 (d, 1H, *J* 13.2 Hz), 3.09 (d, 1H, *J* 13.2 Hz), 6.93–7.23 (m, 9H); MS: 226 (<1, M^+), 208 (100), 193 (95), 179 (13), 178 (51), 165 (12), 152 (5), 135 (53), 119 (6), 117 (78), 116 (68), 115 (74), 105 (4), 103 (9), 92 (10), 91 (50), 89 (21), 77 (10); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.137.

2-(4-Methylphenyl)-1-phenyl-2-propanol (**3**–α,4), from benzyl chloride and 4-methylacetophenone. IR: 3605, 3600–3200, 1165 cm^{-1}; ^1H NMR: δ 1.51 (s. 3H), 1.85 (s, 1H, OH), 2.32 (s, 3H), 2.99 (d, 1H, *J* 13.2 Hz), 3.09 (d, 1H, *J* 13.2 Hz), 7.06–7.62 (m, 9H); MS: 226 (<1, M^+), 208 (16), 193 (12), 179 (3), 178 (9), 165 (6), 152 (3), 135 (100), 119 (34), 117 (23), 116 (12), 115 (24), 105 (9), 103 (4), 93 (4), 92 (27), 91 (100), 89 (20), 77 (20); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.138.

1-(2-Methylphenyl)-2-phenyl-2-propanol (**3**–α,2′), from 2-methylbenzyl chloride and acetophenone. IR: 3605, 3600–3200, 1170 cm^{-1}; ^1H NMR: δ 1.55 (s, 3H), 1.91 (s, 1H, OH), 2.12 (s, 3H), 3.06 (br s, 2H), 6.93–7.37 (m, 9H); MS: 226 (<1, M^+), 208 (67), 193 (65), 179 (24), 178 (34), 165 (10), 152 (4), 130 (15), 121 (100), 117 (5), 116 (6), 115 (33), 106 (57), 105 (27), 103 (43), 92 (3), 91 (30),

89 (10), 77 (38); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.136.

1-(3-Methylphenyl)-2-phenyl-2-propanol (**3**–α,3′), from 3-methylbenzyl chloride and acetophenone. IR: 3600, 3600–3200, 1170 cm^{-1}; ^1H NMR: δ 1.53 (s, 3H), 1.85 (s, 1H, OH), 2.25 (s, 3H), 2.97 (d, 1H, *J* 13.5 Hz), 3.06 (d, 1H, *J* 13.5 Hz), 6.81–7.61 (m, 9H); MS: 226 (<1, M^+), 208 (86), 193 (100), 179 (18), 178 (50), 165 (13), 152 (6), 130 (23), 121 (58), 117 (4), 116 (7), 115 (44), 106 (37), 105 (28), 103 (52), 92 (3), 91 (28), 89 (12), 77 (42); mol. weight: calcd. for $C_{16}H_{18}O$ 226.136, found 226.136.

1-(4-Methylphenyl)-2-phenyl-2-propanol (**3**–α,4′) from 4-methylbenzyl chloride and acetophenone. IR: 3595, 3600–3200, 1170 cm^{-1}; ^1H NMR: δ 1.54 (s, 3H), 1.96 (s, 1H, OH), 2.28 (s, 3H), 2.98 (d, 1H, *J* 11.9 Hz), 3.08 (d, 1H, *J* 11.9 Hz), 6.81–7.47 (m, 9H); MS: 226 (<1, M^+), 208 (95), 193 (100), 179 (14), 178 (45), 165 (10), 152 (4), 130 (19), 121 (53), 117 (4), 116 (7), 115 (41), 106 (70), 105 (43), 103 (60), 92 (3), 91 (29), 89 (13), 77 (41); mol. weight; calcd. for $C_{16}H_{18}O$ 226.136, found 226.137.

2-(2,6-Dimethylphenyl)-1-(4-methylphenyl)ethanol was synthesized according to the general procedure from 2,6-dimethylbenzyl chloride and 4-methylbenzaldehyde in 79 % yield. IR: 3635, 3600–3200, 1100 cm^{-1}; ^1H NMR: δ 1.89 (b s, 1H, OH), 2.30 (br s, 6H), 2.34 (s, 3H), 2.96–3.13 (m, 2H), 4.78–4.93 (m, 1H), 7.02–7.21 (m, 7H); MS: 240 (1, M^+), 222 (29), 207 (28), 192 (29), 179 (3), 178 (4), 165 (5), 152 (2), 130 (19), 121 (92), 120 (100), 119 (23), 115 (19), 105 (41), 93 (52), 91 (44), 77 (37); mol. weight: calcd. for $C_{17}H_{20}O$ 240.151, found 240.152.

Dehydration of **3**; *general procedure.* A solution of **3** (3.40 g, 15 mmol) and *p*-toluenesulfonic acid (0.30 g, 1.5 mmol) was heated under reflux for 4 h with a Dean-Stark trap attached to the reaction flask. The organic phase was then washed with satd. aqueous $NaHCO_3$ and dried ($MgSO_4$). Normal work-up gave a residue which was an essentially pure mixture of the *Z* and *E* isomers of the corresponding stilbene. The mixture was analysed by GLC prior to final purification by gravity-flow circular TLC, using 2 % ethyl acetate in hexane as solvent.

All the dimethylated 1,2-diarylethanols were converted to the corresponding dimethylstilbenes according to this procedure. All dimethylstilbenes (**7**) were obtained as *E*/*Z* mixtures (Table 3) in essentially quantitative yields.

2,2′-Dimethylstilbene (**7**-2,2′), [33,39] from **3**–2,2′. Recrystallization from methanol gave pure (*E*)–**7**–2,2′ in 72 % yield; m.p. 81.4 °C.

2,3′-Dimethylstilbene (**7**–2,3′), from **3**–3,2′. IR: 3010, 1625, 960 cm^{-1}; ^1H NMR: δ 2.18 and 2.35 (2s in a ratio of 6:94, 3H), 2.25 and 2.40 (2s in a ratio of 7:93, 3H), 6.83–7.41 (m, 10H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (7), 193 (62), 192 (16), 191 (11), 189 (6), 179 (11), 178 (48), 165 (9), 152 (4), 129 (3), 128 (5), 116 (26), 115 (27), 103 (8), 102 (10), 91 (10), 89 (12); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.126.

2,4′-Dimethylstilbene (**7**–2,4′), from **3**–4,2′. IR: 3010, 1630, 960 cm^{-1}; ^1H NMR: δ 2.33 (s, 3H), 2.39 (s, 3H), 6.83–7.61 (m, 10H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (7), 193 (65), 192 (15), 191 (10), 189 (6), 179 (11), 178 (50), 165 (8), 152 (4), 129 (2), 128 (4), 116 (24), 115 (26), 103 (9), 102 (11), 91 (12), 89 (13); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.124.

3,3′-Dimethylstilbene (**7**–3,3′),[13,40] from **3**–3,3′. Column chromatography (neutral Al_2O_3/benzene) gave pure (*E*) – **7**–3,3′ in 79 % yield; m.p. 54–55 °C. The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (11), 193 (53), 192 (22), 191 (13), 189 (6), 179 (9), 178 (42), 165 (8), 152 (4), 128 (2), 116 (3), 115 (12), 103 (6), 102 (9), 91 (7), 89 (9).

3,4′-Dimethylstilbene (**7**–3,4′), from **3**–4,3′. IR: 3010, 1630, 960 cm^{-1}; ^1H NMR: δ 2.36 (br s, 6H), 7.04–7.44 (m, 10H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (10) 193 (53), 192 (23). 191 (14), 189 (4), 179 (11), 178 (48), 165 (9), 152 (5), 129 (1), 128 (3), 116 (5), 115 (16), 103 (10), 102 (13), 91 (11), 89 (16); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.122.

4,4′-Dimethylstilbene (**7**–4,4′),[39,41] from **3**–4,4′. Column chromatography (neutral Al_2O_3/ben-

zene) gave pure (*E*) – **7**–4,4′ in 80 % yield; m.p. 181.7 °C. The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (9), 193 (41), 192 (20), 191 (13), 189 (6), 179 (9), 178 (38), 165 (8), 152 (4), 128 (3), 116 (4), 115 (16), 103 (10), 102 (12), 91 (11), 89 (15).

2-(2-Methylphenyl)-1-phenyl-1-propene (**7**–α,2), from **3**-α,2. IR: 3010, 1635, 860 cm^{-1}; ^1H NMR: δ 2.11 and 2.17 (br s and d, respectively, in a 1:3 ratio, 3H, *J* 1.5 Hz), 2.23 and 2.34 (2s in a 1:3 ratio, 3H), 6.37 and 6.47 (q and br s, respectively, in a 3:1 ratio, 1H, *J* 1.5 Hz), 7.00–7.37 (m, 9H); MS (*E*): 208 (100, M^+), 207 (4), 193 (98), 192 (7), 191 (8), 189 (4), 179 (16), 178 (49), 165 (7), 130 (4), 129 (3), 116 (5), 115 (27), 103 (1), 102 (1), 91 (9), 89 (4); MS (*Z*): 208 (87, M^+), 207 (4), 193 (100), 192 (10), 191 (11), 189 (7), 179 (21), 178 (60), 165 (14), 152 (6), 130 (15), 129 (12), 128 (10), 127 (4), 117 (35), 116 (21), 115 (80), 103 (13), 102 (8), 95 (11), 94 (6), 91 (44), 90 (7), 89 (29); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.125.

2-(3-Methylphenyl)-1-phenyl-1-propene (**7**–α,3), from **3**–α,3. IR: 3010, 1625, 855 cm^{-1}; ^1H NMR: δ 2.17 and 2.25 (2d in a ratio of 14:86, 3H, *J* 1.5 Hz), 2.27 and 2.37 (2s in a 15:85 ratio, 3H), 6.43 and 6.81 (2q in a 15:85 ratio, 1H, *J* 1.5 Hz), 7.11–7.35 (m, 9H) MS (*E*): 208 (100, M^+), 207 (10), 193 (17), 192 (17), 191 (10), 189 (5), 179 (9), 178 (38), 165 (8), 152 (3), 129 (2), 128 (2), 116 (7), 115 (17), 103 (3), 102 (2), 91 (6), 89 (6): MS (*Z*): 208 (100), 207 (12), 194 (16), 193 (99), 192 (22), 191 (12), 189 (7), 180 (4), 179 (18), 178 (59), 166 (6), 165 (19), 152 (7), 151 (10), 129 (5), 128 (8), 123 (12), 117 (23), 116 (30), 115 (78), 111 (11), 110 (10), 109 (24), 103 (17), 102 (17), 101 (6), 97 (20), 96 (20), 95 (44), 92 (7), 91 (55), 89 (51); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.126.

2-(4-Methylphenyl)-1-phenyl-1-propene (**7**–α,4), from **3**–α,4. IR: 3010, 1630, 860 cm^{-1}; ^1H NMR: δ 2.16 and 2.24 (2d in a ratio of 14:84, 3H, *J* 1.2 and 1.5 Hz, respectively), 2.30 and 2.34 (2s in a 15:85 ratio, 3H), 6.43 and 6.81 (br s and q, respectively, 1H, *J* 1.5 Hz), 7.06–7.45 (m, 9H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (8), 193 (68), 192 (16), 191 (9), 179 (8), 178 (38), 165 (6), 116 (6), 115 (18), 103 (1), 102 (1), 91 (6), 89 (5); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.126.

1-(2-Methylphenyl)-2-phenyl-1-propene (**7**–α,2′), from **3**–α,2′. IR: 3010, 1610, 865 cm^{-1}; ^1H NMR: δ 2.09 (br s, 3H), 2.26 (br s, 3H), 6.51 and 6.83 (2 br s in a ratio of 12:88, 1H), 7.06–7.48 (m, 9H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (9), 193 (89), 192 (13), 191 (12), 189 (7), 179 (37), 178 (48), 165 (11), 152 (4), 130 (8), 129 (9), 128 (8), 116 (5), 115 (36), 103 (18), 102 (6), 91 (18), 89 (17); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.122.

1-(3-Methylphenyl)-2-phenyl-1-propene (**7**–α,3′), from **3**–α,3′. IR: 3010, 1625, 850 cm^{-1}; ^1H NMR: δ 2.15 and 2.26 (2d in a 1:4 ratio, 3H, *J* 1.4 and 1.2 Hz, respectively), 2.35 (br s, 3H), 6.41 and 6.79 (2 br s in a 1:4 ratio, 1H), 7.06–7.55 (m, 9H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (11), 193 (75), 192 (17), 191 (10), 189 (5), 179 (10), 178 (39), 165 (8), 152 (3), 130 (2), 129 (4), 128 (3), 116 (2), 115 (19), 103 (8), 102 (2), 91 (6), 89 (7); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.127.

1-(4-Methylphenyl)-2-phenyl-1-propene (**7**–α,4′), from **3**–α,4′. IR: 3010, 1625, 870 cm^{-1}; ^1H NMR: δ 2.16 and 2.26 (2d in a 1:9 ratio, 3H, *J* 1.2 Hz), 2.30 and 2.34 (2s, 3H), 6.44 and 6.79 (2 br s in a 12:88 ratio, 1H), 7.06–7.45 (m, 9H). The mass spectra of the *Z* and the *E* isomers were essentially identical; MS: 208 (100, M^+), 207 (12), 193 (80), 192 (21), 191 (14), 189 (3), 179 (12), 178 (47), 165 (11), 152 (4), 130 (3), 129 (6), 128 (5), 116 (5), 115 (27), 103 (13), 102 (5), 91 (11), 89 (12); mol. weight: calcd. for $C_{16}H_{16}$ 208.125, found 208.125.

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