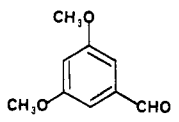

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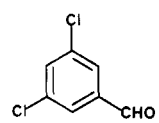

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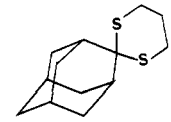

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In summary, while the conversion of aldehyde to ester is often straightforward, the methods which effect this transformation *without the presence of a heavy metal* are rare.[13,14] We believe that the method reported here may be valuable in the oxidation of other systems sensitive to common oxidants.

Experimental Section[10]

Tricarbonyl(methyl 1–4-η-1,3-cyclobutadiene-carboxylate)iron (2a). A 112.0-mg sample of aldehyde 1 in 3 mL of CCl_4 was treated with 60.0 mg of *tert*-butyl hypochlorite. After being stirred for 2 min, a mixture of 0.10 mL of CH_3OH and 0.10 mL of pyridine was added. The reaction mixture was then stirred for 30 min and poured into 10 mL of H_2O and extracted with ether; the ether was dried and evaporated. The brownish oil was distilled [60 °C (1.0 mm)] to give 114 mg (90%) of **2a**: IR (neat) 4.8, 5.0, 5.78 μm; NMR (CCl_4) δ 3.65 (s, 3 H, OCH_3), 4.3 (s, 1 H, para H), 4.6 (s, 2 H, ortho H); mass spectrum (*m/e*) 250 (28), 222 (39), 194 (41), 166 (36), 138 (18), 136 (33), 108 (100), 82 (41), 81 (27), 56 (42).

Tricarbonyl(isophoryl 1–4-η-1,3-cyclobutadienyl-carboxylate)iron (2b). A 50-mg sample of 1 (0.23 mmol) and 2 mL of CCl_4 were stirred at 25 °C, while 28.0 mg of *tert*-butyl hypochlorite in 0.25 mL of CCl_4 was added. After the mixture was stirred for 2 min, 0.1 mL of pyridine and 40.0 mg (0.29 mmol) of isophorol were added. The mixture was stirred for 90 min until TLC analysis showed the reaction was complete. Then 10 mL of H_2O was added and the mixture was extracted twice with 15-mL portions of ether. After the mixture was dried with $MgSO_4$, the solvents were removed under reduced pressure, and the crude product was purified by preparative TLC (7% ether/pentane). Collection of the band at R_f 0.39 gave 32 mg (39%) of compound **2b**: IR (neat) 4.81, 5.0, 5.8, 5.95 μm (w); NMR (CCl_4) δ 0.98 (s, 3 H, CH_3), 1.0 (s, 3H, CH_3), 1.7 (br s, 3 H, CH_3), 4.18 (s, 1 H, para H), 4.42 (s, 2 H, ortho H), 5.27 (m, 1 H, vinyl H); mass spectrum, *m/e* 358 (5), 274 (8), 236 (21), 208 (62), 180 (100), 152 (37), 123 (68), 117 (83), 91 (43), 81 (33).

Methyl Cinnamate (Entry 4). To a solution of 264 mg (2mmol) of cinnamaldehyde in about 8 mL of CCl_4 was added 216 mg of *tert*-butyl hypochlorite by syringe. After the mixture was stirred for 4 h at room temperature, 25 drops of triethylamine and 25 mL of CH_3OH were added. The mixture was then refluxed for 45 min. After the mixture cooled, ether was added and the organic phase was washed with 10% HCl, saturated $NaHCO_3$ solution, and water and then dried with $MgSO_4$, and the solvents were evaporated. Distillation at 85 °C (1 mm) gave pure methyl cinnamate (79%) whose IR, NMR, and mass spectra were identical with those of an authentic sample.

Acknowledgment. We thank the National Institutes of Health (GM26039) and the Petroleum Research Fund (11243-AC1) for support of this research.

Registry No. 1, 33056-62-1; **2a**, 52571-40-1; **2b**, 80583-61-5; **3** (R = Ph), 100-52-7; **3** (R = PhCH=CH), 104-55-2; **3** (R = MeO-*m*-C_6H_4), 591-31-1; **3** (R = 2-furanyl), 98-01-1; **5** (R = Ph; R′ = Me), 93-58-3; **5** (R = PhCH=CH; R′ = Me), 103-26-4; **5** (R = MeO-*m*-C_6H4; R′ = Me), 5368-81-0; **5** (R = 2-furanyl; R′ = Me), 611-13-2; **9**, 7311-34-4; **10**, 10203-08-4; **11**, 80573-02-0; *tert*-butyl hypochlorite, 507-40-4.

Supplementary Material Available: Complete spectral data for compounds **2a** and **2b** (6 pages). Ordering information is given on any current masthead page.

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Photocyclization of 1,2-Diarylethylenes in Primary Amines. A Convenient Method for the Synthesis of Dihydro Aromatic Compounds and a Means of Reducing the Loss of Methyl Groups during the Cyclization of *o*-Methylstilbenes

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One of the most useful photochemical processes in organic synthesis is undoubtedly photocyclization. Specifically, the conrotatory ring closure of *cis*-hexatrienes leading to the cyclohexadienes followed by oxidation or elimination is one of the best known and most exploited photoelectrocyclic reactions.[1,2]

The number of applications of this type of photoreaction is very large, especially for the synthesis of polycyclic aromatic compounds, the classical example being the stilbene–phenanthrene photoconversion.[3]

Nevertheless it has been shown that stilbenes which have one[4] or two[5] electron-withdrawing enolizable substituents on the double bond, when irradiated in protic solvents under nonoxidative conditions, yield 9,10-dihydrophenanthrenes. The mechanism of these reactions has been clarified recently by Laarhoven,[6,7] but their scope was restricted by the substituents required. A new method for preparation of 5,6-dihydrohexahelicenes by photocylization of 2,7-distyrylnaphthalenes under anaerobic conditions has also been recently described by the same author but "the procedure remains rather capricious due to experimental difficulties".[8]

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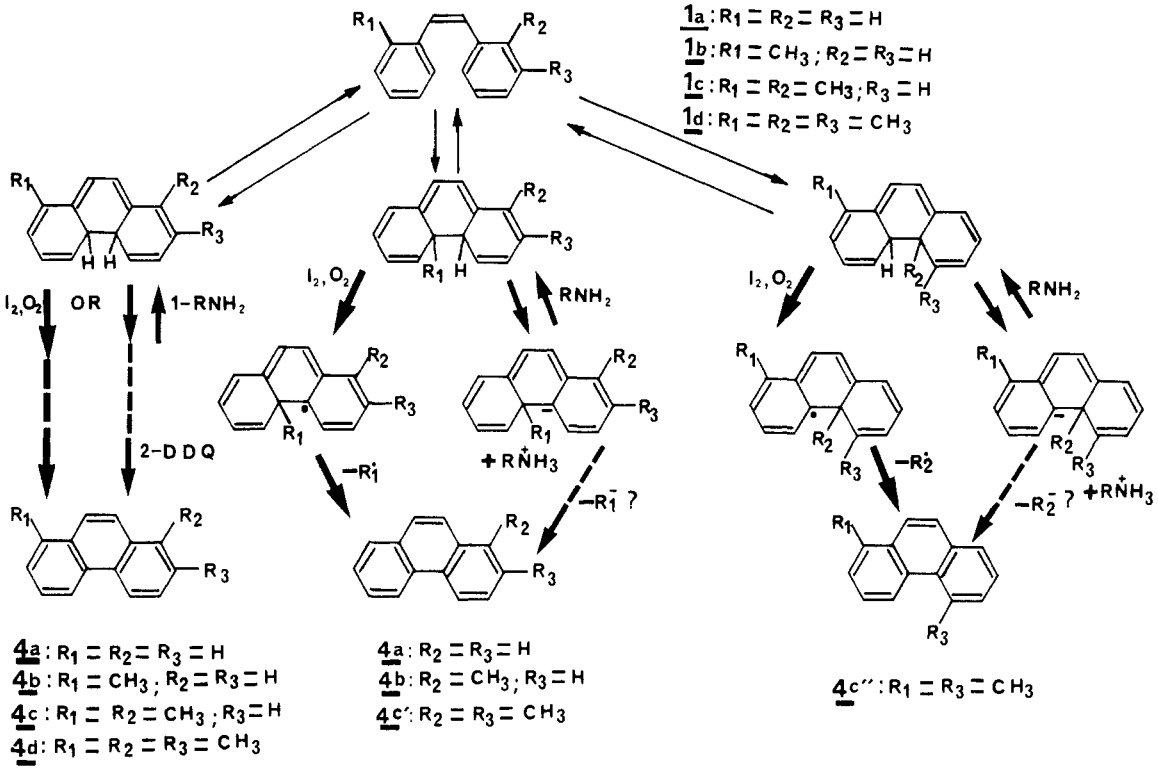
Scheme I



The recent findings that primary amines can induce the nonoxidative photocyclization of 1,2-diarylethylenes[9] and 1,1-diarylethylenes[10] to dihydro aromatic compounds promised wider applications.

We describe here an extension of the use of primary amines for the synthesis of dihydro aromatic compounds and the discovery of the reduced loss of methyl groups during the photocyclization of *o*-methylstilbenes in the presence of these amines.

We have discussed in our preceeding papers[10,11] the mechanism of interaction of primary amines with the arylethylenes which cyclized; labeling experiments particularly are in favor of an abstraction of the proton located on the carbon atoms which have given rise to the new bond while the resulting alkylammonium cation protonates another position. We have indeed established that the 4a,4b-dihydrophenanthrene derivatives generated in neutral solvent[12] yield, in the absence of light and after addition of the primary amines under anaerobic conditions, a small amount of the same dihydro aromatic compounds as those obtained upon direct irradiation of the corresponding 1,2-diarylethylenes in the presence of these amines.[13] We believe that in every case the amine solvent under oxygen-free conditions forces the reaction to an ionic pathway rather than the radical pathway usually invoked in the oxidative process.

Table I

compd irradiated	rel amt of photoproducts under oxidative and nonoxidative conditions	
	I_2 and O_2	1-RNH_2 and 2-DDQ
1b	65/35 4b/4a	90/10 4b/4a
1c	70/30 4c/4b	95/5 4c/4b
1d	65/35 4d/(4c' + 4c'')	95/5 4d/(4c' + 4c'')

If this mechanism was operating, we speculated that photocyclization of *o*-alkylstilbenes might occur with little or no loss of the alkyl groups since if the radical dealkylation can be considered in the classical oxidative photochemical process, the loss of an alkylanion is far less likely, so that the reversibility of the cyclization and of the protonation of the intermediate should favor the nondealkylated compounds (Scheme I). We have irradiated solutions of 2-methyl- (**1b**), 2,2'-dimethyl- (**1c**), and 2,3,2'-trimethylstilbenes (**1d**) (5×10^{-3} M) in *n*-propylamine, oxidized the crude product (mainly 1,4-dihydrophenanthrene derivatives[9]) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and compared the fraction of methyl loss in the phenanthrene products with the oxidative cyclization produced with the general procedure.[3] The results are reported in Table I.

As anticipated, the loss of the *o*-methyl groups is reduced with amine, and the residual dealkylation could be due to

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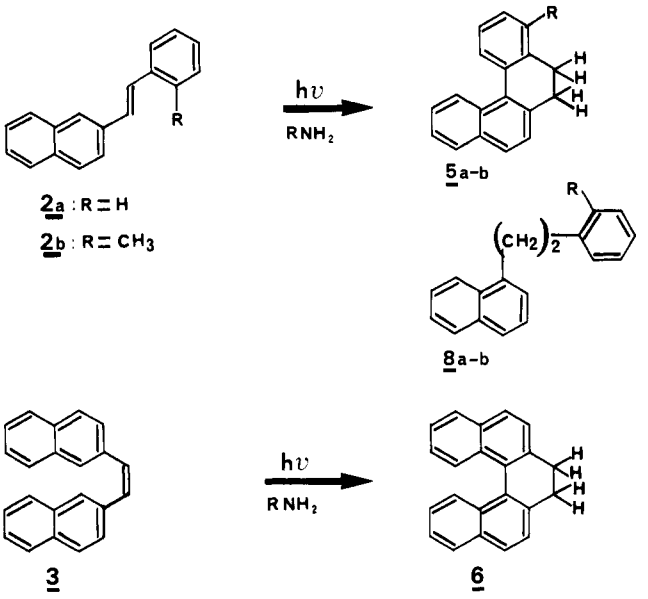
Scheme II



an imperfect degassing. The reversibility of the deprotonation reaction was unambiguously established by the presence of deuterium in the stilbenes (cis and trans) remaining after short-time irradiation carried out on **1b** in N-deuterated amine.

This two-step conversion of *o*-alkylstilbenes to alkylphenanthrenes should be used when the oxidative photocyclization yields dealkylated phenanthrenes difficult to separate from the expected 1-alkylphenanthrenes. As another example, the oxidative photocylization of 2-(*o*-methyl-β-styryl)naphthalene (**2b**) yields a 65/35 mixture of 8-methyl-3,4-benzophenanthrene (**7**) and 3,4-benzophenanthrene. When the irradiation is carried out in *n*-propylamine, oxidation of the crude product with DDQ furnishes exclusively the methylated aromatic compound.

Since the mechanism proposed was a tautomerism of the initial product of the photocylization, it was interesting to investigate the primary products formed during irradiation in amine medium of 2-(β-styryl)naphthalene (**2a**), 2-(*o*-methyl-β-styryl)naphthalene (**2b**), 1,2-bis(2-naphthyl)ethylene (**3**, Scheme II). The irradiations were carried out in *n*-propylamine or in benzene or THF with 1,2-diaminopropane (see Experimental Section). In all cases 9,10-dihydro compounds (**5a,b** and **6**, respectively) were obtained with fairly good yields. The chemical syntheses of **5a**[15] and **6**[16] undertaken to obtain authentic samples are long and tedious.

The structure of the photoproducts is different from that obtained from the parent stilbene[9] (1,2-dihydro vs. 1,4-dihydro), but even if we cannot yet foresee the structure of the dihydro derivative which will be produced by irradiation of a new 1,2-diarylethylene, these results show that the photocyclization of diarylethylenes in primary amines can improve the very useful stilbene–phenanthrene conversion and provide an easy route to specific dihydro aromatic compounds.

Experimental Section

General Methods. Spectra data were obtained with Perkin-Elmer 456 infrared spectrometer, a Perkin-Elmer NMR instrument, and a Cary 219 UV spectrophotometer. For column chromatography neutral alumina (Merck, 70–230 mesh) was used with pentane as the eluent. Quantitative analyses of the reaction products were effected by GLC, using an Intersmat IGC 12 equipped with a 2.1-m column filled with Chromosorb W-HP (80–100 mesh) coated with 3% OV-1.

The amines were refluxed over potassium hydroxide and distilled immediately before use.

Starting Materials. 2-Methyl- (**1b**), 2,2′-dimethyl- (**1c**), and 2,3,2′-trimethylstilbenes (**1d**) were prepared in three steps as already described for 4,4′-dimethylstilbene:[17] free radical bromination of *o*-xylene with slightly less than a molar ratio of *N*-bromosuccinimide, reaction in situ with triphenylphosphine to produce the phosphonium salt, and Wittig reaction in methanol with the appropriate aldehyde with lithium methoxide as base.

2-Methylstilbene (1b). Triphenyl(*o*-xylyl)phosphonium bromide (22.35 g, 0.05 mol) was dissolved in a solution of lithium methoxide (0.1 mol) in methanol (200 mL) with stirring, benzaldehyde (5.3 g, 0.05 mol) was added, and the reaction mixture was stirred at room temperature 18 h. Water was added and the solution extracted with ether. The methylstilbenes obtained (7.3 g, 75%) were a mixture of trans (60%) and cis (40%) isomers (GLC). Column chromatography of the crude product on alumina with pentane as the eluent afforded the cis [NMR (CCl_4) δ 7 (9 H, m), 6.5 (2 H, s), 2.17 (3 H, s)] and trans [NMR (CCl_4) δ 7 (11 H, m), 2.33 (3 H, s)] isomers.

2,2′-Dimethylstilbene (1c). The same reaction as above with *o*-tolualdehyde gave a mixture of cis and trans isomers of 2,2′-dimethylstilbene[18] (6.6 g, 64%).

2,2′,3-Trimethylstilbene (1d). 2,3-Dimethylbenzaldehyde was prepared according to Carruthers.[19] The Wittig reaction, as described but with half the quantities afforded (2.8 g, 50%) of **3** (cis/trans ratio of 2/3). The cis isomer was eluted before trans on an alumina column: UV (cyclohexane) λ_{max} cis 260 nm (ε 10 000), trans 291 (26 000); NMR (CCl_4) cis δ 6.73 (7 H, m), 6.6 (2 H, s), 2.23 (6 H, s), 2.13 (3 H, s), trans δ 7 (9 H, m), 2.37 (3 H, s), 2.3 (6 H, s).

2-(β-Styryl)naphthalene (2a). This compound was synthetized, according to the procedure of Everett[20] by reaction of the Grignard reagent of benzyl chloride with 2-naphthaldehyde. The crude carbinol was treated with phosphoric oxide in boiling benzene and chromatographed on neutral alumina with benzene as the eluent. **2a** was recrystallized from 95% ethanol; mp 146 °C.

2-(*o*-Methyl-β-styryl)naphthalene (2b). Triphenyl(*o*-xylyl)phosphonium bromide (8.9 g, 0.02 mol) was dissolved in a solution of lithium methoxide (0.04 mol) in methanol (100 mL) with stirring, 2-naphthaldehyde (3.12 g, 0.02 mol) was added, and the reaction mixture was stirred at room temperature 22 h. Water was added (40% by volume), and the precipitated product was filtered off and crystallized in ethanol.

The pure trans isomer was obtained: 3.2 g (65%); mp 90 °C (lit.[20] mp 88 °C); NMR (CCl_4) δ 7.35 (13 H, m), 2.42 (3 H, s). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.34; H, 6.62.

1,2-Bis(2-naphthyl)ethylene[21] (3). 2-(Bromomethyl)-naphthalene was prepared in 90% yield by bromination of 2-methylnaphthalene with NBS.[22] Reaction of this compound with triphenylphosphine in boiling benzene during 3 h gave after filtration a quantitative yield of [(2-naphthyl)methyl]triphenylphosphonium bromide. The Wittig reaction with 2-naphthaldehyde with the same quantities as described for **2b** gave **3** (3.37 g, 60%) with a cis/trans ratio of 3/2. The trans isomer is almost insoluble in ether: mp 257–258 °C; NMR (CCl_4) δ 7.53 (14 H, m) 6.7 (2 H, s).

Photocyclization of 1,2-Diarylethylenes in Primary Amines. The photolyses of **1b–d**, **2a,b**, and **3** were carried out in a quartz reactor fitted with dry nitrogen inlet. The solutions (100 mL), each containing diarylethylene (5×10^{-3} M) in *n*-propylamine [except **3** which was dissolved in benzene (100 mL)

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and 1,3-diaminopropane (1 mL)], were degassed by bubbling nitrogen through them for 2 h and were subsequently irradiated with eight Rul 2537-Å lamps (or 3000-Å lamps for **2a,b** and **3**) for 18 h. The reaction mixture was evaporated to dryness. The crude product of the photolysis of **1b–d** were treated with DDQ (15 min in boiling benzene), and the various components were evaluated by subsequent NMR and GLC analyses and comparison with authentic samples obtained by the oxidative photocylization of **1b–d** according to Mallory[3] (Table I). The photoreaction mixtures obtained by irradiation of **2a,b** and **3** were purified by chromatography on a neutral alumina column with pentane as the eluent.

1-Methylphenanthrene (4b). After photocyclization of **1b** in *n*-propylamine and dehydrogenation with DDQ, the total yield of phenanthrenic compounds was 82%, with a **4b/4a** ratio of 9/1 (GLC and NMR). Mallory reported a 57% yield of **4b** by oxidative photocylization of **1b**.[23] We repeated this reaction and found a ratio of **1b/1a** of 65/35.

1,8-Dimethylphenanthrene (4c). Irradiation of **1c** in *n*-propylamine followed by dehydrogenation with DDQ gave **4c**[24] with a chemical yield of 70% and a **4c/4b** ratio of 95/5. The oxidative photocyclization gave a **4c/4b** ratio of 7/3.

1,2,8-Trimethylphenanthrene (4d). After irradiation of **1d** GLC gave a **4d**/(**4c′** + **4c″**) ratio of 95/5. Crystallization gave a 60% yield of **4d**:[25] mp 144 °C; NMR (CCl_4) δ 8.26 (2 H, m), 7.93 (2 H, s), 7.26 (3 H, m), 2.66 (3 H, s) 2.6 (3 H, s), 2.46 (3 H, s).

8-Methyl-3,4-benzophenanthrene (7). After photocyclization of **2b** in *n*-propylamine and dehydrogenation with DDQ,[26] **7** was obtained with a 85% yield after recrystallization in ethanol: mp 63 °C (lit.[27] mp 64–65 °C); NMR ($CDCl_3$) δ 7.5 (11 H, m), 2.45 (3 H, s). Irradiation of **2b** under oxidative conditions furnished a 65/35 ratio of **7**/3,4-benzophenanthrene. Nagel[21] reported an 87% yield of **7** by oxidative photocyclization of **2b**. An authentic sample of 3,4-benzophenanthrene was prepared indifferently by oxidative photocyclization of **2a** or by dehydrogenation of the corresponding 9,10-dihydro derivative prepared as further described.

9,10-Dihydro-3,4-benzophenanthrene (5a). The crude product of the irradiation of **2a** purified by column chromatography first gave **8a** (6%). It was identical with a sample prepared by catalytic reduction of **2a** in methanol with activated Pd and hydrogen in the usual manner. Compound **5a** (86%) was eluted next, and its structure was determined by comparison with an authentic sample synthesized according to the procedure of Bergman:[15] NMR ($DCCl_3$) δ 7–8.5 (10 H, m), 2.85 (4 H, s).

8-Methyl-9,10-dihydro-3,4-benzophenanthrene (5b). Irradiation of **2b** gave **8b** (5%), identical with an authentic sample prepared as described above, and **5b** (84%) which were separated by column chromatography. **5b**: NMR ($CDCl_3$) δ 6.9–7.5 (9 H, m), 2.6 (4 H, m), 2.86 (3 H, s). Anal. Calcd for $C_{19}H_6$: C, 93.40; H, 6.60. Found: C, 93.28; H, 6.55.

GLC analysis reveals total absence of **5a** in the crude irradiation product of **2b** in the amine.

9,10-Dihydro-3,4,5,6-dibenzophenanthrene (6). Irradiation of 3 gave **6** (60%) identical (IR, NMR, melting point) with the authentic sample synthesized according to the procedure of Hall:[16] NMR (CCl_4) δ 7.5 (12 H, m), 2.83 (4 H, s).

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Registry No. *cis*-**1b**, 53423-25-9; *trans*-**1b**, 22257-16-5; *cis*-**1c**, 20657-42-5; *trans*-**1c**, 36888-18-3; *cis*-**1d**, 80663-23-6; *trans*-**1d**, 80663-24-7; **2a**, 2039-70-5; **2b**, 80663-25-8; *cis*-**3**, 2633-08-1; *trans*-**3**, 2753-11-9; **4a**, 85-01-8; **4b**, 832-69-9; **4c**, 7372-87-4; **4c′**, 20291-72-9; **4c″**, 66271-87-2; **4d**, 20291-75-2; **5a**, 80663-26-9; **5b**, 80663-27-0; **6**, 7427-84-1; **7**, 4076-40-8; **8a**, 36707-32-1; **8b**, 80663-28-1; triphenyl(*o*-xylyl)phosphonium bromide, 1530-36-5; benzaldehyde, 100-52-7; *o*-tolualdehyde, 529-20-4; 2,3-dimethylbenzaldehyde, 5779-93-1; benzyl chloride, 100-44-7; 2-naphthaldehyde, 66-99-9; 2-(bromomethyl)-naphthalene, 939-26-4; triphenylphosphine, 603-35-0; [(2-naphthyl)methyl]triphenylphosponium bromide, 35160-95-3; 3,4-benzophenanthrene, 195-19-7.

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Orientation in Base-Promoted Dehydrochlorination of 2,2,3-Trichlorobutane

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Although the pronounced effect of base association upon geometrical orientation in base-promoted eliminations from 2-alkyl halides and tosylates was demonstrated nearly a decade ago,[1,2] the mechanism through which base association exerts its influence remains uncertain.[3] For rationalization of the marked diminution of *trans*-2-alkene/*cis*-2-alkene ratios which is noted for eliminations from $CH_3CH(X)CH_2R$ under conditions favorable to base association, transition state structures **1** and **2**, where Y = H, have been postulated.[3] In comparison with anti elimination transition states for formation of *trans*-2-alkene and *cis*-2-alkene, using dissociated bases, the relative free energy difference between **1** and **2** is reduced by a more efficient "solvation" of the leaving group with the solvated base ion pair in **2** than in **1**. This solvation in **2** is stronger than in **1** due to steric repulsions between the substituent R and the bridging base ion pair solvate in **1**.

To test this explanation, we have investigated the influence of base association on geometrical orientation in base-promoted eliminations from 2,2,3-trichlorobutane (**3**). Because of the much larger dimensions of Y = Cl for this substrate compared with Y = H for a 2-alkyl halide, steric interactions of α- and β-substituents with the solvated base ion pair in **1** and **2** should be quite similar and the special facilitation of (*Z*)-alkene formation by base association should disappear. Although the introduction of both α- and β-chlorine substituents into transition-states **1** and **2** may also exert electronic effects and modify the character of the E2 transition state,[3,4] a pronounced steric effect should also be operative. A strong preference for anti elimination from **3** is anticipated.[3]

Eliminations from **3** promoted by MeONa–MeOH, *t*-BuOK–*t*-BuOH, and *t*-BuOK–18-crown-6–*t*-BuOH were studied under conditions where solvolytic elimination and the isomerization or decomposition of the product 2,3-dichloro-2-butenes were demonstrated to be absent. In the base-promoted eliminations, the yields of 2,3-dichloro-2-butenes were >90% and the formation of the positional isomer 2,3-dichloro-1-butene was not detectable. Results are recorded in Table I.

The effects of base–solvent system and base concentration variations upon the geometrical orientation observed in eliminations from **3** are in complete accord with

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