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1-Hydroxymethyl-2,2-diphenylethyl 2,4,6-trimethylphenyl ketone

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.108
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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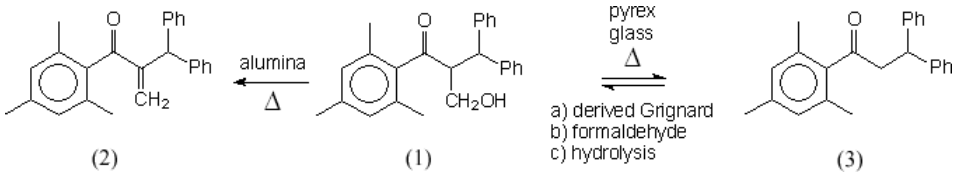
The title compound, $C_{25}H_{26}O_2$, was isolated and characterized as a stable intermediate in the conversion of 2,2-diphenylethyl 2,4,6-trimethylphenyl ketone to its formaldehyde-derived enone.

Comment

The title compound, (1) (Fig. 1), was obtained as an intermediate from which the enone (2) could be obtained by loss of water. Since loss of formaldehyde by a pyrolytic retro-aldol condensation to produce the ketone (3) was an undesirable competing reaction, a study of the behavior of (1) on heating under various conditions was carried out in order to maximize formation of the enone (2). A maximum yield of of 97% of (2) could be obtained by heating (1) in contact with alumina particles. Heating (1) in contact with Pyrex glass particles gave a 66% yield of (3). The synthesis of (1) was carried out by reaction of formaldehyde with the derived Grignard product from compound (3) (see scheme).



(2) (1) (3)

The torsion angle C22—C17—C1—O1 is −68.0 (2)° (Table 1), which compares with the analogous angle of 65.6° for 2,2-diphenylethyl mesityl ketone (Pinkus *et al.*, 1984). For compounds with *tert*-butylmesityl keto groupings, such as 2,4,6-trimethyl-3-pivaloylbenzoic acid (X-ray study; Bear *et al.*, 1973) and *tert*-butylmesityl and *tert*-butylduryl ketones (dipole moment studies; Pinkus & Custard, 1970, 1975), the corresponding angles are 90° or close to it. An H atom on the carbon attached to the carbonyl group causes a decrease in the angle compared with a *tert*-butyl group attached to the carbonyl in the ketones cited in the references. The hydroxyl group is found to hydrogen bond to its symmetry equivalent, holding two molecules together in the crystal structure (Table 2). All of the bond lengths and angles of compound (1) are within expected ranges.

Experimental

Formaldehyde was generated by heating paraformaldehyde (3.1 g, 0.10 mol) in a stream of dry nitrogen and added to approximately 0.075 mol of the vigorously stirred derived bromomagnesium compound of benzalacetomesitylene [(3); 2,2-diphenylethyl 2,4,6-trimethylphenyl ketone]. After all the paraformaldehyde had been

decomposed to formaldehyde by heating, the reaction mixture was stirred vigorously for 6 h and then hydrolyzed in 2 l of cracked ice and approximately 150 ml of a saturated solution of ammonium chloride. The separated aqueous layer was extracted twice with diethyl ether (150 ml × 2). The combined organic layers were extracted twice with distilled water and the organic layer was dried over anhydrous magnesium sulfate, followed by removal of the drying agent by filtration. The solvent was removed by rotary evaporation to obtain a crystalline solid which was recrystallized from cyclohexane (m.p. 426–427 K; yield, 50.9%); analysis calculated for $C_{25}H_{26}O_2$: C 83.76, H 7.31%; found: C 84.01, H 7.49% (Galbraith Labs., Knoxville, TN 39721). IR (cm^{-1}; nujol): 3630, 3590 (O—H stretching); 2940, 2870 (C—H stretching); 1690 (C═O stretching); 1615 (Ar C═C stretching); ^{1}H NMR (60 MHz, hexadeuteroacetone, TMS, p.p.m.): 2.07 (*s, o*-Me), 2.15 (*s, p*-Me), 3.70 (*d*, CH_2), 4.08 (*dt*), 4.63 (*d*, $CHPh_2$), 5.64 (*s*, OH), 6.64 (*s*, *m*-H), 7.04, 7.30 (*m*, Ph_2); ^{13}C (22.50 MHz, hexadeuteroacetone, TMS, p.p.m.): 50.998 [CH(C═O)], 57.48 [$CH(Ph_2)$], 61.43 [CH_2(OH)], 208.842 (C═O).

Crystal data

$C_{25}H_{26}O_2$
M_r = 358.46
Monoclinic, $P2_1/c$
a = 11.7361 (7) Å
b = 10.5700 (7) Å
c = 16.0857 (10) Å
β = 95.574 (3)°
V = 1986.0 (2) Å^3
Z = 4
D_x = 1.199 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4193 reflections
θ = 2.5–26.3°
μ = 0.07 mm^{-1}
T = 273 (2) K
Needle, colorless
0.31 × 0.11 × 0.08 mm

Data collection

Bruker X8 APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.991, T_{max} = 0.994
21 735 measured reflections
4054 independent reflections
3118 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 26.4°
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.108
S = 1.05
4054 reflections
247 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.8613P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2153 (18)	C4—C11	1.528 (2)
O2—C3	1.413 (2)	C4—C5	1.531 (2)
C1—C17	1.512 (2)	C18—C23	1.513 (2)
C1—C2	1.529 (2)	C20—C24	1.508 (2)
C2—C4	1.550 (2)	C22—C25	1.518 (2)
C2—C3	1.556 (2)		
O1—C1—C17	119.98 (13)	C17—C1—C2	118.35 (12)
O1—C1—C2	121.54 (13)		
C22—C17—C1—O1	−68.0 (2)		

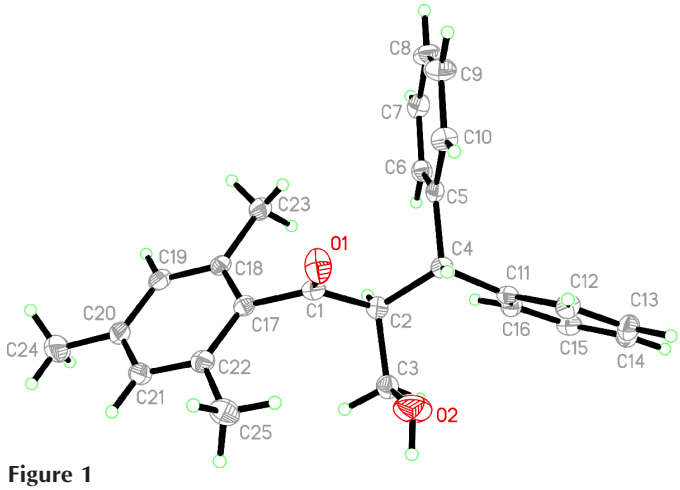


Figure 1
A view of the molecular structure of (1). Displacement ellipsoids are drawn at the 50% probability level

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···O2^{i}	0.83	2.45	2.862 (2)	111

Symmetry code: (i) $1-x, 2-y, -z$.

Atom H1 was located in a difference map and refined. All other H atoms were included in calculated positions (C—H = 0.93 Å) and refined as riding; their isotropic displacement parameters were fixed [U_{iso}(H) = 1.2U_{iso}(C)].

Data collection: *APEX*2 (Bruker, 2003); cell refinement: *APEX*2; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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