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3-Benzoyl-1,2,4,5-tetraphenylpentane-1.5-dione. A molecular paddlewheel

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Abstract—Racemic (2*R*,4*R*)-, (2*S*,4*S*)-3-benzoyl-1,2,4,5-tetraphenylpentane-1,5-dione results from the alkali-induced condensation of acetophenone with desoxybenzoin in the presence of air. The structure which resembles that of an irregular five-bladed paddlewheel is confirmed by X-ray crystallography.

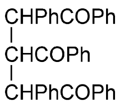
1. Introduction

Desoxybenzoin **4** and acetophenone were reported by Klingemann[1] to react together in ethanolic potassium hydroxide in the presence of air to give a compound $C_{36}H_{28}O_3$. Callow and Hill[2] later suggested that this is the 'phenacylidenedideoxybenzoin' **1** but their arguments, based solely on C and H analyses and a somewhat dubious postulated reaction sequence, appeared to us to be inconclusive and we have therefore reinvestigated the reaction.

2. Results and discussion

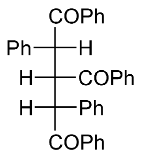
The major product, for which we confirmed the molecular formula $C_{36}H_{28}O_3$, proved to be a racemic mixture of the (*R*,*R*)- and (*S*,*S*)- forms of the triketone **1** (shown as their Fischer projections **1a** and **1b**). The NMR spectrum exhibits signals for 25 aromatic and three aliphatic protons the latter appearing from their chemical shifts and coupling constants to be attached to three adjacent carbon atoms each of which is linked to a carbonyl group as in the part structure **2**. The coupling constants J_{ab} and J_{bc}, each 10 Hz, are consistent with a *transoid* arrangement in each case. Of the three signals, that for H_b lies at lowest field suggesting that this proton is further deshielded by the nearby β-carbonyl groups. The different shifts for H_a and H_c establish that they are in different environments and that the molecule cannot be symmetrical. A 'Catalin' model shows that the presence of the five phenyl groups produces an exceptionally crowded molecule.

To establish the conformational details of the molecule we performed an X-ray crystal structure determination, details of which are given in Section 3. The compound crystallises in the space group *Pc* with two chemically identical but crystallographically independent molecules. The molecules selected for inclusion in the asymmetric unit have, by choice, opposite chirality, and Figure 1 shows one of them

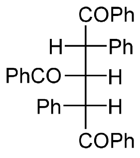


$$\begin{array}{l}\mathrm{CHPhCOPh}\\ |\\ \mathrm{CHCOPh}\\ |\\ \mathrm{CHPhCOPh}\end{array}$$

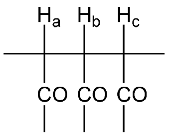
1: *rac*



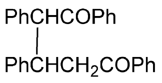
1a: *RR*



1b: *SS*



2



$$\begin{array}{l}\mathrm{PhCHCOPh}\\ |\\ \mathrm{PhCHCH_2COPh}\end{array}$$

3

Keywords: ketone; autoxidation; condensations; trione; X-ray crystal structure.

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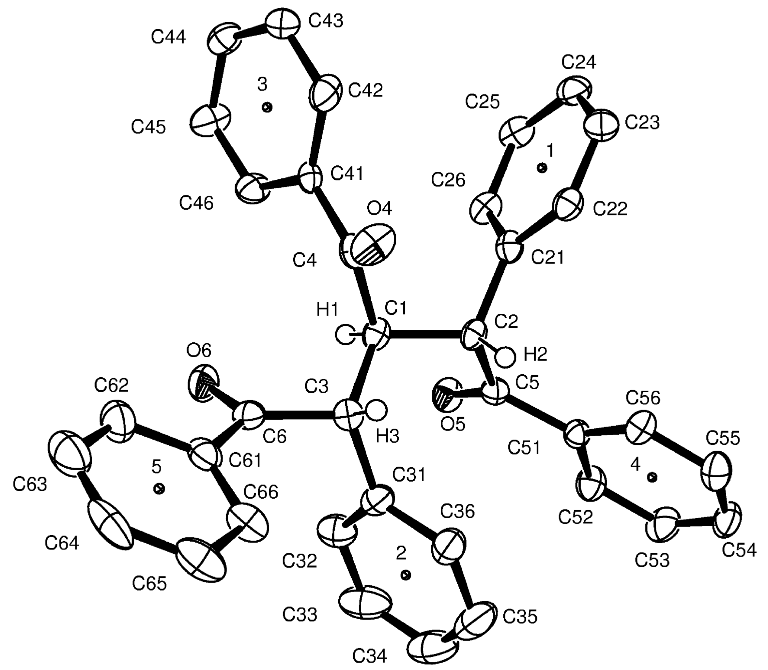
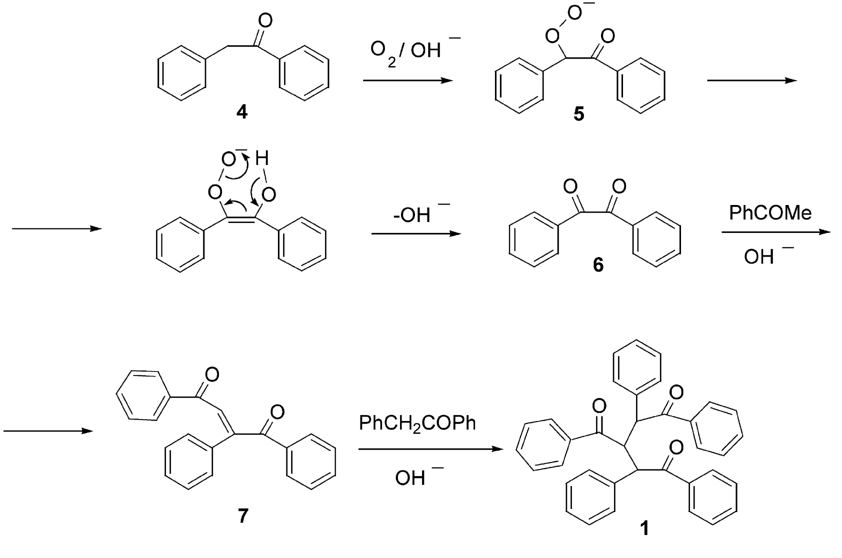


Figure 1. The (2R,4R) molecule, molecule A, showing the atom labelling scheme which applies equally to the (2S,4S) enantiomer, molecule B. Aryl hydrogen atoms have been omitted for clarity. Ring centroids (small circles) are designated numerically only. Aromatic C–C, aliphatic C–C and C=O bond lengths are in the ranges 1.368(6)–1.399(5), 1.480(4)–1.557(4) and 1.216(3)–1.228(3)Å, respectively, for both molecules.

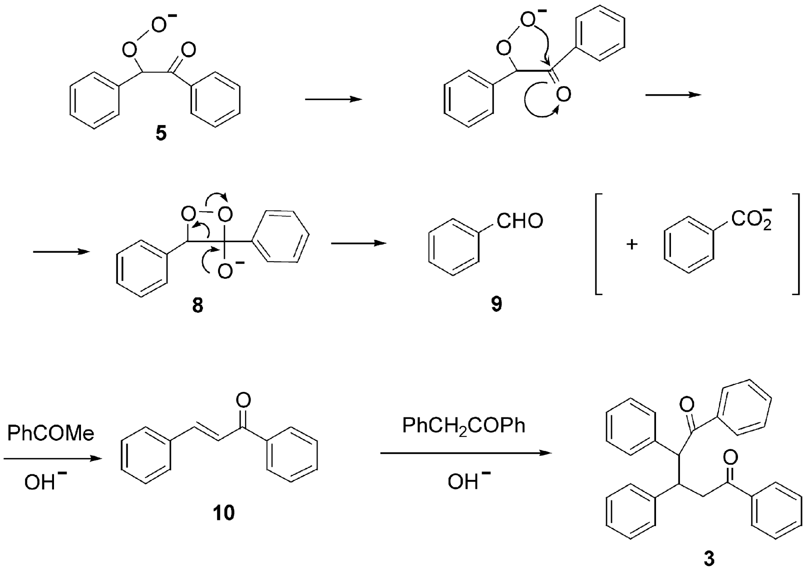
and the labelling scheme common for both. The bond lengths and angles are entirely as expected for a molecule of this kind, which in this case, takes the form of an irregular five-bladed paddlewheel, the five aromatic rings being steeply inclined to the general plane of the molecule. There is no intramolecular interaction between the well separated phenyl rings, the shortest distance between ring centroids of 4.370(2)Å being well in excess of that (~3.5 Å) typically associated with $\pi\cdots\pi$ interaction. There are, however, a number of intermolecular C–H$\cdots\pi$ and C–H$\cdots$O interactions.

In both enantiomers, the proton H1, corresponding to H_b above, is adjacent to the carbonyl groups at C5 and C6 consistent with the marked downfield shift in its NMR signal noted earlier. The environments of protons H2 and H3, corresponding to H_a and H_c above, clearly differ e.g. in terms of the number and proximity of nearest neighbour phenyl groups. Thus H2 has three H/phenyl contacts, to ring centroids 1, 2, and 4, of less than 3.9 Å while H3 has only two, to centroids 2 and 5, in the same range. In both cases the protons lie within the deshielding region of each ring. This is in conformity with the observed NMR signals suggesting that the molecule retains a similar conformation in solution.

A second, minor product was obtained from the desoxybenzoin–acetophenone reaction by Callow and Hill[2] who suggested that it was an isomer of the triketone **1**. We did not find this in our own preparation but instead succeeded in



Scheme 1.



Scheme 2.

isolating a very small quantity of a product $C_{29}H_{24}O_2$ which we identified as the diketone **3** by comparison with an authentic specimen prepared[3] from desoxybenzoin **4** and 1,3-diphenylpropenone **10**.

The formation of the above products appears to be a consequence of the initial ready autoxidation of desoxybenzoin **4** in alkaline solution (Scheme 1) to form the alkylperoxide ion **5** which can lose hydroxide with the production of benzil **6**. Reaction of this with acetophenone gives the enedione **7** which finally undergoes conjugate addition of desoxybenzoin **4** to form the triketone **1**. The alternative mode of decomposition of the alkylperoxide ion **5**, possibly via the dioxetan **8** shown in Scheme 2, provides benzaldehyde **9** and a benzoate ion. Reaction of the former with acetophenone produces the enone **10** which undergoes conjugate addition of desoxybenzoin to give the diketone **3**. Support for these pathways comes from the high (75%) yield of the triketone **1** which results from the alkali-induced reaction of benzil with acetophenone and desoxybenzoin in the *absence* of oxygen and from the ready reaction[3] of the enone **10** with desoxybenzoin under similar conditions to give the diketone **3**.

The shape of the triketone **1** coupled with its ease of preparation make it of potential interest as a hub in the formation of discotic liquid crystals.

3. Experimental

NMR spectra were measured in $CDCl_3$ at 400 MHz on a Varian Unity Inova or at 250 MHz on an A. C. Bruker 250 instrument using, respectively, residual $CHCl_3$ (7.27 ppm) and tetramethylsilane as internal standards. FTIR spectra were measured with an ATI Mattson Genesis spectrophotometer for KBr discs and UV absorption spectra with a Perkin–Elmer Lambda 15 for methanolic solutions. Mass spectra were obtained by EI at 70 eV with an AEI MS30 spectrometer or by ES using a Finnigan Navigator. TLC was performed using Merck Kieselgel GF_{254}.

3.1. Reaction of desoxybenzoin with acetophenone

3.1.1. In the presence of oxygen. A solution of potassium hydroxide (2 g, 35.7 mmol) in ethanol (100 ml) was added to a solution of desoxybenzoin (5 g, 25.5 mmol) and acetophenone (3 g, 25.0 mmol) in the same solvent (50 ml) and the mixture was kept for one week at room temperature with free access of air and occasional stirring. The resulting solid was collected, washed with ethanol and then with water to remove potassium compounds and crystallised from ethanol to give racemic (2*R*,4*R*)-, (2*S*,4*S*)-3-benzoyl-1,2,4,5-tetraphenylpentane-1,5-dione **1a** and **1b** (1.516 g, 2.98 mmol; 23%) as colourless monoclinic crystals mp 198–199°C (lit.,[2] 199–200°C) [Found: C, 85.15; H, 5.52%, $(M+H)^+$ (ES), 509.0. $C_{36}H_{28}O_3$ requires C, 85.01; H, 5.55%, (M+H), 509.2. Found: $(M-H_2O)^+$, 490.1953. $C_{36}H_{26}O_2$ requires M, 490.1953]; *m*/*z* 490 (0.2%, $M-H_2O$), 403 (2, M−PhCO), 386 (3, 403-OH), 313 (9, M−PhCHCOPh), 300 (7, $M-C_{15}H_{12}O$), 105 (100, PhCO), and 77 (23, Ph); λ_{max}/nm 251 (log ε 4.538); ν_{max}/cm^{-1} 1670 (aromatic C=O); δ_H 5.00 (1H, d, *J*=10 Hz, CHC*H*Ph), 5.44 (1H, d, *J*=10 Hz, CHC*H*Ph), 5.83 (1H, dd, *J*=10, 10 Hz, CHC*H*CH), 6.80–7.13 (8H, m, ArH), 7.13–7.53 (13H, m, ArH) and 7.73–7.91 (4H, m, ArH). Acidification of the aqueous washings afforded benzoic acid (1.69 g, 8.2 mmol), mp 121°C, identical with an authentic specimen.

Concentration of the ethanolic mother-liquors gave a solid which on being subjected to repeated TLC using chloroform gave 1,2,3,5-tetraphenylpentane-1,5-dione **3** (5 mg, 0.04 mmol) identical (MS, NMR) with an authentic specimen mp 194–196°C (lit.,[3] 189°C) [Found: M^+ (EI), 404. Calcd for $C_{29}H_{24}O_2$: M, 404.2. Found: $(M+H)^+$ (ES), 405.6. Calcd for $C_{29}H_{25}O_2$: M, 405.2]; *m*/*z* 404 (0.4%, M), 284 (4, $M-PhCOCH_3$), 196 (13, $PhCOCH_2Ph$), 180 (25, PhCH=CHPh), 105 (100, PhCO) and 77 (25, Ph); δ_H 2.92 (1H, dd, *J*=3.5, 16.4 Hz) and 3.10 (1H, dd, *J*=10.2, 16.4 Hz) (both $CHCH_2CO$), 4.26 (1H, ddd, *J*=3.5, 10.2, 10.8 Hz, $CHCHCH_2$), 5.05 (1H, d, *J*=10.8 Hz, PhCOC*H*CH), 6.88–7.36 (14H, m, ArH), 7.36–7.42 (2H, m, ArH), 7.49–7.54 (2H, m, ArH) and 7.65–7.70 (2H, m, ArH)

3.1.2. With benzil in the absence of oxygen. A solution of potassium hydroxide (2 g, 35.7 mmol) in ethanol (100 ml) was added to a solution of desoxybenzoin (2.5 g, 12.7 mmol), acetophenone (3 g, 25.0 mmol), and benzil (2.5 g, 11.9 mmol) in the same solvent (50 ml) under nitrogen and kept out of contact with oxygen for seven days at room temperature. The resulting solid was collected, washed successively with ethanol, water, and ether and crystallised from ethanol to give the triketone **1** (4.53 g, 8.93 mmol, 75%) identical (mp mixed mp and IR) with that described above.

3.2. X-ray structure determination

Crystal data of triketone **1**: $C_{36}H_{28}O_3$, M=508.58, monoclinic, space group Pc (no. 7), a=17.8644(6) Å, b=13.1829(3) Å, c=11.7387(3) Å, β=106.2220(10)°, V=2654.45(13) Å^3, Z=4 (Z^1=2), D_c=1.273 Mg/m^3, λ=0.71073 Å, μ=0.080 mm^{-1}, T=120 K. X-ray data for a colourless rod 0.22×0.04×0.04 mm^3 were obtained with the Enraf Nonius KappaCCD area detector diffractometer of the EPSRC's Crystallography Service at Southampton. The data were corrected for absorption using SORTAV:[4,5] 15,121 reflections were collected, 4837 (merged) unique, R(int)=0.056. The structure was solved by direct methods with SHELXS-86[6] and refined by least squares on merged (MERG 3) F^2 with SHELXL-97[7] Merging of the data due to the absence of any atom of higher atomic number than that of oxygen leaves the absolute structure (the direction of the polar axis c) indeterminate. Nevertheless refinement proceeded smoothly to the values given with all hydrogen atoms placed in calculated positions and refined using a riding model. In the final stages the refinement (703 parameters) converged to $R1$=0.0427 [for 3915 observed reflections with $I>2\sigma(I)$] and $R1$ and $wR2$ (for all 4837 reflections) 0.0635 and 0.0862 respectively.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 206174. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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