

reported^{3,4} for dehydrohalogenating agents⁵⁻⁹ 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) and 1,5-diazabicyclo[4.3.0]nonene-5 (DBN).

The generality of the dehydrobrominating reagent is demonstrated by the application of *N*-phenylbenzamidine to the two bromides 1-bromoheptane and bromocyclohexane. A mixture of 3.5 equiv of *N*-phenylbenzamidine and 1 equiv of the appropriate bromide was dissolved in 25 equiv of *o*-xylene and refluxed (148°) for 8 hr. The resulting olefins were obtained in 98% yield by glc analysis and were identical by ir, nmr, and glc comparison with authentic samples.

Attempts to bring about dehydrochlorination with *N*-phenylbenzamidine gave poor yields of products. Thus *N*-phenylbenzamidine is a relatively mild and selective dehydrobrominating agent.

Experimental Section

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained using a Jeolco minimar spectrometer. Tetramethylsilane was used as an internal standard. Infrared spectra were obtained using a Perkin-Elmer Model 137 G spectrophotometer. Gas-liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 0.25 in. o.d.) bent in a U shape and packed with 3% SE-30 on 100/120 mesh GCQ at a column temperature of 270 or 60° with a helium flow rate of 90 ml/min was used for all glc analyses.

Dehydrobromination of Bromo Ketone 1 in *o*-Xylene.—Bromo ketone 1 (250 mg, 0.63 mmol) was added to a solution of *N*-phenylbenzamidine (412 mg, 2.22 mmol) and 1.87 ml of *o*-xylene. The reaction solution was refluxed (148°) for 3 hr. The ether extract of the acidified (5% HCl) reaction mixture was washed with 5% aqueous sodium carbonate and water, dried over anhydrous sulfate, and evaporated *in vacuo*. Crystallization of the residue from aqueous methanol solution yielded 181 mg (91%) of the crystalline solid **3**: mp 175–177° (lit.² mp 173–175°); $\lambda_{\text{max}}^{\text{KB}} 1725, 1645, 1600, 1575 \text{ cm}^{-1}$; δ nmr (CHCl₃) 1.56 (3 H), 1.76 (3 H), 4.33 (3 H), 4.58 (3 H), 7.71 (1 H), 8.15 (2 H, multiplet), 9.58 (1 H, d, *J* = 8 Hz). *Anal.* Calcd for C₁₅H₂₂O₄: C, 72.50; H, 7.01. Found: C, 72.86; H, 7.14.

Dehydrobromination of Bromo Ketone 1 in Benzene.—Bromo ketone 1 (250 mg, 0.63 mmol) was added to a solution of *N*-phenylbenzamidine (412 mg, 2.22 mmol) and 2.05 ml of benzene which was refluxed (83°) for 48 hr. Following work-up in the manner described above, crystallization from aqueous methanol yielded 180 mg (90.5%) of the crystalline solid **3**, mp 175–177°.

General Procedure for Dehydrobromination. 1-Bromoheptane and Bromocyclohexane.—A mixture of *N*-phenylbenzamidine (996 mg, 5.37 mmol) and 1.53 mmol of the appropriate bromide was dissolved in 4.58 ml of *o*-xylene and refluxed at 148° for 8 hr. The usual work-up of the ether extract of the acidified reaction mixture yielded the corresponding olefin (98% glc) which was identical by ir, nmr, and glc comparison with authentic samples.

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Registry No.—1, 37931-64-9; **3**, 37931-65-0; *N*-phenylbenzamidine, 1527-91-9.

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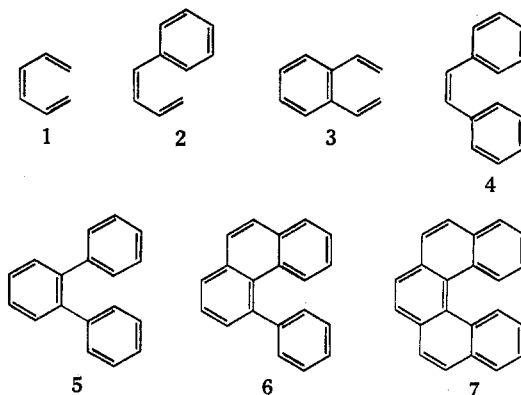
The Photochemistry of 2-Vinylbiphenyl and 4-Vinylphenanthrene¹

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The photochemistry of hexatriene (1) and the related compounds, 1-phenyl-1,3-butadiene (2), 1,2-divinylbenzene (3), stilbene (4), *o*-terphenyl (5), 4-phenylphenanthrene (6), and dibenzo[*c,g*]phenanthrene (7),



whose structures may be considered as possessing a disguised hexatriene system, have been investigated.² In these compounds the hexatriene system gradually loses its separate identity by successive fusion of benzene rings. We now wish to report some observations on the photochemistry of the other two members of this series: 2-vinylbiphenyl (8) and 4-vinylphenanthrene (12).

The relative ease of photocyclization of hexatriene analogs has been related to the sum of the free-valence indices in the first excited state, ΣF^* , at the two positions which become bonded during the cyclization.^{3,4} Generally, photocyclization is only observed if $\Sigma F^* > 1.0$. The photocyclization of both **8** and **12** at the two positions indicated as a and b should be very favorable since ΣF^* is 1.63 and 1.48 for **8** and **12**, respectively. These values are calculated for planar molecules in the usual way and are based on the HMO approximation.

Irradiation of a benzene solution of **8** for 1 hr, in the presence of atmospheric oxygen (aerobic irradiation), gave complete conversion to 9,10-dihydrophenanthrene (10); there was no evidence of the formation of phen-

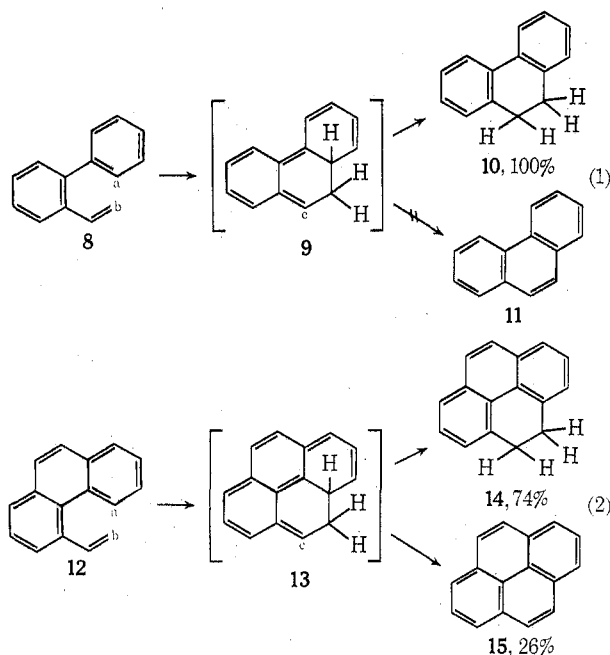
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anthrene (11) (eq 1), the product expected under oxidative conditions.

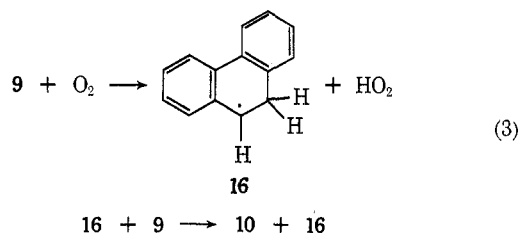


Irradiation of a solution of 12 under the conditions described for 8 gave a mixture consisting of 26% pyrene (15) and 74% rearrangement product, 4,5-dihydropyrene (14) (eq 2). Two control experiments were run to determine the origin of pyrene. In the first a 10^{-2} M solution of 12 in benzene was degassed and irradiated for 1 hr (anaerobic irradiation). Gas chromatographic analysis showed the presence of 14; there was no evidence of pyrene. In the second experiment a 5×10^{-4} M solution of 14 in benzene, containing 1% pyrene, was subjected to aerobic irradiation. No increase in the pyrene concentration was observed. These experiments demonstrate that oxygen is required for the formation of pyrene and that pyrene is not formed from a photoreaction of 4,5-dihydropyrene (14).

We assume that dihydrophenanthrene (9) and dihydropyrene (13) are intermediates in the photocyclization of 8 and 12, respectively, and these intermediates lead to isolable compounds by ground-state reactions. Anaerobic irradiation of 8 and 12 did not, however, give spectroscopically detectable quantities of the dihydroforms 9 and 13. The formation of 10 from 9 and 14 from 13 may be explained by a rapid 1,5-sigmatropic shift of the tertiary hydrogens to position c, an allowed ground-state process.⁵ A similar rearrangement in a more complicated hexatriene system has also been reported.⁶

A possible alternate mechanism for the formation of 10 and 14 involves a radical-chain mechanism. Thus, if oxygen were to abstract a hydrogen atom from 9, 16 would be produced which could then act as a chain carrier (eq 3). A radical reaction has been shown to occur in the photochemical isomerization of suitably substituted stilbenes to 9,10-dihydrophenanthrenes.⁷

However in separate experiments it was shown that, after 0.5 hr of aerobic irradiation of 8, no H_2O_2 was



present,⁸ and the presence of PhSe radicals,⁹ generated from the irradiation of solutions containing Ph₂Se₂, had no effect on the reaction.

It is not clear why 12 gives both 14 and 15, whereas 8 gives only the dihydro product 10. If the rate of the 1,5-sigmatropic rearrangement in 9 were faster than in 13, some of the latter could persist long enough to undergo oxidative dehydrogenation to pyrene. However, it is not clear why the rate of migration of the tertiary hydrogens in 9 and 13 to positions of similar electron density should be significantly different.¹⁰ The thermal abstraction of a tertiary allylic hydrogen from 9,10-cyclopentano-4a,4b-dihydrophenanthrene by molecular oxygen has been shown to have a rather large negative entropy of activation.⁸ The slight structural difference between 9 and 13 may be sufficient to produce a significant difference in the configuration of the transition states for hydrogen abstraction, and hence a larger negative entropy of activation, for the conversion of 9 relative to that of 13.

Experimental Section

Melting points are uncorrected. Uv absorption spectra were obtained on a Cary 14 spectrophotometer and, for the pmr spectra, a Varian T60 instrument was used. Gas chromatographic analyses were performed on a Varian Model 1200 flame ionization instrument using a 3 ft \times 1/8 in. glass column packed with 2% Versimid 900 on 100–120 Chromosorb W. Gas chromatographic retention times and the pmr spectra of 10, 14, and 15 were checked against those of authentic samples. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. A 550-W medium-pressure mercury arc (Hanovia 673A) contained in a water-cooled Vycor jacket was used as the light source. In some experiments a merry-go-round apparatus surrounded the light source and contained the sample tubes. The sample tubes were Pyrex test tubes (1-cm o.d.) fitted with an adapter for attachment to a high-vacuum line when necessary. For anaerobic irradiations the samples were degassed by five freeze-pump-thaw cycles at 10^{-5} Torr.

2-Vinylbiphenyl.—This compound was prepared by a published procedure.¹¹

4-Phenanthrenecarboxaldehyde.—A mixture of 4.5 g of 4-methylphenanthrene,¹² 4.63 g of *N*-bromosuccinimide, 50 mg of benzoyl peroxide, and 100 ml of carbon tetrachloride was stirred and refluxed for 2 hr. Succinimide was removed by filtration and the filtrate evaporated *in vacuo* on a steam bath. The residue of crude 4-bromomethylphenanthrene was dissolved in 50 ml of acetic acid–water (1:1), and 6.6 g of hexamethylenetetraamine added. The mixture was stirred and refluxed for 2 hr. Hydrochloric acid (20 ml) was then added and refluxing continued for 15 min. After cooling to room temperature, the mixture was extracted with 300 ml of chloroform, the extract washed with water, dried over magnesium sulfate, and filtered, and the filtrate evaporated to dryness. The crude aldehyde was recrystallized three times from ether–hexane: yield 2.4 g (49.9%), mp 82–84°.

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Anal. Calcd for $C_{17}H_{10}O$: C, 87.35; H, 4.98. Found: C, 87.47; H, 5.00.

4-Vinylphenanthrene.—A mixture of 175 mg of methyltriphenylphosphonium bromide, 0.25 ml of 1.91 *M* phenyllithium, and 20 ml of dry ether were stirred and refluxed under nitrogen for 0.5 hr. A solution of 100 mg of 4-phenanthrenecarboxaldehyde in 20 ml of ether was added dropwise over a period of 15 min, and the mixture was then stirred and refluxed for 2 hr. The reaction mixture was filtered, the filtrate diluted with 200 ml of ether, washed with water, dried, and filtered, and the ether removed *in vacuo*. The residue was chromatographed on alumina using hexane as the eluent to give an oil which was further purified and analyzed *via* the picrate: 125 mg (59.1% yield), mp 112–113°.

Anal. Calcd for $C_{22}H_{15}N_3O_7$: C, 60.97; H, 3.49; N, 9.70. Found: C, 60.85; H, 3.49; N, 9.53.

Photocyclization of 2-Vinylbiphenyl.—A 10^{-3} *M* solution of **8** in benzene was placed in a Pyrex test tube and irradiated under aerobic conditions for 1 hr. Gas chromatographic analysis of the reaction mixture showed it to consist entirely of **10**. In a second experiment a solution of 2.0 g of **8** in 1 l. of benzene was stirred and irradiated through a Vycor immersion well. The course of the reaction was followed using pmr and uv spectroscopy. The reaction was stopped after 12 hr, at which point it was ~70% complete. Judging by the color of the solution, considerable photodecomposition had occurred. The solvent was removed *in vacuo* and the residual liquid vacuum distilled to give 400 mg [bp 181–183° (4.5 Torr)] of material. A pmr spectrum of this mixture showed it to consist of **8** and **10**. No further attempts were made to isolate the low melting **10**.

Photocyclization of 4-Vinylphenanthrene.—A 10^{-2} *M* solution of **12** in benzene was placed in a Pyrex test tube and irradiated under aerobic conditions for 1 hr. The reaction mixture was analyzed by gas chromatography and contained $26 \pm 2\%$ **15** and $74 \pm 2\%$ **14**. There was no detectable amount of starting material or other compounds present. Irradiation of solutions of **12** under anaerobic conditions, followed by gas chromatographic analysis, showed the presence of **14**; there was no evidence of pyrene.

Isolation of 4,5-Dihydropyrene.—Four 20-ml benzene solutions, each 2×10^{-3} *M* in **12**, were placed in Pyrex test tubes, degassed, and irradiated for 0.5 hr. The solutions were combined, the solvent was removed *in vacuo*, and the residue was sublimed. 4,5-Dihydropyrene, **14**, sublimed at 75° (2.0 Torr): mp 132–134° (lit.¹³ 131–132°); pmr δ 3.29 (s, 4 H), 7.55 (m, 8 H).

Registry No.—**8**, 1587-22-0; **12**, 41498-39-9; **12** picrate, 41498-40-2; **14**, 6628-98-4; 4-methylphenanthrene, 832-64-4; 4-phenanthrenecarboxaldehyde, 41498-43-5.

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Photosensitized Cyclodimerization of Phenyl Vinyl Ethers

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Recently we have reported that aromatic esters, substituted with electron-withdrawing groups, undergo photocycloadditions to olefins to yield oxetanes^{1a,b} or ladder compounds,^{1c} and that these esters are readily photoreduced by various aromatic hydrocarbons.² In

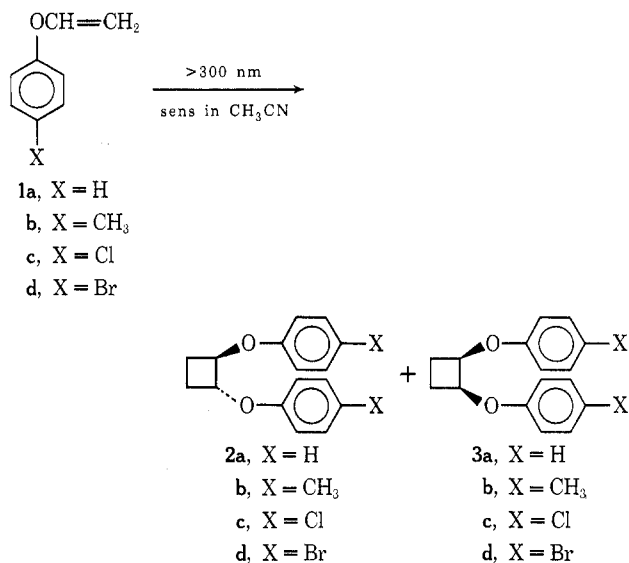
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the course of a continuing study we also found that aromatic esters acted as sensitizers for cyclodimerization of phenyl vinyl ether **1a** to give its head-to-head cyclodimers **2a** and **3a**.³ For some olefins having an electron-withdrawing group, such as acrylonitrile, photosensitized cyclodimerization is well known,⁴ but, for olefins having an electron-donating group, such a reaction is very unique.

In this paper, we wish to report that in the presence of aromatic esters some para-substituted phenyl vinyl ethers **1b–d** also undergo photosensitized cyclodimerizations to afford head-to-head cyclodimers. Furthermore, we examined the availability of various sensitizers to effect this reaction and the quenching efficiency of a sensitizer's (dimethyl terephthalate, **4**) fluorescence by the ethers **1a–e** in order to clarify the reaction mechanism.

Irradiation of an acetonitrile solution of **1** and a sensitizer such as dimethyl terephthalate (**4**) gave a mixture of *trans*- and *cis*-1,2-di-*para*-substituted phenoxycyclobutanes **2** and **3** (3:4) as the result of head-to-



head cyclodimerization of **1**. The structures of the cyclodimers were determined by their mass and nmr spectra. From mass spectra, they were characterized to be the head-to-head cyclodimers due to the reverse [2 + 2] cleavage ($M^+ - C_2H_4$). The stereochemistry of **2** and **3** was confirmed by comparison of their nmr spectra with those of *trans*- and *cis*-1,2-dibromocyclobutanes. A methine proton chemical shift of **2** was more upfield by *ca.* 0.2 ppm than that of **3**. In addition, the former had a broad four-proton methylene peak, while the latter had a sharp and sometimes distinct triplet methylene peak. These features of nmr spectra are very similar to those of *trans*- and *cis*-1,2-dibromocyclobutanes whose stereochemistry is confirmed.⁵ On the basis of these nmr data, **2** and **3** were assigned to the *trans* and *cis* isomers, respectively.

On the other hand, irradiation of **1** without the sensitizer gave no cyclodimer but only polymers.⁶ This indicates that the cyclodimerization of **1** proceeds ex-

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(6) Cyclodimers **2** and **3** remained unchanged upon similar irradiation.