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RELATIVE STABILITY OF CROWDED ISOMERIC ENOLS: 2-MESITYL-2-PHENYLETHENOLS AND THEIR METHYL ETHERS

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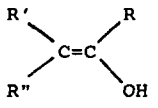
The structure of 2-mesityl-2-phenylethenol (7) obtained by reduction of mesityl phenyl ketene with $LiAlH_4$ and by acid-catalysed rearrangement of 1-mesityl-2-phenylethylene glycol was determined by x-ray crystallography to be *Z* [(*Z*)-7]. In contrast with a literature report, the reduction of 2-acetoxy-2-mesityl-2-phenylacetaldehyde did not provide the *E* isomer [(*E*)-7], but a mixture of (*Z*)-7 and 2-mesityl-2-phenylethenol. An (*E*)-7–(*Z*)-7 mixture of 1:5 was obtained starting from pure (*Z*)-7 at 80 °C in dimethyl sulphoxide. The lower stability of (*E*)-7 was ascribed to higher steric effects due to a smaller Ph–C=C compared with Mes–C=C torsional angle and a preferred intramolecular π(Mes)–OH in (*Z*)-7 over π(Ph)–OH hydrogen bonding. In order to dissect the effects, the corresponding 2-mesityl-2-phenylvinyl methyl ethers (*E*)-15 and (*Z*)-15, where hydrogen bonding is absent, were prepared and equilibrated in chlorobenzene. The (*Z*)-15:(*E*)-15 ratio of *ca* 3:1 between 58° and 132° ($\Delta G = 0{\cdot}8$ kcal mol^{-1}) gives $\Delta H \approx 0{\cdot}6$ kcal mol^{-1} and $\Delta S \approx 0{\cdot}5$ e.u. It was concluded that steric effects contribute *ca* 1 kcal mol^{-1} and hydrogen bonding *ca* 1·5 kcal mol^{-1} to the higher stability of (*Z*)-7 over (*E*)-7. The unknown mesitylphenylacetaldehyde 16 was obtained from (*Z*)-7 at 135 °C in 31% yield.

Stable simple enols having two different β-substituents can exist in two geometrical isomers, **1** and **2**. In the aliphatic series[1] and for singly β-aryl-substituted systems[2], both isomers were spectroscopically observed, although not isolated. When both R′ and R″ are aromatic groups of similar bulk, e.g. R = R′ = Mes, R″ = 2,6-Me_2-4-*t*-BuC_6H_2[3] or R″ = 3-MeO-2,4,6-Me_3C_6H,[4] both isomers can be observed but only one was isolated on crystallization. In these two cases an $E \rightleftharpoons Z$ isomerization whose rate depends on the nature of the solvent was observed. In contrast, the acetates of these enols and the isopropyl ethers of the latter are more stable and both isomers were isolated.[3,4]



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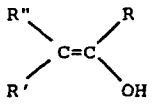

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When R′ and R″ are aromatic substituents with different bulk, only one isomer is usually observed and isolated.[5] Presumably, if the other isomer is initially formed it then isomerizes rapidly, as demonstrated with 1,2-dimesityl-2-phenylethenol (**3**). Addition of mesityl-MgBr to mesityl phenyl ketene probably involves an initial formation of the (*E*)-enolate **4**, since capture by Ac_2O gives the (*E*)-acetate (*E*)-**5**. However, protonation gives enol (*Z*)-**3** which should be formed by a rapid isomerization of an initially formed but not observed (*E*)-**3** [equation (1)].[5,6] The geometries of (*Z*)-**3**, (*E*)-**5** and (*Z*)-**5** were established by x-ray crystallography.[6] Interestingly, the mass spectral fragmentation of acetates (*E*)-**5** and (*Z*)-**5** form the same species which gives the cleavage pattern of enol (*Z*)-**3**.[7]

There is evidence[4] that the isomerization may be due to abstraction of the enolic hydrogen either as a radical or as a proton. The intermediate, having a carbon–carbon bond order lower than two, is then prone

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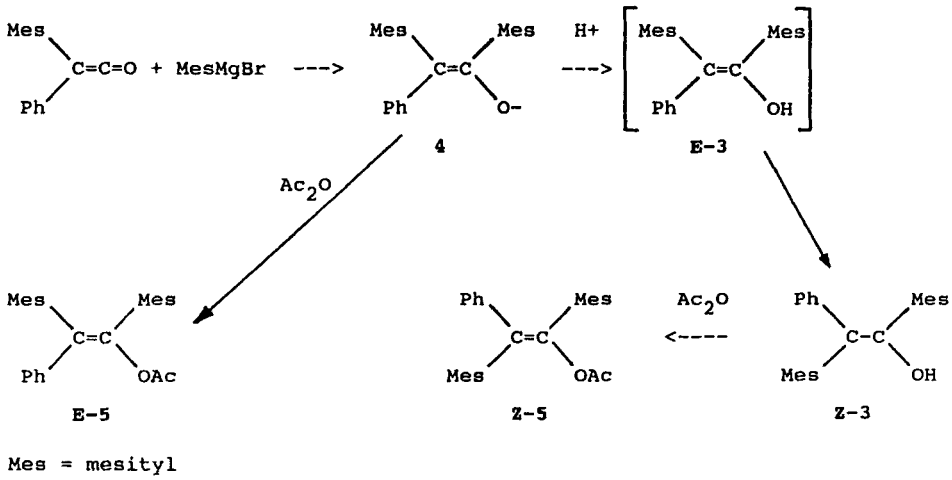
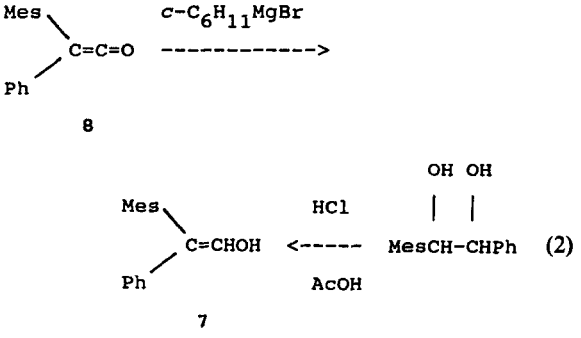


(1)

to isomerization. Alternatively, resonative electron donation by the vinylic oxygen may also reduce the bond order of **1** via the hybrid structure **6**. In order to

distinguish between these routes, we investigated the 2-mesityl-2-phenylvinyl-OR (R = H, Me) system since Fuson *et al.*[5] had claimed the isolation of two isomeric enols. One stable enol **7** (m.p. 114–115 °C) was obtained by reduction of mesityl phenyl ketene **8**[8] or by dehydration of 1-mesityl-2-phenylethylene glycol[9] [equation (2)]. Treatment of **7** with $Pb(OAc)_4$ gave the acetoxy aldehyde **9**[5] which according to Fuson *et al.* gave with isobutylmagnesium bromide the geometrical isomer **10** of the precursor enol **7** [equation (3)].[5] The configurations of **7** and **10** were not determined. Fuson *et al.* suggested that the reduction gives 1-phenyl-1-



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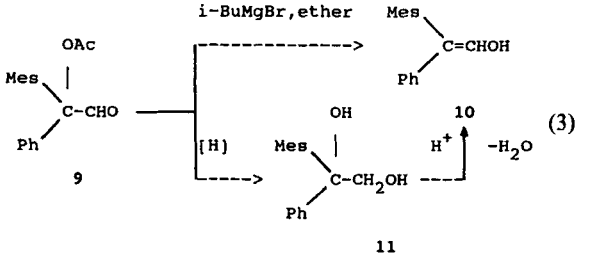


(3)

mesitylethylene glycol (**11**), which undergoes dehydration to **10** [equation (3)].

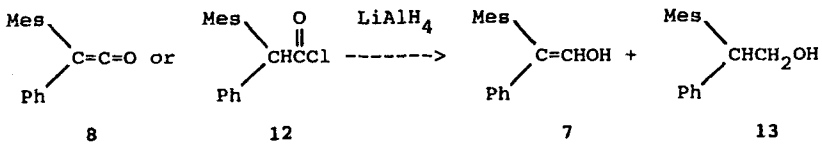
The formation of two isomeric enols seemed reasonable in view of the reduced steric hindrance of **7**/**10** compared with (*E*)-**3**/(*Z*)-**3**. We therefore tried to repeat Fuson *et al*'s. synthesis[5] in order to characterize the two enols by modern methods and to investigate their stability to mutual isomerization. In parallel we synthesized the two isomeric methyl enol ethers of **7**/**10** in order to compare their relative stability with that of the parent enols.

RESULTS AND DISCUSSION

Preparation of 7 and its further reduction

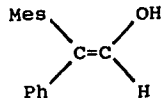
Ketene **8** was obtained by a modification of Fuson *et al.*'s method,[10] since the ketene prepared by the original procedure from mesitylphenylacetic acid and $SOCl_2$ and then pyridine in benzene was always admixed with a substantial quantity of mesitylphenylacetyl chloride (**12**).

When we reduced an **8**/**12** mixture with $LiAlH_4$, two products were obtained, enol **7** and 2-mesityl-2-phenylethanol (**13**) [equation (4)]. In contrast, reduction of pure **8** with $LiAlH_4$ gave a 89% yield of **7**, m.p. 112 °C, in a procedure similar to its reduction with



(4)

c-$C_6H_{11}MgBr$.[8] Compound **7** was also obtained from 1-mesityl-2-phenylethylene glycol, thus confirming Fuson *et al.*'s results.[9]



Z-7

Failure to obtain 10

When 2-acetoxy-2-mesityl-2-phenylacetaldehyde (**9**)[5] was reduced with *i*-BuMgBr, following exactly Fuson *et al.*'s procedure, TLC and ^{1}H NMR showed that the oily yellowish solid formed is a 6:1 mixture of **7** and **13**. Crystallization gave a solid which by ^{1}H NMR was a 3·3 (**7**):1 (**13**) mixture the IR spectrum of which resembled that of **7**. It is likely that this mixture was mistaken by Fuson *et al.*[5] as a second isomeric enol **10**.

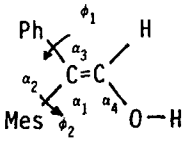
X-ray structure of 7

The structure of the enol **7** was determined by x-ray crystallography as that of the formally more crowded *Z*-isomer (*Z*)-**7**. Selected data are given in Table 1 and the ORTEP drawing and the stereoscopic view are given in Figures 1 and 2, respectively [bond lengths and angles, positional and thermal parameters and structure factors of (*Z*)-**7** have been deposited at the Cambridge Crystallographic Data Centre]. An NOE experiment showed an interaction between an *o*-Me of the mesityl ring and the OH group, indicating a (*Z*)-**7** configuration also in solution.

The crystal structure displays several interesting features. (a) The Ph—C=C torsional angle (28·4°) is much smaller than the Mes—C=C torsional angle (74·8°). This is reminiscent of the corresponding angles in (*E*)-**3**, (*E*)-**5** and (*Z*)-**5**.[6] Although (*Z*)-**7** is formally more crowded than its *E* isomer, owing to these torsional angles the steric interaction of vicinal *cis* OH/Mes in (*Z*)-**7** seems lower than that of *cis* OH/Ph in (*E*)-**7**.

(b) The bond angles at the enol C=C bond are around 120°, the largest being the Mes—C=C, as expected. The MesCPh angle of 116·2° is noteworthy.

Table 1. Selected bond lengths and angles for enol (*Z*)-**7**



Bond	Length (Å)	Bond angle	Angle (°)
C(1)—C(2)	1·33(1)	α_1 [C(1)—C(2)—C(9)]	123·1(7)
C(1)—O	1·365(9)	α_2 [C(3)—C(2)—C(9)]	116·2(6)
C(2)—C(3)	1·49(1)	α_3 [C(1)—C(2)—C(3)]	120·6(7)
C(2)—C(9)	1·50(1)	α_4 [O—C(1)—C(2)]	121·9(7)
C—C(Ph)	1·34(1)–1·41(1)[a]	C—C—C(Ph)	118·9(8)–120·9(8)
		C—C—C(Mes)	118·7(8)–122·1(8)
		C—C_{ipso}—Me	119·6(7)–121·5(7)
C—C(Mes)	1·37(1)–1·41(1)	(C(3)C(2)C(9))(HC(1)O)	10·2
C_{Ar}—C_{Me}	1·50(1)–1·51(1)	ϕ_1	28·4
		ϕ_2	74·8
		Mes_{ring}—Ph_{ring}	92·7
O—H	1·04		
H···O[b]	1·85(1)	O—H···O[b]	147·9(5)

[a] C(6)—C(7) = 1·34 Å; C(4)—C(5), C(7)—C(8) = 1·41 Å.
[b] Intermolecular hydrogen bond.

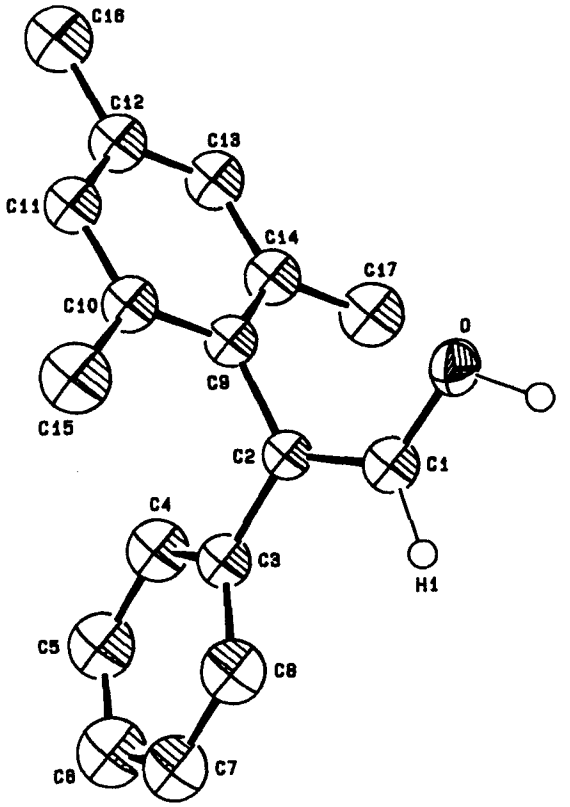


Figure 1. ORTEP drawing of (*Z*)-7

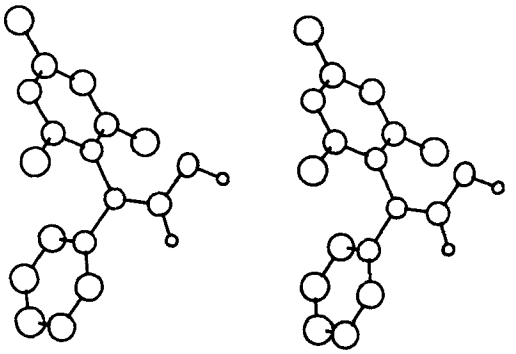


Figure 2. Stereoscopic view of (*Z*)-7

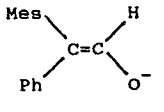
Angles $< 120°$ were found in other crowded enols[6,11,12] which are substituted at C_α. However, in (*Z*)-7 it is still smaller than the 'normal' sp^2 value in spite of the small steric effect at C_α.

(c) The torsional angle of the double bond itself is 10°. This seems appreciable considering the degree of steric hindrance between the two parts of the double bond.

(d) The unit cell (Figure 3) shows a net of four intermolecularly bonded OH groups which are in an *anti* arrangement in relation to the double bond. Similar intermolecular hydrogen bonds were found in other 2,2-diaryl-1-*H*-ethenols,[11,12] whereas an OH—π (Ar) interaction is observed in the solid state of the analogous 1-substituted systems.[6]

Stereochemistry of the reduction

Formation of (*E*)-**5** in equation (1) suggests that the Mes—C=C torsional angle in **8** is larger than the Ph—C=C angle and that **4** is formed initially by addition of the nucleophile to **8** from its least hindered side. Likewise, the enolate ion initially formed on $LiAlH_4$ reduction of **8** should be **14**, whose protonation should lead to the (*E*)-enol (*E*)-**7** and not, as observed [equation (4)], to (*Z*)-**7**. Consequently, as for (*Z*)-**3**, we believe that a rapid acid catalysed (*E*)-**7** → (*Z*)-**7** isomerization took place after protonation of **14**.



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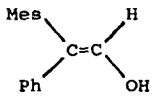


E-7

Methoxy ethers as a probe for dissecting steric and hydrogen bonding effects of the enols

If a facile route for (*E*)-**7** ⇌ (*Z*)-**7** isomerization is available the thermodynamic preference for formation of (*Z*)-**7** should be $\geq 2{\cdot}5$ kcal mol^{-1} (1 kcal = 4·184 kJ) at room temperature. This could result from two different reasons. (a) It may be a mere steric effect. (b) In non-hydrogen bond-accepting solvents, a *syn*-C=C—O—H conformation is present, and a stronger OH—π(Mes) than OH—π(Ph) hydrogen bonding should contribute to the stabilization of (*Z*)-**7**. This is due to a better electron donation by the mesityl ring and a better alignment of the π-Ar and the OH. Fortunately, the influence of both effects can easily be tested.

To elucidate the steric effect of mesityl vs phenyl in (*E*)- and (*Z*)-**7**, the intramolecular hydrogen bonding should be removed. We have synthesized the two isomeric enol ethers (*Z*)-**15** and (*E*)-**15** where such hydrogen bonding is absent and determined their relative stability. MMP2 calculations[13] indicate that the conformation around the C=C—O—Me group is *anti* in both enol ethers, as demonstrated by their heats of formation (kcal mol^{-1}): *syn*-(*Z*)-**15** (+1·5), *anti*-(*Z*)-**15** (−0·8), *syn*-(*E*)-**15** (>8; no local minimum found) and *anti*-(*E*)-**15** (0·4). The preference for the *anti* conformation in **15** is in contrast to that observed in simple

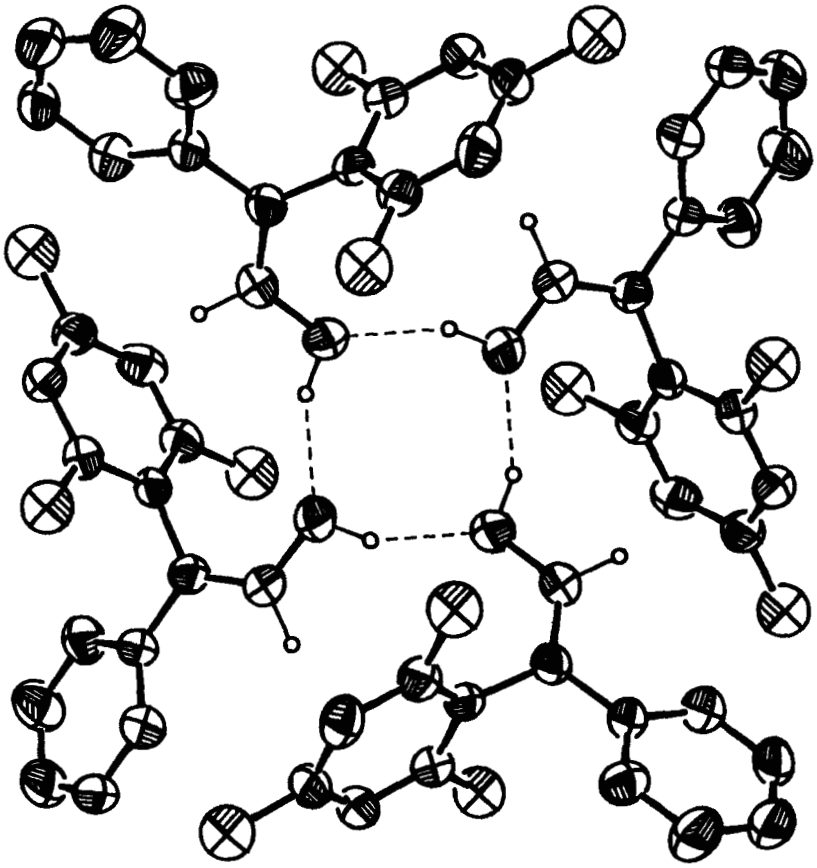


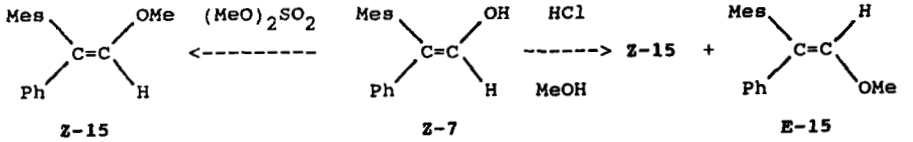
Figure 3. Unit cell of (*Z*)-7

enol ethers, where non-bonded attraction favours the *syn* conformer.[14]

When enol (*Z*)-**7** was reacted with dimethyl sulphate[15] we obtained methyl enol ether (*Z*)-**15**. Although Fuson *et al.*[9] reported formation of a single ether from the reaction of **7** with methanolic hydrogen chloride, the reaction gave in our hands two isomeric enols, (*Z*)-**15** and (*E*)-**15** [equation (5)]. After chromatography the isolated yields were (*Z*)-**15** 47% (yellow liquid) and (*E*)-**15** 21% (white crystals).

The main difference in their ^{1}H NMR spectra is the downfield shift of the vinylic hydrogen in (*Z*)-**15** ($CDCl_3$): δ 6·71 [(*Z*)-**15**] and 6·07 [(*E*)-**15**], while in cyclic voltammetry the $E_{1/2}$(SCE) are similar: 1·20 V [(*Z*)-**15**] and 1·23 V [(*E*)-**15**]. The configuration assignment of the ethers is based on the assumed retention of configuration in the reaction of (*Z*)-**7** with $(MeO)_2SO_2$ [equation (5)], so that the ether formed is only (*Z*)-**15**. Apparently, Fuson *et al.* were unable to separate (*Z*)-**15** and (*E*)-**15**.

(*E*)-**15** can be formed in equation (5) by (a) an HCl-catalysed isomerization of (*Z*)-**7** to the less stable (*E*)-**7**, which undergoes faster etherification, (b) a ketene acetal or hemiacetal formation followed by loss of MeOH or H_2O or (c) a partial isomerization of an initially formed (*Z*)-**15**.



(5)

The relative stability of (*Z*)-**15** and (*E*)-**15** was determined in hexane and chlorobenzene with *p*-toluenesulphonic acid as a catalyst. Starting from either (*Z*)-**15** or (*E*)-**15** the same (*Z*)-**15**:(*E*)-**15** ratio of 75 ± 2:25 ± 2 was obtained at about 60 °C in both solvents. With chlorobenzene as a solvent, the (*Z*)-**15**:(*E*)-**15** ratio was found to be almost independent of temperature between 58 and 132 °C ($\Delta G =$ 0·8 kcal mol^{-1}), giving $\Delta H \approx 0{\cdot}6$ kcal mol^{-1} and $\Delta S \approx 0{\cdot}5$ e.u. for the (*Z*)-**15** ⇌ (*E*)-**15** equilibrium.

Obviously, the smaller difference in stability of (*Z*)-**15** and (*E*)-**15** compared with (*Z*)-**7** and (*E*)-**7** implies that steric effects are not solely responsible for the thermodynamic preference of enol (*Z*)-**7**. Most likely hydrogen bonding effects are also operative. As a prerequisite, the conformation of enol (*Z*)-**7** in solution needs to be *syn* in contrast to the solid-state data. To probe the conformation in solution, we determined the ^3J(HCOH) coupling constants as a function of the hydrogen bond accepting ability of the solvents. In line with earlier ^{1}H NMR studies on $Mes_2C{=}CHOH$,[16] the values obtained for (*Z*)-**7** indicate that in deuterated dimethyl sulphoxide (DMSO-d_6) (where $^3J = 6{\cdot}5$ Hz) the conformation is *anti* with a dihedral angle of >30° whereas in $CDCl_3$ ($^3J = 13{\cdot}5$ Hz) a *syn* conformation prevails.

Formation of (*E*)-7 and mesitylphenylacetaldehyde 16

Obviously the stronger hydrogen bond to DMSO replaces the intramolecular OH—π(Ar) hydrogen bond to the mesityl ring. Consequently, in DMSO the relative stability of the two enols (*Z*)-**7** and (*E*)-**7** is mainly controlled by steric effects, which should result in approximately the same ΔH[(*Z*)-**7** ⇌ (*E*)-**7**] value as for the two isomeric enol ethers (*Z*)-**15** and (*E*)-**15**. On dissolution of (*Z*)-**7** in DMSO-d_6 at room temperature still only the signals for (*Z*)-**7** δ(DMSO-d_6) 7·06 (=CH, $J = 6{\cdot}5$ Hz) and 8·93 (OH, $J = 6{\cdot}5$ Hz) were observed in the ^{1}H NMR spectrum. However, after heating the solution for 5 h at 80 °C, signals of two new compounds emerged in both the ^{1}H and ^{13}C NMR spectra. According to ^{1}H NMR integration both compounds are isomers to (*Z*)-**7**. The minor isomer was formed to about 1%. The major new isomer has signals at δ (DMSO-d_6) 6·45 (=CH, d, $J = 6{\cdot}5$ Hz) and 9·50 (OH, $J = 6{\cdot}5$ Hz), i.e. a lower field hydroxy proton and a higher field vinylic hydrogen than for (*Z*)-**7**. The similar ^3J (HCOH) coupling and the ^{1}H and ^{13}C NMR spectra indicate that the new compound is (*E*)-**7**. From the (*Z*)-**7**:(*E*)-**7** ratio of 5:1 at 80 °C, which does not change after cooling to room temperature for 24 h, but which is 7:1 after 72 h, a ΔG value of *ca* 1·1 kcal mol^{-1} at 80 °C was derived. This value is close to that observed for the corresponding enol ethers. Consequently, we believe that this energy difference between either (*Z*)-**7**/(*E*)-**7** or for (*Z*)-**15**/(*E*)-**15** is mainly due to a differential steric interaction of the OR (R = H, Me) with the mesityl and the phenyl groups.

At 100 °C the (*Z*)-**7**:(*E*)-**7** ratio is 3·6:1 and the minor isomer, which is formed in 3% yield, could be spectrally identified as the unknown mesitylphenylacetaldehyde (**16**).

MesCH(Ph)CHO

16

It exhibits signals at δ (DMSO-d_6) 9·90 (CHO) and 5·30 (CH) with $^3J < 1$ Hz and $\nu_{CO} = 1725$ cm^{-1} (in $CHCl_3$). All attempts to obtain **16** by oxidation of **13** by using MnO_2,[17] SeO_2,[18] TEMPO–O_2–CuCl[19] or Swern's reagent[20] resulted in the formation of mesityl phenyl ketone and enol (*Z*)-**7**. However, reduction of **12** (Pd–$BaSO_4$–H_2,[21] LiAlH(O-*t*-Bu)$_3$[22]) afforded (*Z*)-**7**, **13** and up to 13% of **16**. Finally, **16** was obtained in 31% yield by heating neat (*Z*)-**7** for 5 h at 135 °C. Although the aldehyde may be an intermediate in the (*Z*)-**7** ⇌ (*E*)-**7** transformation, this issue was not investigated further.

Our AM1 calculations[23] of the enthalpies of formation (kcal mol^{-1}) of enols *syn*-(*Z*)-**7** (−3·6), *anti*-(*Z*)-**7** (+2·2), *syn*-(*E*)-**7** (−2·6) and *anti*-(*E*)-**7** (+2·0) and of aldehyde **16** (−1·1) agree qualitatively with the experimental data. The observed stability order is (*Z*)-**7** > (*E*)-**7** (*syn* isomers in $CDCl_3$) and aldehyde **16** has a higher energy than the tautomeric enols (in a non-polar solvent).

CONCLUSIONS

In contrast to Fuson *et al.*'s report, only one, rather than two, configurationally stable 2-mesityl-2-phenylethenols is formed and isolated from light petroleum. The isolated enol (*Z*)-**7**, where the Mes—C=C torsional angle is larger than the Ph—C=C angle, is less destabilized by Ar–OH steric interactions and in $CDCl_3$ is also stabilized by an internal OH—π(Ar) hydrogen bond to the mesityl group when compared with its (*E*)-isomer (*E*)-**7**. In DMSO, where the intramolecular hydrogen bond is replaced by hydrogen bonding to the solvent, both isomers could be detected and (*Z*)-**7** is favoured by about 1·1 kcal mol^{-1} over (*E*)-**7** at 80 °C. From the slightly smaller stability difference of the isolable enol ethers (*Z*)-**15** and (*E*)-**15**, we estimate that steric effects contribute *ca* 1 kcal mol^{-1} to the difference in stability of the isomeric enols, while intramolecular hydrogen bonding in the *syn*-enol (*Z*)-**7** contributes an additional ≥1·5 kcal mol^{-1}.

EXPERIMENTAL

General. For general information, see Refs 11 and 24. The AM1[23] and MMP2[13] calculations were per-

formed on a MicroVAX computer (Digital Equipment) using MOPAC 6·00 (Quantum Chemistry Program Exchange No. 455).

2-Mesityl-2-phenylethenol [(*Z*)-7]. (i) From **8**. To obtain the pure, orange–yellow ketene **8**, prepared according to the procedure given by Fuson *et al.*,[10] it was distilled twice (at 150–155 °C/13–14 mm Hg and at 125–126 °C/3 mm Hg) to remove the corresponding acid chloride. To an ice-bath cooled solution of **8** (4 g, 16·95 mmol) in dry THF (60 ml) under argon was added in portions $LiAlH_4$ (1 g, 26·32 mmol). The ice-bath was then removed and the mixture was stirred at room temperature under argon for 2·5 h. The cooled mixture was then decomposed in water (20 ml) and then 10% H_2SO_4 (100 ml). Extraction with diethyl ether (4 × 75 ml), drying ($MgSO_4$) and evaporation of the solvent yielded (*Z*)-**7** (3·59 g, 89%) as a white solid. Recrystallization (light petroleum ether, b.p. 60–80 °C) yielded **7**, m.p. 112 °C (lit.[9] m.p. 114–115 °C). IR: ν_{max} (CCl_4) = 3621 (OH, v w), 3518 (OH, s), 3462, 3402 (OH, v w), 1630 (C=C, s) (lit.[9] ν_{OH} = 3623 and 3521 cm^{-1}). The spectrum was identical at 5–13% concentrations in CCl_4. UV: λ_{max} (hexane) = 212 nm sh (ε 25 000), 257 (13 300). ^1H NMR (CD_2Cl_2): δ 2·10 (s, 6H, Mes-*o*-Me), 2·32 (s, 3H, Mes-*p*-Me), 4·42 (d, 1H, J = 13·2 Hz, OH), 6·96–7·22 (s + m, 8H, Ar—H + =C*H*). Mass spectrum (EI, 70 eV, room temperature): *m/z* (relative abundance, assignment) = 238 (100, M), 223 (12, M – Me), 220 (7, M – H_2O), 209 (33, MesCHPh), 195 (12, MesCHPh – CH_2), 179 (17, MesCHPh – 2Me), 165 (1H, MesCPh – 3Me), 119 (7, Mes), 105 (5, PhCO), 91 (10, $PhCH_2$), 77 (7, Ph).

(*ii*) *By acid-catalysed rearrangement of 1-mesityl-2-phenylethylene glycol.* According to the procedure described by Fuson *et al.*[9] we obtained (*Z*)-**7**, m.p. 108–110 °C (lit.[9] m.p. 114–115 °C); GC, 25 m SE-30 column programmed from 125 °C (5 min) to 250 °C at 10 °C min^{-1}, retention time = 14·70 min (purity 97%), in 79% yield. IR (KBr): ν = 3450–3200 (s, OH), 2900 (m, CH), 1650 (m), 1620 (w), 1590 (m, C=C). ^1H NMR ($CDCl_3$): δ 2·09 (s, 6H, Mes-*o*-Me), 2·31 (s, 3H, Mes-*p*-Me), 4·30 (d, ^3J = 13·5 Hz, 1H, OH), 6·95 (s, 2H, Mes—H), 7·07 (d, ^3J = 13·5 Hz, 1H, C*H*OH), 7·09–7·30 (m, 5H, Ph—H). ^{13}C NMR ($CDCl_3$): δ 19·79 (C-17/C-15), 21·18 (C-16), 117·12 (C-9), 124·61 (C-4/C-8), 125·91 (C-6), 128·65 (C-5/C-7), 129·07 (C-11/C-13), 129·79 (C-3), 137·91 (C-12), 138·04 (C-2), 138·50 (C-10/C-14), 139·05 (C-1). Mass spectrum (CI, NH_4^+): *m/z* (relative abundance, assignment) = 256 (100, M + NH_4^+), 238 (20, M^+).

Reduction of a mixture of 8 and 12. Formation of (Z)-7 and 13. To a mixture of phenyl mesityl ketene (**8**) and phenylmesitylacetyl chloride (**12**) (2·5 g, 0·01 mol if the mixture was pure **8**) in dry THF (40 ml) under argon was added $LiAlH_4$ (0·96 g, 0·025 mol) and the reaction mixture was refluxed for 30 min. After cooling, the ice-bath cooled mixture was carefully decomposed with several drops of water, $MgSO_4$ was added and the THF solution was filtered. Dilute (3%) HCl (50 ml) was added to the filtrate and the aqueous solution was extracted with diethyl ether (5 × 15 ml) and dried ($MgSO_4$). The combined organic layers were evaporated, giving a white solid (1·81 g). TLC [20% diethyl ether–80% light petroleum (b.p. 40–60 °C)] showed mainly two spots. ^1H NMR ($CDCl_3$) indicated the presence of a mixture of (*Z*)-**7** and **13** in a 1 : 1·5 ratio. A 1·3 g amount of the mixture was separated into two fractions on an Si-60 (230–400 mesh) pressure column with 20% diethyl ether–80% light petroleum (b.p. 40–60 °C) as eluent. The first fraction was a white solid (202 mg, 15%). Two recrystallizations of 101 mg from light petroleum (b.p. 60–80 °C) afforded 41 mg of (*Z*)-**7** as a white solid, m.p. 112 °C.

The second fraction was a white solid (668 mg, 48%). Recrystallization from light petroleum (b.p. 60–80 °C) afforded pure **13** (504 mg) as a white solid, m.p. 75·5 °C. UV: λ_{max} (hexane) = 211 nm sh (ε 14 000), 262 (760). IR: ν_{max} (Nujol) = 3260 (OH, br s), 2980–2820 (CH, s), 1590 (C=C, w). ^1H NMR (CD_2Cl_2): δ 1·52 (br s, 1H, OH), 2·14 (br s, 6H, Mes-*o*-Me), 2·24 (s, 3H, Mes-*p*-Me), 4·10–4·19 (dd, 1H, one H of $CHCH_2$), 4·44–4·53 (dd, 1H, one H of $CHCH_2$), 4·71–4·79 (dd, 1H, one H of $CHCH_2$), 6·84 (s, 2H, Mes—H), 7·11–7·30 (m, 5H, Ph—H). Mass spectrum (EI, 70 eV, room temperature): *m/z* (relative abundance, assignment) = 240 (23, M), 238 (5, M – H_2), 209 (100, MesCHPh), 194 (11, MesCHPh – Me), 179 (20, MesCHPh – 2Me), 165 (6, MesCPh – 3Me), 119 (2, Mes), 115 (2), 91 (6, C_7H_7), 77 (4, Ph). Analysis for **13**: calculated for $C_{17}H_{20}O$, C 84·96, H 8·39; found, C 84·72, H 8·15%.

2-Acetoxy-2-mesitylphenylacetaldehyde, 9. Compound **9**, m.p. 130 °C, was prepared by Fuson *et al.*'s procedure.[5] Glacial AcOH (Riedel-de Haën, 99–100% pure) solvent was dried by distillation from triacetylborate. IR: ν_{max} = 2950–2830 (C-H, s), 1740 (AcO, s), 1720 (CO, s), 1600 (C=C, w) cm^{-1} [lit.[5] 1762 ($OCOCH_3$), 1733 (CHO) cm^{-1}]. ^1H NMR (CD_2Cl_2): δ 2·16 (s, 6H, Mes-*o*-Me), 2·21 (s, 3H, AcO or Mes-*p*-Me), 2·26 (s, 3H, AcO or Mes-*p*-Me), 6·85 (s, 2H, Mes—H), 7·25–7·39 (m, 5H, Ph—H), 9·67 (s, 1H, CHO). Mass spectrum (EI, 70 eV, 85 °C): *m/z* (relative abundance, assignment) = 296 (7, M), 237 (6, M – OAc), 225 [66, Mes(Ph)CH_2CH_3], 209 (6, MesCHPh), 194 (4, MesCHPh – Me), 178 (12, MesCPh – 2Me), 165 (9, MesCPh – 3Me), 147 (13, MesCO), 119 (13, Mes), 115 (6), 105 (100, PhCO), 91 (14, C_7H_7), 77 (49, Ph).

Reduction of 9. (*i*) *with* i-*BuMgBr.* Fuson *et al.*'s

procedure[5] using *i*-BuMgBr in a five-fold excess relative to **9** was followed exactly. TLC (40% diethyl ether–60% light petroleum) and the ^{1}H NMR (CD_2Cl_2) showed that the oily yellowish solid formed (1·13 g) was an approximately 6·6:1 mixture of **7** and **13**. Crystallization (light petroleum) afforded a white solid (0·36 g), the ^{1}H NMR (CD_2Cl_2) of which corresponds to a 3·3:1 ratio of **7** to **13**. The IR spectrum (Nujol) and the TLC pattern correspond to those of **7**. No enol isomer [i.e. (*E*)-**7**] to (*Z*)-**7** was obtained.

(*ii*) *with LiAlH*$_4$. To **9** (200 mg, 0·68 mmol) dissolved in dry diethyl ether (10 ml) under argon was added $LiAlH_4$ (51 mg, 1·34 mmol). The reaction was followed by taking small samples after 1·5, 2 and 3 h, decomposing with water, extraction with diethyl ether, drying ($MgSO_4$) and evaporating. TLC (40% CH_2Cl_2–60% light petroleum) showed a spot with an R_f much lower than that of either **7** or **9**. After 3·5 h of reflux the mixture was cooled in an ice-bath and decomposed with water (10 ml) and then with aqueous NH_4Cl (20 ml), followed by extraction with diethyl ether (3 × 35 ml), drying ($MgSO_4$) and evaporation. A colourless, clear oil was obtained (175 mg). Recrystallization from diethyl ether–light petroleum (b.p. 40–60 °C) yielded a white solid (63 mg), m.p. 87·5 °C (**10** melts at 100–102 °C[8]). From the ^{1}H NMR (CD_2Cl_2) spectrum it is not clear whether this is an enol or a diol: δ 2·22, 2·26 (2 s, 9 H, Mes—Me), 4·02–4·07 (d, 1H, J = 11·3 Hz, CH or OH?), 4·25–4·31 (d, 1H, J = 11·3 Hz, CH or OH), 6·81 (s, 2H, Mes—H), 7·23–7·35 (m, 4·75H, Ph—H). In the mass spectrum (EI, 70 eV, 75 °C) there are small peaks at *m/z* 256 (13, **11**?) and 238 (**7**). The base peak is at *m/z* 225 [$MesC^+$(Ph)OH].

The microanalysis does not correspond to **11** or to enol **7**. Analysis for **11**: calculated, C 79·65, H 7·86; found, C 75·50, H 7·48%.

Z-2-Mesityl-2-phenylvinyl methyl ether [(*Z*)-*15*].[15,24] A mixture of **7** (1·0 g, 4·2 mmol) and redistilled dimethyl sulphate (2·75, 28·9 mmol) in methanol (9 ml) was heated to reflux and to the hot solution was added with vigorous stirring, in small portions, a solution of KOH (2·4 g, 43 mmol) in methanol (15 ml). The suspension was then refluxed with stirring for 30 min, poured into water (60 ml) and 2 M HCl (10 ml), extracted with diethyl ether (100 ml) and then with water (100 ml), dried (Na_2SO_4) and the solvent was evaporated. Chromatography on silica gel M60 using 3:1 cyclohexane–CH_2Cl_2 as eluent gave 185 mg (17%) of (*Z*)-**15** as an oil (lit.[16] m.p. 44–45 °C). GC, 35 m OV-17 column programmed from 60 °C (1 min) to 250 °C at 10 °C min^{-1}: retention time = 22·28 min. IR (neat): ν_{max} = 3000 cm^{-1} (w, C—H), 2900 (vs, CH), 1630 (s, C=C), 1600 (m, C=C), 1220 (vs), 1140 (s), 1100 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2·09 (s, 6H, Mes-*o*-Me), 2·30 (s, 3H, Mes-*p*-Me), 3·68 (s, 3H, OMe), 6·71 (s, 1H, =CH), 6·90 (s, 2H, Mes—H), 7·05–7·23 (m, 5H, Ph—H), ^{13}C NMR ($CDCl_3$): δ 20·07 (C-17/C-15), 21·24 (C-16), 60·39 (OMe), 118·21 (C-9), 124·99 (C-4/C-8), 125·86 (C-6), 128·26 (C-5/C-7), 128·54 (C-11/C-13), 133·30 (C-3), 136·65 (C-12), 136·97 (C-10/ C-14), 138·93 (C-2), 145·43 (C-1). Mass spectrum (EI), *m/z* (relative abundance, assignment): 252 (100, M), 238 (4, M – Me), 220 (20), 147 (100, MesCO), 119 (28, Mes), 105 (20, PhCO), 77 (16, Ph), 51 (8); (CI): 270 (100, M + NH_4^+), 147 (25, MesCO). Analysis for (*E*)-**15**: calculated, C 85·67, H 7·99; found, C 85·69, H 7·92%.

(*Z*)- and (*E*)-*2-mesityl-2-phenylvinyl methyl ethers* [(*Z*)-*15 and* (*E*)-*15*] *from* (*Z*)-*7 and HCl–MeOH*. To MeOH (80 ml) saturated with dry HCl was added (*Z*)-**7** (1·8 g, 7·6 mmol) and the mixture was refluxed for 11 h. After cooling it was poured into water (500 ml) and the product was extracted with diethyl ether (300 ml) and then washed with water (100 ml). The organic phase was dried (Na_2SO_4), the solvent was evaporated and the remainder was chromatographed on silica gel M-60, giving two fractions, at R_f 0·6 [the (*Z*)-enol ether (*Z*)-**15**] (900 mg, 47%) and at R_f 0·67 [the (*E*)-enol ether (*E*)-**15**] (400 mg, 21%). The chromatographic and spectral data for (*Z*)-**15** were identical with those reported above. (*E*)-**15**: m.p. 80–81 °C; GC, 25 cm OV-17 programmed from 60 °C (1 min) to 250 °C at 10 °C min^{-1}, retention time = 20·45 min. IR (film): ν_{max} = 3000 (C—H, w), 2900 (C—H, vs), 1630 (C=C, s), 1600 (C=C, m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2·13 (s, 6H, Mes-*o*-Me), 2·30 (s, 3H, Mes-*p*-Me), 3·77 (s, 3H, MeO), 6·07 (s, 1H, =CH), 6·91 (s, 2H, Mes—H), 7·10–7·30 (m, 3H, Ph—H), 7·42 (2H, Ph—H). ^{13}C NMR: δ 20·36 (C-17/C-15), 21·13 (C-16), 60·54 (OMe), 115·68 (C-9), 125·05 (C-6), 125·94 (C-4/C-8), 128·08 (C-5/C-7), 128·27 (C-11/C-13), 128·55 (C-10/C-14), 135·70 (C-3), 136·64 (C-10/C-14), 137·25 (C-12), 138·68 (C-2), 147·43 (C-1). Mass spectrum (EI), *m/z* (relative abundance, assignment): 238 (4, M – Me), 147 (100, MesCO), 119 (28, Mes), 105 (20, PhCO), 77 (16, Ph), 51 (8); (CI): 270 (100, M + NH_4^+), 147 (25, MesCOO). Analysis for (*E*)-**15**: calculated, C 85·67, H 7·99; found, C 85·43, H 8·18%.

Cyclic voltammetry of (*Z*)-*15 and* (*E*)-*15*. A 1 mM solution of the enol ether [(*Z*)-**15** or (*E*)-**15**] in dry CH_2Cl_2 (6 ml) containing tetra-*n*-butyl ammonium hexafluorophosphate (0·1 M) was prepared under nitrogen. Ferrocene was used as a reference ($E_{1/2}$ = 0·304 V vs SCE).[25] At −10 °C quasi-reversible waves were recorded using scan rates between 500 and 10 mV s^{-1}, providing $E_{1/2}$ [(*Z*)-**15**] = 1·23 V vs SCE (lifetime 1·0 s) and $E_{1/2}$ [(*E*)-**15**] = 1·20 V vs SCE (lifetime 2·0 s).

High-temperature equilibration study of enol ethers (Z)-15 and (E)-15. A 0·01 M solution of both enol ethers and *p*-toluenesulphonic acid in chlorobenzene was heated at various temperatures until no change in the (*Z*)-**15** : (*E*)-**15** ratio was observed by GC. The following (*Z*)-**15** : (*E*)-**15** equilibrium ratios were obtained by starting either from (*Z*)-**15** or (*E*)-**15**: 58·6 °C (76 : 24), 70·5 °C (77 : 23), 80·0 °C (75 : 25), 90·6 °C (76 : 24), 106·6 °C (73 : 27), 119·4 °C (74 : 26) and 131·7 °C (74 : 26). A similar experiment at 57 °C with hexane as solvent led to a (*Z*)-**15** : (*E*)-**15** ratio of 75 : 25.

High-temperature study of (Z)-7. Only the signals of (*Z*)-**7** were observed in the ^{1}H NMR and ^{13}C NMR spectra when it was dissolved in DMSO-d_6 under a nitrogen atmosphere at 25 °C. ^{1}H NMR (DMSO-d_6): δ 2·01 (s, 6H, Mes-*o*-Me), 2·25 (s, 3H, Mes-*p*-Me), 6·86 (s, 2H, Mes—H), 7·06 (d, ^3J = 6·5 Hz, 1H, C*H*OH), 7·15–7·25 (m, 5H, Ph—H), 8·93 (d, ^3J = 6·5 Hz, 1H, OH). ^{13}C NMR (DMSO-d_6): δ 19·63 (C-17/C-15), 20·60 (C-16), 114·62 (C-9), 123·89 (C-4/C-8), 124·75 (C-6), 127·74 (C-5/C-7), 128·28 (C-11/C-13), 133·69 (C-3), 135·21 (C-12), 136·48 (C-10/C-14), 139·46 (C-2), 140·26 (C-1).

When the solution was heated under a nitrogen atmosphere for 5 h at 80 °C and analysed at 25 °C by NMR, it displayed two sets of signals in a ratio of 5 : 1. One corresponded to those of (*Z*)-**7**, while the other was ascribed to the isomeric enol (*E*)-**7**. After 24 h at room temperature the ^{1}H NMR spectrum still showed a (*Z*)-**7** : (*E*)-**7** ratio of 5 : 1 in DMSO that increased to 7 : 1 after 72 h. Data for (*E*)-**7**: ^{1}H NMR (DMSO-d_6): δ 2·06 (s, 6H, Mes-*o*-Me), 2·22 (s, 3H, Mes-*p*-Me), 6·45 (d, ^3J = 6·5 Hz, 1H, C*H*OH), 6·86 (s, 2H, Mes—H), 7·06 (m_c, 1H, Ph—H), 7·15–7·25 (m, 2H, Ph—H), 7·37 (m_c, 2H, Ph—H), 9·50 (d, ^3J = 6·5 Hz, 1H, OH). ^{1}H NMR ($CDCl_3$): δ 5·12 (d, 1H, J = 13·5 Hz, OH), 6·41 (d, 1H, J = 13·5 Hz, CH). ^{13}C NMR (DMSO-d_6): δ 19·85 (C-17/C-15), 20·52 (C-16), 111·62 (C-9), 123·88 (C-4/C-8), 124·67 (C-6), 127·06 (C-5/C-7), 127·83 (C-11/C-13), 133·64 (C-3), 135·15 (C-12), 137·74 (C-10/C-14), 140·02 (C-2), 142·33 (C-1). Signals for aldehyde **16** (1%) as described below were also observed.

A ^{1}H NMR spectrum of the (*Z*)-**7**–(*E*)-**7** mixture at 100 °C showed broadening of the OH doublet due to coalescence. (*Z*)-**7**: ^{1}H NMR (DMSO-d_6): δ 2·01 (s, 6H, Mes-*o*-Me), 2·25 (s, 3H, Mes-*p*-Me), 6·86 (s, 2H, Mes—H), 7·06 (s, 1H, C*H*OH), 7·15–7·25 (m, 5H, Ph—H), 8·36 (br s, 1H, OH). (*E*)-**7**: ^{1}H NMR (DMSO-d_6): δ 2·06 (s, 6H, Mes-*o*-Me), 2·22 (s, 3H, Mes-*p*-Me), 6·45 (s, 1H, C*H*OH), 6·86 (s, 2H, Mes—H), 7·06 (m_c, 1H, Ph—H), 7·15–7·25 (m, 2H, Ph—H), 7·37 (m_c, 2H, Ph—H), 9·00 (br s, 1H, OH).

Synthesis of aldehyde 16. Pure enol (*Z*)-**7** was heated at 135 °C in a sealed glass ampoule for 5 h, affording 31% of aldehyde **16**. IR ($CHCl_3$): ν = 2715 (CHO), 1725 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2·21 (s, 6H, Mes-*o*-Me), 2·38 (s, 3H, Mes-*p*-Me), 5·19 (br s, 1H, CH), 7·07 (s, 2H, Mes—H), 7·13–7·41 (m, 5H, Ph—H), 10·03 (br s, 1H, CHO). Although it was possible to separate **16** from enol **7** by HPLC [Merck LiChrosorb RP-18, 7 μm, acetonitrile–water (80 : 20) as eluent] no pure **16** (**16** : **7** = 4 : 1) has been obtained so far, presumably because of follow-up tautomerization. ^{1}H NMR (DMSO-d_6): δ 2·08 (s, 6H, Mes-*o*-Me), 2·24 (s, 3H, Mes-*p*-Me), 5·30 (br s, 1H, CH), 6·85 (s, 2H, Mes—H), 6·97–7·22 (m, 5H, Ph—H), 9·90 (br s, 1H, CHO).

Crystallographic data for (Z)-7. $C_{17}H_{18}O$, M = 238·5, space group $P\bar{4}2_1c$, a = 20·545(5) Å, c = 6·509(2) Å, V = 2747·4(8) Å^3, Z = 8, $\rho_{calc.}$ = 1·15 g cm^{-3}, μ(Mo Kα) = 0·37 cm^{-1}, number of unique reflections = 1012, number of reflections with $I \geqslant 2\sigma(I)$ = 674, R = 0·076, R_w = 0·076, $w^{-1} = \sigma_F^2 + 0{\cdot}000206F^2$.

X-ray crystal structure analysis. Data were measured on a Philips PW1100/20 four-circle computer-controlled diffractometer. Mo Kα (λ = 0·71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 22 centred reflections in the range $10 \leqslant \theta \leqslant 13$ °. Intensity data were collected using the $\omega - 2\theta$ technique to a maximum 2θ of 45 °. In the scan width, $\Delta\omega$, for each reflection was $1{\cdot}00 + 0{\cdot}35 \tan\theta$ with a scan speed of 3·0 ° min^{-1}. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis.[26] After several cycles of refinements the positions of the hydrogen atoms were calculated, and added with a constant isotropic temperature factor of 0·08 Å^2 to the refinement process (all crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 Structure Determination Package). Refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0·3 e Å^{-3} scattered about the unit cell without a significant feaure.

The discrepancy indices,

$$R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$$

were presented with other pertinent crystallographic data.

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