Synthesis and X-Ray Structure of *cis*-4b,9b-Diphenyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene-5,10-dione

Baburao M. Bhawal, Abdul Rakeeb Desmukh, Hongming Zhang, Subhash P. Khanapure and Edward R. Biehl*

Department of Chemistry, Southern Methodist University, Dallas, TX 75275, USA

The X-ray structure of the title compound **3** and a possible mechanism for its formation from the reaction of bromobenzene and the trimethylsilyl enolate of methyl phenylacetate **2** with lithium diisopropylamide in tetrahydrofuran are presented.

Recently, we treated bromobenzene with the trimethylsilyl enolate of methyl phenylacetate **2** under typical aryne-forming conditions [*i.e.* lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at −70 °C for 10 min then at room temperature for 1 h]. After proton quench and the usual work-up of the reaction mixture, a crystalline solid (20%) was obtained as one of the products, which was identified as the title compound **3**; m.p. 288–289 °C, IR ($CHCl_3$) 1710 cm^{-1}, ^1H NMR ($CDCl_3$) δ 6.64 (m, 4 H), 6.95 (m, 6 H), 7.75 (m, 2 H), 7.83 (m, 4 H) and 7.99 (m, 2 H). Obtaining a fused alicyclic ring junction from a base-mediated reaction of a halogenoarene and ester enolate is unprecedented.

The structure of **3** was further confirmed by single-crystal X-ray analysis† from which the ORTEP[1] drawing (Fig. 1) shows the presence of a *cis* alicyclic ring junction in spite of the steric bulk of the *cis*-4b and 9b phenyl groups. Preliminary theoretical calculations estimate the difference in energy content between the more stable *cis*-diphenyl **3** and the less stable *trans*-diphenyl diastereoisomer to be approximately 16 kcal mol^{-1} (1 cal = 4.184 J).[2]

Although a detailed understanding of the reaction mechanism must await additional investigation, radicals are probably involved in at least one of the steps to account for the construction of the 4b,9b carbon–carbon bond in **3**. A possible mechanism shown in Scheme 1, consists of the addition of radical **2a**, perhaps generated by trace amounts of oxygen remaining in the THF solvent, to **1** to give the cycloadduct **4**. The yield of **3** is reduced, but not eliminated, when the reaction is carried out in degassed THF. Solutions containing strong base are apt to give oxidation products if traces of oxygen are present. The reaction of bromobenzene with methyl phenylacetate and LDA gives normal aryne products, indicating that the trimethylsilyl enolate is required for the formation of compound **3**. For convenience, we have shown

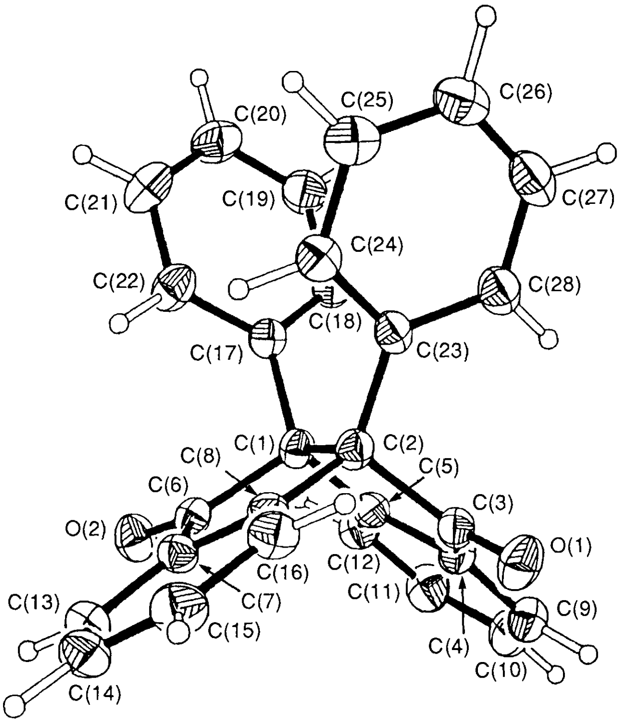
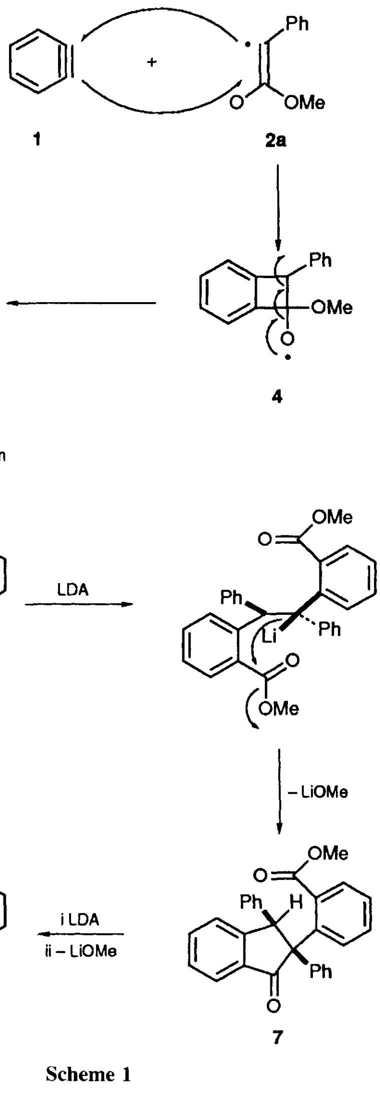


Fig. 1 ORTEP drawing of compound **3**



Scheme 1

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† *Crystal data* for **3**: $C_{28}H_{18}O_2$, M = 386.45, monoclinic, space group $P2_1/n$, a = 8.285(3), b = 14.708(6), c = 16.325(6) Å, β = 92.93(3)°, U = 1987(1) Å^3, Z = 4, D_c = 1.29 g cm^{-3}. R = 0.030 for 2192 reflection [$I \geq 3\sigma(I)$ 2.50° ≤ 2θ ≤ 46.00°]. Intensity data were collected on a Nicolet R3m/v diffractometer with graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods with program package SHELXTL-*PLUS* (G. M. Sheldrick, Structure Determination Softaware Programs; Nicolet Instrument Corp., USA, 1988) and refined by full-matrix least-squares analysis using anisotropic thermal parameters for all non-H atoms. All hydrogen atoms were located from difference maps and their positions were refined with fixed U = 0.08 Å^2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the cycloaddition occurring in one step; it probably is a two-step process given the diradical nature that benzyne exhibits in [2 + 2] cycloadditions with certain alkenes.[3] Adduct **4** then undergoes ring opening to the stabilized benzyl radical **5** which then dimerizes to the *anti* diphenylethane adduct **6**. Successive deprotonation by LDA and cyclization of **6** yields the *cis*-diphenylcyclopentanone **7**, which then undergoes a similar two-step process to give compound **3**. In a separate experiment, methyl 2-(phenylmethyl)benzoate was treated with LDA using dry, but not 'degassed' THF to see if the anion of the methyl ester was converted to radical **5** and subsequently to **3** under the reaction conditions used in the original experiment. That **3** was not formed indicated that the anion derived from **5** was not an intermediate in that reaction.

Work is in progress to determine the scope of the pentalene synthesis, and the results will be reported in due course.

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