

## Synthesis and X-Ray Crystal Structures of Some Hindered Polyphenylated Ketones

Derek H. R. Barton, M. Teresa Barros Papoula, Jean Guilhem, William B. Motherwell, Claudine Pascard, and Elise Tran Huu Dau

*Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France*

The synthesis, properties, and X-ray structures of two highly hindered polyphenylated ketones, 2,2,6,6-tetraphenylcyclohexanone and pentaphenylacetone, are described, both being obtained using bismuth(v) chemistry.

We have previously shown that the reaction of a preformed potassium enolate with triphenylbismuth carbonate is a general method for  $\alpha$ -arylation of the carbonyl group.<sup>1</sup> Although controlled mono-arylation can be achieved *via* the intermediacy of a  $\beta$ -keto ester,<sup>1</sup> the enhanced acidity of the  $\alpha$ -proton on a monoarylated ketone usually leads to the facile introduction of a second phenyl group. Thus, for example, reaction of 4,4-dimethylcholest-5-en-3-one (**1**) gave the diaryl-

ated ketone (**2**).<sup>1</sup> Acetophenone was likewise readily converted into phenyl triphenylmethyl ketone.<sup>1</sup> As part of our general interest in the preparation of highly hindered functional groups,<sup>2</sup> we have now extended this facile arylation to cyclohexanone and dibenzyl ketone. Sequential treatment of cyclohexanone with an eight-fold excess of potassium hydride and triphenylbismuth carbonate in tetrahydrofuran gave the polyphenylated ketone (**3**) in virtually quantitative yield (93%)

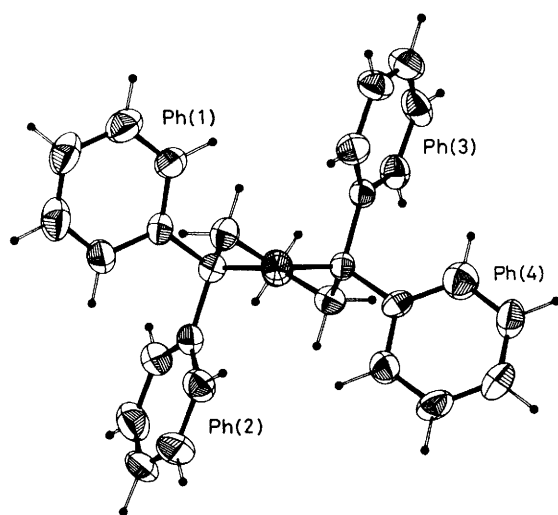
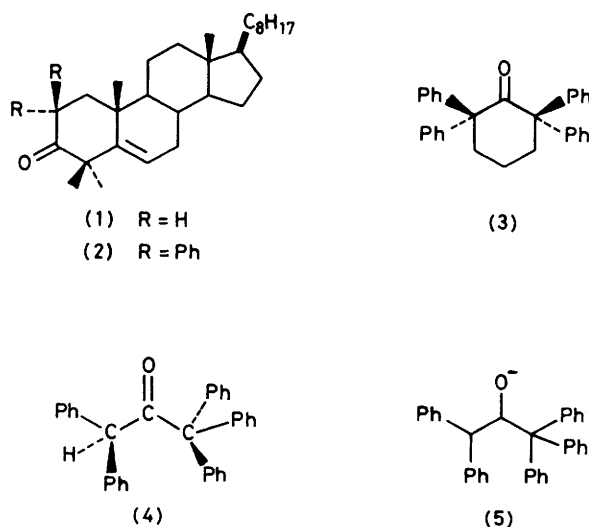


Figure 1. X-Ray crystal structure of (3).

[m.p. 222–224 °C;  $\nu_{\max}$  (CHCl<sub>3</sub>) 1705 cm<sup>-1</sup>]. In an analogous manner, reaction of dibenzyl ketone gave pentaphenylacetone (4) (60%) [m.p. 180–181 °C;  $\nu_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 1710 cm<sup>-1</sup>]. The unknown hexaphenylacetone was not detected in this reaction or in a separate experiment involving treatment of pentaphenylacetone with potassium hydride and triphenylbismuth carbonate. This may be a consequence either of the formation and subsequent stability of the potassium enolate or of the instability of the product ketone. Reduction of pentaphenylacetone with lithium aluminium hydride gave the corresponding alcohol (70%) [m.p. 212–213 °C;  $\nu_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 3550 cm<sup>-1</sup>]. No elimination of triphenylmethyl anion was detected<sup>3</sup> so the alcoholate anion (5) must be stable.

The X-ray analysis of these hindered highly phenylated ketones confirmed their structures and showed a number of interesting conformational effects.<sup>4</sup>

**Crystal data:** (3), monoclinic,  $P2_1/c$ , with  $a = 10.930(2)$ ,  $b = 19.326(3)$ ,  $c = 10.442(2)$  Å,  $\beta = 101.48(2)^\circ$ ,  $Z = 4$ ; (4), triclinic,  $P\bar{1}$ , with  $a = 13.152(3)$ ,  $b = 11.122(2)$ ,  $c = 9.230(2)$  Å,  $\alpha = 112.29(1)^\circ$ ,  $\beta = 89.85(1)^\circ$ ,  $\gamma = 105.49(1)^\circ$ ,  $Z = 2$ .

The experimental data were collected with a Philips 4-circle diffractometer, using graphite-monochromated Cu-K $\alpha$  radi-

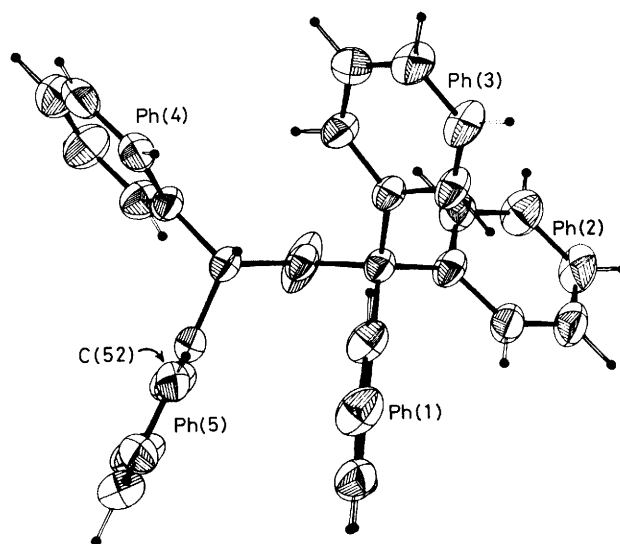


Figure 2. X-Ray crystal structure of (4).

ation ( $\lambda = 1.5418$  Å). From 3948 measured independent reflections, 1835 were significant [ $I > 3\sigma(I)$ ] for (3) and 3507 from 4345 for (4). The structures were solved using local direct methods programs (Riche<sup>5</sup>). Hydrogen atoms were located from Fourier-difference maps and kept at calculated positions. The refinements were performed using the least-squares large-blocks method to a discrepancy factor of 5.4% for (3) and 5.1% for (4).<sup>†</sup> Perspective views of the molecules of (3) and (4) are shown in Figures 1 and 2, respectively, looking down the oxygen-carbon double bond.

The 2,2,6,6-tetraphenylcyclohexanone molecule (3) exhibits non-crystallographic symmetry; a two-fold axis runs through C(4)–C(1)–O. The ring has a twist conformation with C(6)–C(1)–C(2) (and the oxygen atom) in one plane ( $\pm 0.001$  Å), making a torsion angle of 33° with the C(3)–C(4)–C(5) plane. The two phenyl rings on each carbon atom are at right angles to each other [Ph(1)/Ph(2): 86°, Ph(3)/Ph(4): 93.5°]. The molecule is in the most extended conformation with the aromatic rings being as far apart as possible; rings Ph(2) and Ph(3) make a dihedral angle of 62° but point in opposite parallel directions. Rings Ph(1) and Ph(4) are facing each other on each side of the carbonyl group with a dihedral angle of 127°, in such a way that the oxygen electron lone pair orbitals are parallel to their planes at a distance of 2.2 Å. The C=O bond is rather long: 1.215(5) Å.

The most striking feature of the pentaphenyl acetone molecule (4) is the superposition of the phenyl rings Ph(1) and Ph(5). They are in nearly parallel planes [Ph(1)/Ph(5): 20°], and their dihedral angles with the plane of the carbonyl group are 86° for Ph(1) and 114° for Ph(5). The rings Ph(1) and Ph(5) are staggered [see Figure 2] with C(52) above the centre of Ph(1) at a distance of 3.6 Å. The plane of the carbonyl group bisects the ring Ph(2); H(3) is practically coplanar with the C=O group [H(3)–C(3)–C(1)–O: 167°] but the C(3)–H(3)

<sup>†</sup> The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

bond points in an opposite direction. Again, there is no interaction between the electron lone pair orbitals of the oxygen and the phenyl ring Ph(2).

Received, 15th March 1982, Com. 293

### References

- 1 D. H. R. Barton, D. J. Lester, W. B. Motherwell, and M. T. Barros Papoula, *J. Chem. Soc., Chem. Commun.*, 1980, 246 and unpublished results.
- 2 T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2079; D. H. R. Barton, J. D. Elliott, and S. D. Gero, *J. Chem. Soc., Chem. Commun.*, 1981, 1136.
- 3 Cf. D. Seebach and R. Locher, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 957.
- 4 Cf. L. A. Paquette, Y. Hanzawa, G. J. Hefferon, and J. F. Blount, *J. Org. Chem.*, 1982, **47**, 265.
- 5 C. Riche, *Acta Crystallogr., Sect. A*, 1973, **29**, 133.