92%): mp 168 °C (from cyclohexane–benzene); ^{1}H NMR δ 1.86 (3 H, d, J = 7 Hz), 2.12 (6 H, s), 2.56 (3 H, s), 4.63 (1 H, q, J = 7 Hz), 6.22 (1 H, s), 7.3–8.0 (5 H, m). Anal. Calcd for $C_{20}H_{19}Cl_2NO_3S$: C, 56.61; H, 4.52; N, 3.30. Found: C, 56.80; H, 4.41; N, 3.13.

Reaction of 1 with Allene 2b. A solution of 1 (5.0 g) and **2b** (4.3 g) in carbon tetrachloride (220 mL) was refluxed for 21 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column (0.7 kg) with benzene as eluent. First fractions gave some solid material (0.4 g; ^{1}H NMR δ 2.0–2.8) followed by 3,3′-bis(3,5-dichloro-2,4,6-trimethylphenyl)-5-methyl-5-(phenylsulfonyl)-4,5′-spirobi(2-isoxazoline) (**8b**) (1.6 g, 11%): mp 240 °C (from hexane–benzene); ^{1}H NMR δ 1.84, 1.87 (9 H, 2 s), 2.44, 2.48, 2.52, 2.59 (12 H, 4 s), 3.32, 4.65 (2 H, AB type, J = 19.5 Hz), 7.5–7.8 (3 H, m), 8.0–8.2 (2 H, m); ^{13}C NMR δ 16.3–19.7, 41.8 (t), 100.0 (s), 101.1 (s), 124.4–136.7, 157.2 (s), 157.6 (s). Anal. Calcd for $C_{30}H_{28}Cl_4N_2O_4S$: C, 55.05; H, 4.24; N, 4.19. Found: C, 54.97; H, 4.32; N, 4.27. Further elution gave isoxazole **5b** (5.1 g, 55%).

Registry No. **1**, 13456-86-5; **2a**, 2525-42-0; **2b**, 13603-90-2; **3a**, 2525-40-8; **3b**, 13603-88-8; **4**, 2525-41-9; **5a**, 96965-01-4; **5b**, 96965-05-8; **6**, 96965-04-7; **7**, 96965-00-3; **8a**, 96965-02-5; **8b**, 96965-06-9; **9**, 96965-03-6; $PhSO_2CH_2COCH_3$, 5000-44-2.

The Photochemistry of 1-Phenyl-1,2-dihydronaphthalene. A Simple Preparation of *cis*-Dibenzobicyclo[3.3.0]octa-2,7-diene

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In a previous paper[1] we reported that 1-phenyl-1,2-dihydronaphthalene (1) irradiated with a broad-spectrum lamp in an apolar solvent yields in 4 h, apart from polymeric material, only one product, viz., *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**4**) (Scheme I).

In the paper mentioned[1] we gave arguments for the supposition that the actual product (*exo*-**4**) originates from the more stable, primary ring opening product cZc-**3**, formed from PE-**1**, via a [π^4a + π^2a] photocycloaddition of cZt-**3**. Furthermore, it was argued that the lifetime of cZc-**2** might be too short to give *endo*-**4** in an analogous way; cZc-**2** should undergo rapid photoisomerization to cZc-**3** or reversal to **1** or both of them.

In further studies devoted to possible photochemical additions of alcohols to unsaturated systems like **1** and **2**, we irradiated **1**, dissolved in methanol, in the presence or absence of an acid, using a ca. 254-nm light source to suppress the formation of *exo*-**4**. On irradiation for 20 h **1** had completely disappeared, and the reaction mixture contained a novel photoproduct, different from *exo*-**4**, which could be readily purified by crystallization. Formation of any photoaddition product could be excluded because the same product was formed even quantitatively when **1** was irradiated with 254-nm light in *hexane* for 24 h.

The mass spectrum (M^+ = 206) showed that the product had the same molecular formula as **1** ($C_{18}H_{14}$). The UV spectrum contained two maxima (272 and 265 nm) of nearly equal height, pointing to a benzene derivative

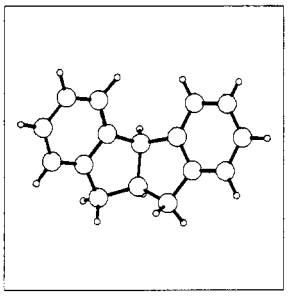
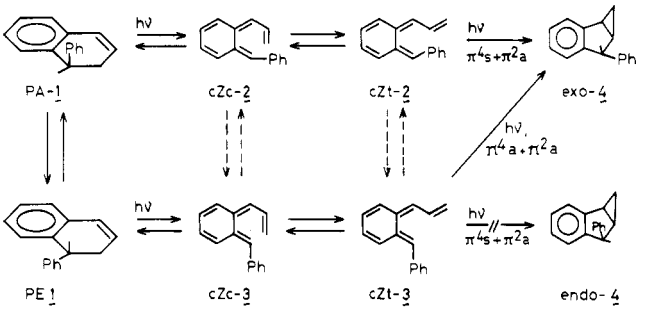
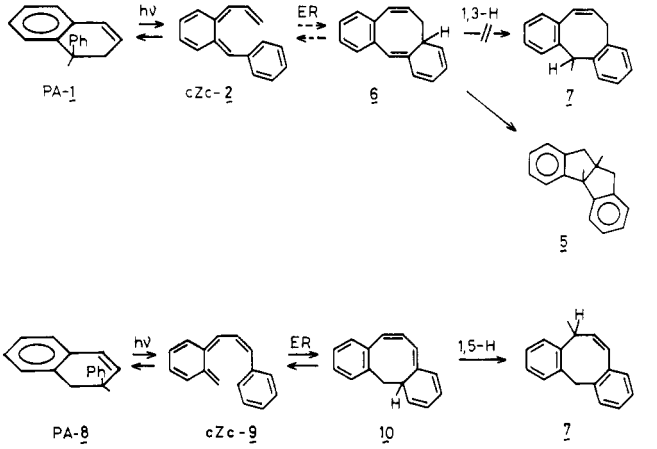


Figure 1. X-ray of **5**.

Scheme I



Scheme II



without extended conjugation. The NMR spectrum, containing two multiplets at δ 2.1–2.9 (2 H) and 3.1–3.6 (3 H), a broadened doublet (δ 4.64, 1 H), and a signal of eight aromatic protons (δ 7.0–7.3), added insufficient information to assign a definite structure. X-ray analysis[2] revealed, however, that the product was *cis*-dibenzobicyclo[3.3.0]octa-2,7-diene (**5**). The molecular configuration is given in Figure 1.

Irradiation of **1**, dissolved in CD_3OD, yielded **5** without any incorporation of deuterium. This excludes that **5** is formed via an ionic or radical process.

A mechanism is given in Scheme II. It implies that the product originates from a primary formed intermediate (cZc-**2**) belonging to the PA conformer of **1**. The electrocyclic reaction cZc-**2** → **6** is similar to the conversion cZc-**9** → **10** (see Scheme II), which was previously proposed[3] to explain the photochemical conversion of 2-phenyl-1,2-di-

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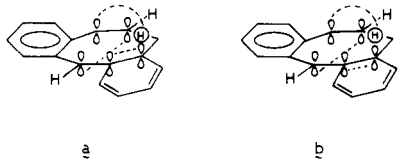

a b

Figure 2.

hydronaphthalene (8) into the dibenzocyclooctatriene 7. In the latter case the end product (7) might arise from 10 via a 1,3- as well as a 1,5-H shift, but irradiation of suitably deuterated 8 revealed that the final step only proceeds by a 1,5-H shift.

A more general reluctance of compounds like 6 and 10 to undergo 1,3-H shifts might explain that photolysis of 1 does not yield the cyclooctatriene derivative 7 because its formation from 6 is only possible via a 1,3-H shift.

Accepting that the product 5 arises from 6, the experimental conditions (254-nm light, no D incorporation) imply that the conversion of 6 → 5 is a thermal, concerted process. Two methods, viz., $\pi^2a + \pi^2a + \sigma^2s$ (Figure 2a) and $\pi^2a + \pi^2s + \sigma^2a$ (Figure 2b), both thermally allowed, are possible to fulfil the steric requirements necessary for the formation of the cis-fused structure of the product 5.

Repeating the analysis of the NMR spectrum of the reaction mixture, obtained by irradiation of 1 in hexane with a broad-spectrum lamp, revealed that 5 is probably also formed under these conditions but in very small amounts (less than 1%).

Apart from the extension of knowledge about the photochemical behavior of phenyl-substituted dihydronaphthalenes, this study may be of some practical value. Two preparations of 5 have been described in the literature. One of them,[4] starting from anthracene, requires a six-step procedure and about 136 working hours to give 5 in 64%; the other[5] starts from cinnamic acid and leads in four steps (ca. 66 h) to an overall yield of 20%. With the photochemical conversion 1 → 5, the latter compound can be obtained in four steps from α-naphthol in 65% yield within 40 h. Especially for the preparation of small samples, it is an attractive, fast, efficient, and simple method.

Experimental Section

The ^1H NMR spectrum was recorded on a Bruker WH90 spectrometer in $CDCl_3$. The mass spectrum was obtained with a VG-7070 mass spectrometer. The UV spectrum was recorded with a Perkin-Elmer 555 instrument.

The preparation of 1 was performed according to the literature.[6] Irradiations were carried out under anaerobic conditions using 10^{-3} M solutions in methanol or hexane. Monochromatic irradiations (254 nm) were done in a Rayonet photochemical reactor fitted with 254-nm lamps or using Philips bactericidal fluorescent tubes. Products were isolated by evaporation of the solvent and crystallization of the residue from methanol. Compound 5 crystallized as colorless needles and melted at 95 °C (lit. mp 95.0–95.5 °C,[5] 95 °C[4]): UV (CH_3OH) λ_{max} (log ϵ) 272 nm (3.40), 265 (3.43), λ_{min} 269 nm (3.06); mass spectrum, m/e 206 (M^+, 100%), 191 (14), 178 (14), 128 (14), 115 (17), 91 (80); NMR (simulated δ from Me_4Si) δ 2.76 (H(4), H(6), $J_{4,5} = J_{5,6} = 3.5$ Hz, $J_{4,4'} = J_{6,6'} = -15.2$ Hz), 3.24 (H(4'), H(6') $J_{4',5} = J_{5,6'} = 7.0$ Hz), 3.40 (H(5) $J_{1,5} = 7.2$ Hz), 4.64 (H(1)), 7.0–7.3 (arom).

Registry No. 1, 16606-46-5; 5, 14090-18-7.

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Asymmetric Reductions by $NaBH_4$ of Ketone–β-Cyclodextrin Complexes

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The asymmetric reduction of prochiral ketones has been successfully achieved by using chirally modified metal hydrides.[1] Significant asymmetric inductions have also been obtained by the use of achiral reagents in a chiral environment: a 32% optical yield (o.y.) (phenyl *tert*-butyl ketone) was observed in the sodium borohydride reduction in the presence of optically active catalysts under phase-transfer conditions,[2] and up to 78% o.y. (propiophenone) was achieved in the sodium borohydride reduction of ketones bound to the chiral domains of bovine serum albumin.[3]

Cyclodextrins may also provide a chiral binding site[4] capable of including guest ketones and induce "template-directed" chiral reductions. One limited study[3a] reported on a very limited success: carbinols in 0–10% o.y. were obtained from three trifluoromethyl aryl ketones in the presence of a ten-fold molar excess of β-cyclodextrin (β-CD) over the substrate in alkaline aqueous solution. A growing number of reports of successful use of cyclodextrins to achieve kinetic resolutions of racemic substrates[5] or optical induction in reactions involving prochiral centers[6] led us to investigate in more detail the use of these host molecules in the sodium borohydride asymmetric reduction of prochiral ketones. Preliminary experiments carried out in a variety of conditions (in aqueous, DMF, Me_4SO solutions) using different ratios of reactants and cyclodextrins resulted in low optical inductions, about 8% and 7% o.y. at best with 1-naphthyl methyl ketone and 4-phenyl-3-buten-2-one.

We found and here report that significant improvements on these inductions can be obtained by reducing preformed 1:1 β-CD–ketone complexes suspended in a sodium borohydride aqueous alkaline (0.2 M sodium carbonate) solution. After disappearance of the ketone, the reactions were extracted with ether and the resulting alcohols analyzed to ascertain their purity and optical activity and evaluate the o.y.'s.[7] In a few cases where the specific rotation of

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