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The factors controlling the reaction of (2,4,6-triisopropylphenyl) methyl ketone with Ph_3Al and structure of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$

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Abstract

The reaction of (2,4,6)-tri-isopropylphenyl methyl ketone with tri-phenylaluminium was investigated. $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ was found to be formed exclusively. The title compound has been characterised by NMR and its crystal structure determined by X-ray diffraction study.

Keywords: (2,4,6-Triisopropylphenyl) methyl ketone; Tri-phenylaluminium; X-ray diffraction study

1. Introduction

To improve a reaction selectivity of organoaluminium compounds with organic molecules a detailed knowledge of mechanisms and the factors controlling product distribution is required. The first step towards this aim is understanding how the steric and electronic effects control the co-ordination, and subsequent reactivity of organic molecules with organoaluminium compounds. One of the most exhaustively studied reactions has been that of tri-alkylaluminium compounds with ketones. The reaction can give products of alkyl addition, reduction or enolisation and usually a mixture of products is found [1,2]. With sterically demanding reagents it is possible to force the reaction to occur in a specific manner. Barron and co-workers have investigated a number of reactions of ketones with $AlR_x(BHT)_{3-x}$, species derived from 2,6-di-*tert*-butyl-4-methylphenol (BHT-H) [3–7]. The monomeric nature of the aluminium aryloxide compounds, arising from the steric hindrance of BHT ligand, is the key factor of their specific reactivity. The aryloxide compounds of aluminium have also been used with success in regio- and stereospecific organic syntheses and catalytic systems [8–11].

Reactions of organoaluminium compounds with sterically hindered ketones are less common but can also be selective [12].

Henderson et al. [13] have investigated the reaction of aromatic ketones with Me_3Al recently. They found that disubstitution of the *ortho* positions on the aromatic ring by methyl groups causes the enolisation reaction to be preferred over alkylation due to steric crowding around carbonyl group of the ketons. In this article the reaction pathway was widely discussed.

Herein we report the synthesis and structure of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$, obtained quantitatively from the reaction of hindered ketone and Ph_3Al. The influence of steric hindrance, C–H···O intramolecular H-bond on conformation of the aluminium enolate and ^1H-, ^{13}C-NMR patterns are shown.

2. Results and discussion

2.1. Synthesis and NMR studies

The reaction of Ph_3Al with an equimolar amount of (2,4,6)-tri-isopropylphenyl methyl ketone yields at the first stage $Ph_3Al{\cdot}O{=}C(Me)(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)$ (**I**) com-

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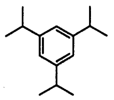
plex (Eq. (1)). The complex has been characterised by IR, ^1H- and ^{13}C-NMR spectroscopy.

$$Ar^*(Me)C{=}O + Ph_3Al \rightleftharpoons \underset{\textbf{(I)}}{Ar^*(Me)C{=}O{\cdot}AlPh_3} \qquad (1)$$

Ar* =



The IR spectrum of complex **I** shows a decrease in the carbonyl stretching frequency from 1698 to 1642 cm^{-1} in comparison to a free ketone. The found $\Delta\nu$ of 54 cm^{-1} is typical for complexed ketones with organoaluminium compounds [5,14].

The ^{13}C-NMR spectra of complex **I** show the carbonyl carbon resonance line at 223.0 ppm. In the uncomplexed ketone a chemical shift of C=O group is at 210.0 ppm.

Complex **I** easily reacts further to give the title compound, $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ (**II**), exclusively (Eq. (2)).

$$\underset{\textbf{(I)}}{2Ar^*(Me)C{=}O\cdot AlPh_3}$$

$$\rightarrow \underset{\textbf{(II)}}{[Ph_2AlO(2,4,6,\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2} + 2PhH \qquad (2)$$

Compound **II** is poorly soluble in toluene and benzene and non-soluble in hexane. The compound **II** is air and moisture sensitive and decomposes quickly giving white powder insoluble in common organic solvents. Cryoscopic molecular weight determination of compound **II** shows that it exists in solution as a dimer ($n = 1.95$).

The ^1H- and ^{13}C-NMR spectra of **II** show an interesting signal pattern of isopropyl groups in high field region. In the ^1H-NMR spectrum three Me doublets of isopropyl groups at 0.59, 0.86 and 1.20 ppm were found. The integration of the signals shows that each doublet contains six protons. The ^{13}C-NMR spectra of compound **II** show three resonances of methyl carbons at 22.7, 24.2 and 26.7 ppm. In contrast, the isopropyl groups of complex **I** showed in the ^{13}C-NMR spectrum two resonance lines of the Me groups at 23.9 and 24.2 ppm.

For complex **I** the ratio of *ortho*- and *para*- Me groups was found to be 2 to 1; i.e. 12H (d) at 1.02 ppm and 6H (d) at 1.10 ppm, respectively.

The observed spectral features indicate that the *ortho*-isopropyl groups of **II** are locked in a non-symmetrical position providing the asymmetric environment which lifts the degeneracy of the Me protons and carbon signals of **II** in the *ortho*- position.

The conclusion is consistent with studies on enantiotopomerisation and conformation of free hindered aryl alkyl ketones carried out by Casarini et al. [15]. A three-Me signal pattern of isopropyl groups in ^{13}C-NMR spectra of (2,4,6)-tri-isopropylphenyl methyl ketone was recorded around −100 °C only. As the temperature was increased, two out of three lines coalesce into a single one, indicating that the magnetic environment is average on the NMR time scale. For (2,4,6)-tri-isopropylphenyl *tert*-butyl ketone three signals of methyl groups in the ^1H-NMR spectrum were found even at 150 °C. Such behaviour was explained by locking the oxygen atom of the carbonyl moiety in the perpendicular plane with respect to the aromatic ring. Hence the presence of a bulky crowded environment near the carbonyl group causes hindered rotation about the Ar*–CO bond.

The analysis of the molecular structure of compound **II** indicates that the barrier to rotation in the studied dimeric form is introduced by two Ph_2Al moieties bonded to the bridging oxygen atom.

2.2. X-ray crystallographic studies of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$

The molecular structure of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The compound crystallises in $P2_1/n$ space group in form of centrosymmetric dimer with two four-coordinate aluminium atoms. The monomeric units are bridged via enolate oxygen atoms O(1) and O(1′) and the central four-membered Al_2O_2 ring in **II** is planar.

The Al–O bond lengths (1.851(2), 1.8687(18) Å) and Al–O–Al and O–Al–O bond angles (100.4 and 79.6(1)°, respectively) are within the ranges reported for other Al_2O_2 rings [see [17] and references therein]. The average value of Al–C bond length in **II** is equal to 1.951 Å.

We were expecting that the π systems present in the molecule: the aromatic ring, the double bond C(1)=C(2) and the oxygen atom O(1), would result in a conjugation depending on their mutual orientation. The presence of the sterically hindering *ortho*-isopropyl groups of the Ar* moiety in **II** forces the sp^2 carbon atom (C(2)) to be in the plane oriented almost perpendicular to the Ar* ring. The dihedral angle between the plane defined as C(1)–C(2)–O(1) and the mean plane of the aromatic ring is 88.3(1)°. For this reason a conjugation cannot occur between the aromatic ring and a *p*-electron pair of oxygen atom O(1) or π-electrons of the C(1)=C(2) bond. On the other hand the relatively short C(2)–O(1) and long C(2)=C(1) bond lengths of 1.401(3) and 1.304(4) Å, respectively, are a consequence of electron delocalisation over this part of the molecule. Unaffected C–O and C=C bonds one can find in $[Me_2Al(\mu\text{-}OCH_2C_6H_2^tBu_3\text{-}2,4,6)]_2$ (1.44 Å [18]) and in $[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2$ (1.24 Å [19]), respectively.

The results worthy of comment are the torsional angles of both *ortho*-^iPr groups and contacts between H(40) and H(80) hydrogen atoms and the O(1) alkoxy oxygen atom. These facts indicate the existence of weak intramolecular C–H···O hydrogen bonds (Fig. 2). The

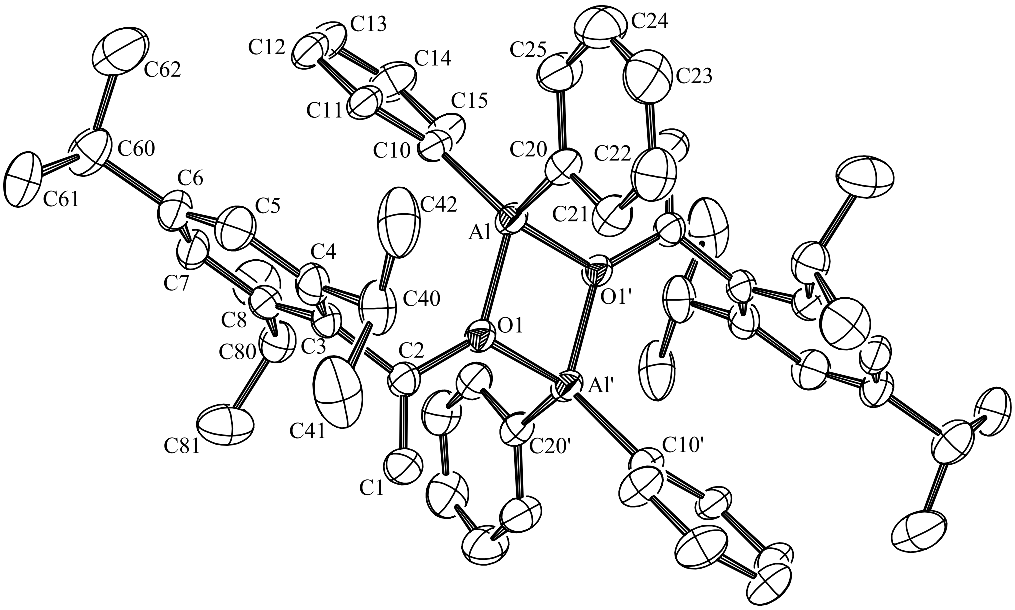


Fig. 1. An ORTEP [16] view of the molecular structure of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ (**II**) showing 40% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ [a]

Bond lengths			
Al–Al′	2.8587(15)	C(2)–C(1)	1.304(4)
Al–O(1)	1.851(2)	C(2)–C(3)	1.494(4)
Al–O(1′)	1.8687(18)	C(2)–O(1)	1.401(3)
Al–C(10)	1.953(3)	Al–C(20)	1.950(3)
Bond angles			
O(1)–Al–O(1′)	79.6(1)	O(1)–C(2)–C(1)	119.9(3)
C(10)–Al–O(1)	116.9(1)	C(3)–C(2)–C(1)	125.0(3)
C(10)–Al–O(1′)	112.9(1)	C(3)–C(2)–O(1)	115.0(2)
C(20)–Al–O(1)	113.6(1)	C(10)–Al–C(20)	117.4(1)
C(20)–Al–O(1′)	110.3(1)		

[a] Atoms labelled with prime belong to the centrosymmetric counterparts of the dimer.

appropriate H···O and C···O distances and C–H···O angles are presented in Table 2. Although observed contacts are rather long, both *ortho*-^{i}Pr groups involved in H-bonds are twisted in a similar fashion. The torsion angles C(3)–C–C–H and C(3)–C–C···O are almost equal (see Table 2), which indicates that the C–H vectors are oriented at the acceptor O atom so as to improve the C–H···O geometry. The similar effect of C–H···O interactions on the torsional conformation of methyl groups was systematically analysed by Steiner [20]. Besides, the influence of intramolecular C–H···O hydrogen bond on the conformation of aluminium aryloxide heterocycles has been published recently [11].

In summary, the formation of a donor–acceptor complex **I** is the first step in the reaction of the studied ketone with Ph_3Al. In the complex **I** due to the Lewis acid nature of an aluminium atom a positive charge on carbonyl carbon atom increases. It causes the Broensted acidity of the studied ketone as well. We suppose that due to the steric crowding around the carbonyl carbon in complex **I** the C=O group is perpendicular to aromatic ring and π electron interaction between the carbonyl group and aromatic ring does not occur. To confirm our assumptions, we have analysed literature data on a structure of aromatic ketones with *ortho*-substituted aromatic ring by alkyl or phenyl groups. The collection of structural data was obtained from the Cambridge Crystallographic Database (CSD version 5.22) using CCDC software [21]. The search was conducted according to the parameters defined in Section 3 and was directed towards unsubstituted, 2-

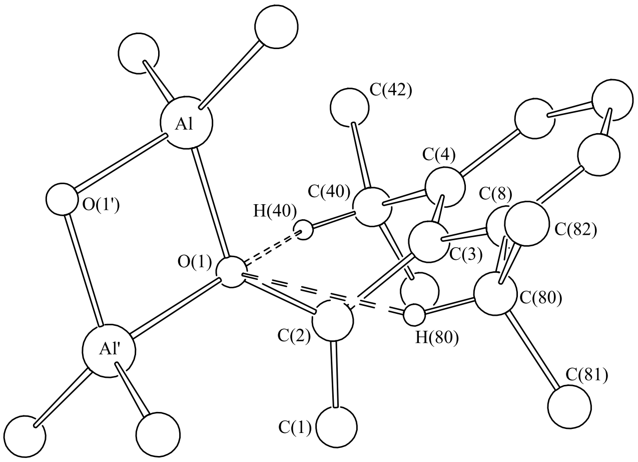


Fig. 2. Structural fragment of **II** showing conformation of alkoxy ligand. Dashed bonds denote hydrogen bonding interactions.

Table 2
C–H···O hydrogen bonding geometry (Å, °)

C–C–H···O(1)	H···O	C···O	C–H···O	C(3)–C–C–H	C(3)–C–C···O
C(4)–C(40)–H(40)	2.87(3)	3.541(4)	127(2)	26.0(19)	23.7(2)
C(8)–C(80)–H(80)	2.87(3)	3.544(4)	128(2)	−24.2(18)	−22.8(2)

monosubstituted and 2,6-disubstituted acetophenone derivatives. The orientation of the C=O carbonyl group was specified by dihedral α angle between the mean plane of the aromatic ring and the plane defined by oxygen and carbon atoms of the C(O)Me group. As we have shown on the scatterplot (Fig. 3), the conformation of acetophenone derivatives is determined by the presence of substituents in *ortho* positions of aromatic ring. For ketones with disubstituted aromatic ring the angles O=C–Ar* of almost 90° are preferred (the average value 79.3°). For unsubstituted aromatic ring a mean value of the angle 5.6° was found. Moreover, the α angle correlates with carbonyl carbon atom–aromatic ring bond length. For the angles about 90° the longest bond lengths of C(O)–Ar have been found.

The studied ketone should be a stronger Broensted acid compared to aromatic ketones in which the π conjugation occurs. For the stronger Broensted acid enolisation reaction is expected to be preferred as discussed by Henderson et al. based on the ab initio molecular orbital calculations [13]. Besides the factors described above, the steric crowding in complex **I** make the approaches of Ph–Al group to carbonyl reacting centre difficult, which again prefers enolisation reaction. For studied reaction of the ketone with Ph_3Al we found that the enolisation proceeds quantitatively.

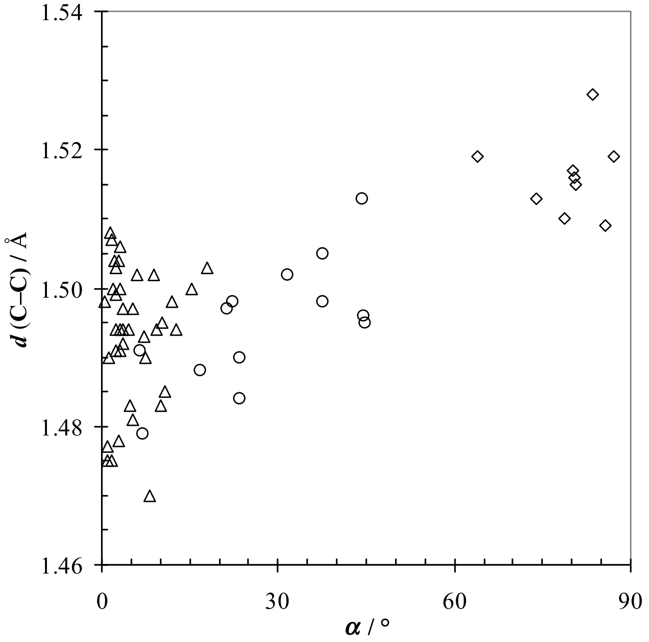


Fig. 3. Scatterplot of the C_{ar}–$C_{carbonyl}$ distance versus the dihedral α angle for acetophenone derivatives. Data retrieved from CSD for *ortho*-unsubstituted (triangles), *ortho*-monosubstituted (circles) and *ortho*-disubstituted (open diamonds) are shown.

3. Experimental

3.1. General procedures

The reactions were carried out under an inert atmosphere using Schlenk line techniques. All the solvents were dried by standard methods. Infrared spectra were obtained using a Carl Zeiss Jena Specord M80 spectrometer. The NMR spectra were taken on a Varian VXR-300 300MHz spectrometer.

3.2. Synthesis of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$

A solution of (2,4,6)-tri-isopropylphenyl methyl ketone (0.7356 g, 2.985 mmol) in toluene (10 ml) was added dropwise to a stirred suspension of tri-phenylaluminium (0.7850 g, 2.978 mmol) in toluene (15 ml). The Ph_3Al dissolved to give clear, light-yellow solution of $Ph_3Al\cdot O{=}C(Me)(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)$ (**I**). The reaction mixture was allowed to stir for 5 days at ambient temperature. During this period crystals of $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ (**II**) are formed. The solution was removed with a syringe and the product (**II**) was washed twice with hexane (5 ml); then dried out under vacuum yielding white crystals of **II**. Yield ~60%.

3.2.1. $Ph_3Al\cdot O{=}C(Me)(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)$ (*I*)

IR (CH_2Cl_2): 1642 cm^{-1}—the complexed $\nu_{C=O}$, 1698 cm^{-1} free $\nu_{C=O}$ of (2,4,6-tri-isopropylphenyl) methyl ketone. ^1H-NMR spectrum (C_6D_6): δ 1.02 (d, 12H, Me), 1.10 (d, 6H, Me), 2.21 (s, 3H, Me), 2.49 (m, 2H, CH), 2.64 (m, 1H, CH), 6.93 (s, 2H, Ar*), 7.32–7.36 and 8.10–8.13 (m, 15H, Ph). ^{13}C-NMR spectrum (C_6D_6): δ 23.9 (Me), 24.2 (Me), 31.6 (Me–C=O), 34.6 (CH), 121.6 (CH, Ar*), 127.6–128.3 (Ph), 138.7 (*para*-C, Ar*), 142.0 (*ortho*-C, Ar*), 146.0 (C, Ar*), 223.0 (C=O).

3.2.2. $[Ph_2AlO(2,4,6\text{-tri-}^iPr\text{-}C_6H_2)C{=}CH_2]_2$ (*II*)

M_w (cryometrically in benzene) 830 ($n = 1.95$). ^1H-NMR spectrum (C_6D_6): δ 0.59 (d, 6H, Me), 0.86 (d, 6H, Me), 1.20 (d, 6H, Me), 2.70 (m, 1H, CH), 3.10 (m, 2H, CH), 4.20 (d, 1H, $H_2C{=}C$), 5.30 (d, 1H, $H_2C{=}C$), 6.86 (s, 2H, Ar*), 7.14–7.30 and 8.81–8.85 (m, 10H, Ph). ^{13}C-NMR spectrum (C_6D_6): δ 22.7 (Me), 24.2 (Me), 26.7 (Me), 31.3 (CH), 34.8 (CH), 100.9 ($H_2\mathit{C}{=}C$), 121.6 (CH, Ar*), 127–129 (Ph), 138.8 (*para*-C, Ar*), 141.3 (*ortho*-C, Ar*), 148.2 (C, Ar*), 151.1 ($H_2C{=}\mathit{C}$).

3.3. X-ray structure determination

Single crystals of **II**, suitable for X-ray diffraction studies, were grown from toluene. A transparent white-pale well-shaped crystal was placed in a thin walled capillary tube (Lindemann glass 0.5 mm) in an inert atmosphere. The tube was plugged with grease, then flame-sealed and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. The selected crystallographic data, the parameters of data collections and refinement procedures are presented in Table 3. The crystal class and the orientation matrix were obtained from the least-square refinement of 41 well-centred reflections randomly selected in the 2θ range 15.6–29.1°. The intensities were collected in the $\omega-2\theta$ mode and corrected for Lorentz-polarisation effects. The structure was solved by direct methods using the SHELXS-97 program [22a] and refined by full-matrix least-squares method against F^2 values (SHELXL-97 [22b]). Neutral-atom complex scattering factors were employed [22c]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Difference Fourier maps calculated at a late stage of the refinement, indicated substantial disorder of the *para*-isopropyl group over two positions (rotated by ~180° about the C(6)–C(60) bond). Both disordered moieties were modelled using similarity restraints for the chemically equivalent C–C distances with refined occupancy factors of 0.70(1) for major conformer. Except for the disordered part of the molecule, all hydrogen atoms were located from the Fourier difference map and isotropically refined.

Table 3
Crystal data, data collection and refinement parameters for [$Ph_2AlO(2,4,6\text{-tri-}^{i}Pr\text{-}C_6H_2)C{=}CH_2]_2$ (**II**)

Empirical formula	$C_{58}H_{70}O_2Al_2$
Formula weight	853.10
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group, number	$P2_1/n$, 14
a (Å)	12.8550(14)
b (Å)	13.9328(17)
c (Å)	15.971(2)
β (°)	112.265(9)
V (Å^3)	2647.2(6)
Z	2
D_{calc} (Mg m^{-3})	1.070
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)
Absorption coefficient (cm^{-1})	0.093
2θ Range (°)	4.0–25.0
Measured reflections	4867
Unique reflections	4656 ($R_{int} = 0.036$)
Reflections with $I > 2\sigma(I)$	2645
Data/parameters/restraints	4656/425/38
Goodness-of-fit (S) [a]	0.962
R_1, wR_2 (all data) [b]	0.1080, 0.1532
R_1, wR_2 ($I > 2\sigma(I)$) [b]	0.0557, 0.1305
Largest difference peak and hole (e Å^{-3})	+0.21 and −0.36

[a] GooF $= S = \{[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_c|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.085P)^2$ where $P = (F_o^2 + 2F_c^2)/3$.

3.4. Cambridge Structural Database search

The collection of structural data was obtained through systematic search of the 5.22 version (October 2001) of the Cambridge Crystallographic Database (CSD) using CCDC software. The searches were performed for *ortho*-unsubstituted, 2-mono- and 2,6-disubstituted aromatic ketones containing –C(Me)=O group. The resulting subsets were sorted and investigated manually. Subsequently, entries with the R factor greater than 0.07 and those with an error flag were rejected. Structures with the following characteristics were also excluded: disordered fragments, charged molecules, fragments with metal coordination and engaged in C=O···H hydrogen bond. Duplicate determinations of the same compound were retained when these represented different polymorphs or structures measured in different temperatures. The dihedral angles α and C–C bond lengths were extracted with the program QUEST.

4. Supplementary material

Listings of crystal and refinement data, atomic coordinates, bond distances and angles, thermal parameters for compound **II** are available from Cambridge Crystallographic Data Centre, CCDC no. 186009. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

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