The Photocyclization of 3,3′-Diphenyl-2,2′-bi-1*H*-indene-1,1′-dione

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The photocyclization of the title compound afforded 14-hydroxy-4b-phenylbenz[*c*]indeno[2,1-*a*]fluoren-13-(4b*H*)-one, which is easily isomerized to 4b,13b-dihydro-4b-phenylbenz[*c*]indeno[2,1-*a*]fluorene-13,14-dione. The hydrogenation of both compounds gave *anti*-4b,8b,13a,13b-tetrahydro-4b-phenylbenz[*c*]indeno[2,1-*a*]fluorene-13,14-dione.

Although the photooxidative cyclizations of stilbenes[1] and 2-styrylthiophenes[2] to phenanthrenes and naphtho-[2,1-*b*]thiophenes respectively have been proposed to proceed *via* 4a,4b-dihydrophenanthrene and 9a,9b-dihydronaphtho[2,1-*b*]thiophene intermediates, such intermediates have not yet been isolated because of their extreme instability. Recently, though, Doyle *et al.*[3] have isolated the keto-form of the 4a,4b-dihydrophenanthrene intermediate in the photocyclization of 3,4-bis-(*p*-hydroxyphenyl)-3-hexene, and Cuppen and Laarhoven[4] have clarified that this photocyclization proceeds in the first excited state and then in a conrotatory manner.

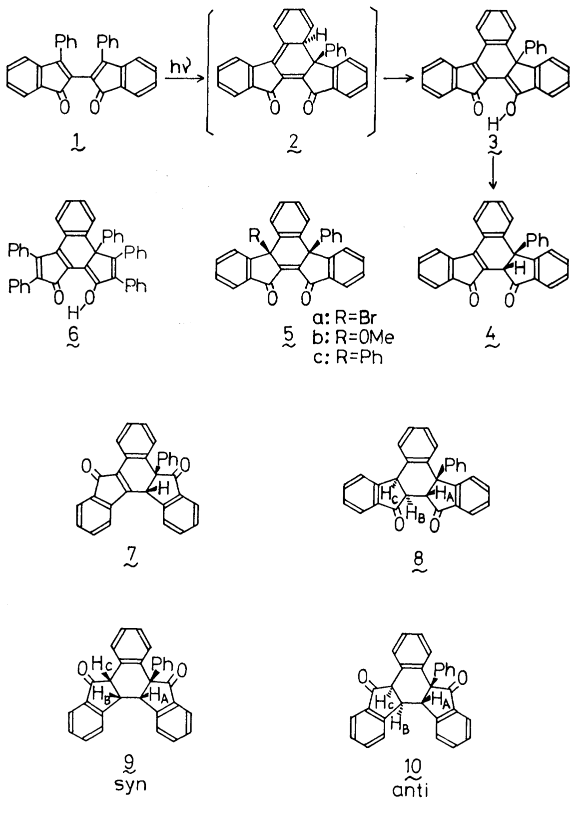
The hypothetical photocyclization product (**2**) of 3,3′-diphenyl-2,2′-bi-1*H*-indene-1,1′-dione (**1**) is expected to be isolable, because **2** has a highly conjugated enone structure, and because the conditions are unfavorable for the elimination of benzene from **2**.

The photolysis of **1**, however, gave a proton-migrated isomer of **2**, 14-hydroxy-4b-phenylbenz[*c*]indeno[2,1-*a*]fluoren-13(4b*H*)-one (**3**). We will report on this photocyclization and an some reactions of **3**.

The irradiation of **1** in benzene for 20 h afforded **3**[5] as blue-black prisms in a 70% yield. Although the νOH band of **3** was not observed, presumably because of a strong intramolecular hydrogen bond, an OH proton signal appeared at δ 9.93. The UV spectral data of **3** (604 nm (ε 2800)) were comparable to those of the analogous compound, **6** (626 nm (ε 4000)).[6,7] The UV spectral data of the acetate of **3** (513 nm (ε 2700)) were also comparable to those of the acetate of **6** (535 nm (ε 3250)).[6] It has previously been reported that the heating of 3,3′,4,4′,5,5′-hexaphenyl-2,2′-bi-2,4-cyclopentadiene-1,1′-dione in boiling benzophenone affords **6** in a 70% yield.[7] However, the heating of **1** under these conditions did not give **3**, and **1** was recovered unchanged. In contrast to the thermal stability of **6**, **3** was easily converted into 4b,13b-dihydro-4b-phenylbenz[*c*]indeno[2,1-*a*]-fluorene-13,14-dione (**4**) by heating in boiling toluene. This ketonization of **3** was performed more easily by treating it with acid. The phenyl group and the hydrogen atom marked in **4** probably bear a *syn* relationship to each other, because the signal due to this hydrogen atom was at a higher magnetic field (δ 4.25), and because the spectral data of **4** were comparable to those of **7** of the *syn*-form.[8]

The treatment of **3** and **4** with Br_2 afforded 4b,8b-dihydro-8b-bromo-4b-phenylbenz[*c*]indeno[2,1-*a*]fluorene-13,14-dione (**5a**) both in 93% yields, on treatment with $AgClO_4$ in MeOH this substance was converted into its methoxy derivative (**5b**). The spectral data of **5a** and **5b** were comparable to those of **5c**.[9] The hydrogenation of **3** and **4** over Pd–C gave *anti*-4b,8b,13a,13b-tetrahydro-4b-phenylbenz[*c*]indeno[2,1-*a*]fluorene-13,14-dione (**8**) in 50 and 25% yields respectively. These hydrogenations of **3** and **4** were performed more easily in 55 and 69% yields respectively, using the recently reported reagent, Zn–$ZnCl_2$–EtOH.[10] Interestingly, this reagent was also effective for the conversion of **5b** and the acetate of **3** into **8** in 48 and 44% yields respectively.

The *anti*-relationship between the indanone rings of **8** was determined by comparing its NMR spectral data with those of **9** of the *syn*-configuration[11] and of **10** of the *anti*-configuration, which had been prepared by the hydrogenation of **7**. The NMR spectral data of **8** (δ 4.01 (d, $J_{BC}=8$ Hz, H_B), 4.07 (s, H_A), 4.92 (d, H_C)) were comparable to those of **10** (δ 4.12 (d, $J_{BC}=$ 6.5 Hz, H_C), 4.61 (s, H_A), and 4.67 (d, H_B)), but not to those of **9**, which shows complex signals of an ABX pattern.[11] The absence of spin-spin coupling between H_A and H_B in **8** and **10** is probably due to the fact that the dihedral angle between the hydrogen bonds is nearly 90°. The examination of the molecular models supports this idea.



Experimental

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$ respectively. The mass spectra were measured with an ionization energy of 75 eV.

*Photocyclization of **1**.* A solution of **1** (2 g) in benzene (400 ml) was irradiated with light from a 400-W high-pressure mercury lamp, filtered through Pyrex glass, at room temperature under N_2 for 20 h. The crude crystals after the evaporation of the solvent were recrystallized from AcOEt to afford **3** as blue-black prisms; 1.4 g (70%); mp 194 °C (dec). IR: 1670, 1615, 1590, 1560, and 1520 cm^{-1}; $\lambda_{\max}$: 297 (35700), 373 (13800), and 604 nm (ε 2800); NMR δ: 7.0—8.4 (m, Ar, 17H) and 9.93 (s, OH, 1H); MS *m/e* (rel intensity): 410 (M^+, 100), 333 (M^+-Ph, 70), and 305 (333$-$CO, 21).

Found: C, 87.51; H, 4.35%. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42%.

The keeping of a solution of **3** (0.1 g) in Ac_2O (0.5 ml)-pyridine (2 ml) at room temperature for 12 h afforded, after recrystallization from CCl_4, the acetate of **3** as purple prisms; 0.105 g (95%); mp 254—256 °C; IR: 1760, 1695, and 1190 cm^{-1}; $\lambda_{\max}$: 285 (30500), 307 (18800), and 513 nm (ε 2700); NMR δ: 2.58 (s, AcO, 3H) and 7.1—8.2 (m, Ar, 17H).

Found: C, 84.74; H, 4.30%. Calcd for $C_{32}H_{20}O_3$: C, 84.94; H, 4.46%.

*Conversion of **3** into **4**.* HCl gas was bubbled through a solution of **3** (0.5 g) in $CHCl_3$ (50 ml) at 0 °C for 10 min. Recrystallization from AcOEt afforded **4** as orange prisms; 0.45 g (90%); mp 245—247 °C (dec); IR: 1710 and 1695 cm^{-1}; $\lambda_{\max}$: 292 (11300), 332 sh (4700), and 430 nm (ε 1700); NMR δ: 4.25 (s, CH, 1H) and 6.9—8.5 (m, Ar, 17H); MS *m/e* (rel intensity): 410 (M^+, 100), 333 (M^+-Ph, 98), and 305 (333$-$CO, 28).

Found: C, 87.55; H, 4.52%. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42%.

The heating under reflux of a solution of **3** (0.1 g) in toluene (10 ml) under N_2 for 24 h afforded, after recrystallization from AcOEt, **4**; 0.06 g (60%).

*Preparation of **5a** and **5b**.* To a solution of **3** (0.69 g) in $CHCl_3$ (25 ml), Br_2 (0.4 g) was added, and then the mixture was stirred for 10 min. Recrystallization from AcOEt-$CHCl_3$ afforded **5a** as yellow prisms; 0.764 g (93%); mp 209—210 °C; IR: 1740 and 1700 cm^{-1}; $\lambda_{\max}$ 301 nm (ε 15600); MS *m/e* (rel intensity): 490 and 488 (M^+, 5) and 409 (M^+-Br, 100).

Found: C, 73.35; H, 3.41%. Calcd for $C_{30}H_{17}O_2Br$: C, 73.63; H, 3.50%.

The treatment of **4** (0.18 g) in $CHCl_3$ (10 ml) with Br_2 (0.1 g) as above afforded **5a**; 0.2 g (93%).

The treatment of a solution of **5a** (0.27 g) in MeOH (10 ml)-tetrahydrofuran (10 ml) with $AgClO_4$ (0.5 g) afforded, after recrystallization from AcOEt, **5b** as yellow needles; 0.22 g (91%); mp 258—260 °C; IR: 1710 and 1640 cm^{-1}; $\lambda_{\max}$: 302 nm (ε 17400); NMR δ: 2.29 (s, OMe, 3H) and 6.9—8.3 (m, Ar, 17H); MS *m/e* (rel intensity): 440 (M^+, 20) and 409 (M^+-OMe, 100).

Found: C, 84.27; H, 4.44%. Calcd for $C_{31}H_{20}O_3$: C, 84.53; H, 4.58%.

*Hydrogenation of **3**, **4**, and **7**.* A mixture of **3** (0.2 g), tetrahydrofuran (30 ml), and a catalytic amount of Pd-C was stirred under H_2 at room temperature for 12 h. The filtrate after the filtration of Pd-C was evaporated to dryness to leave crude crystals. The recrystallization of the crude crystals from AcOEt afforded **8** as colorless prisms; 0.11 g (50%); mp 233 °C; IR: 1720 cm^{-1}; $\lambda_{\max}$ 247 (23200) and 295 nm (ε 4200); NMR δ: 4.01 (d, $J_{BC}=8$ Hz, H_B, 1H), 4.07 (s, H_A, 1H), 4.92 (d, $J_{BC}=8$ Hz, H_C, 1H), and 6.5—8.0 (m, Ar, 17H); MS *m/e* (rel intensity): 412 (M^+, 100), 335 (M^+-Ph, 16), and 307 (335$-$CO, 15).

Found: C, 87.63; H, 4.66%. Calcd for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89%.

The same treatment of **4** as described above afforded **8** in a 25% yield.

The same treatment of **7** as described above afforded **10** as pale yellow needles in a 58% yield; mp 263—265 °C; IR: 1700 cm^{-1}; $\lambda_{\max}$: 249 (23800), 290 (4600), 326 (800), and 340 nm (ε 800); NMR δ: 4.12 (d, $J_{BC}=6.5$ Hz, H_C, 1H), 4.61 (s, H_A, 1H), and 4.67 (d, $J_{BC}=6.5$ Hz, H_B, 1H).

Found: C, 87.55; H, 4.68%. Calcd for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89%.

The treatment of **3**, **4**, and **7** with Zn-$ZnCl_2$-EtOH by the previously reported procedure[10] afforded **8** (55), **8** (69), and **10** (69%) respectively.

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