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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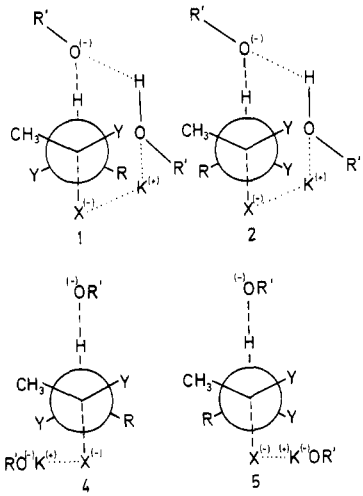
Table I. Geometrical Orientation in Base-Promoted Dehydrochlorination of 2,2,3-Trichlorobutane[a] at 35 °C

entry	base-solvent	[base], M	(E)-/(Z)-2,3-dichloro-2-butene
1	MeONa-MeOH	0.50	6.73 ± 0.10[b]
2	MeONa-MeOH	1.0	6.71 ± 0.03
3	*t*-BuOK-*t*-BuOH	0.25	1.45 ± 0.26
4	*t*-BuOK-*t*-BuOH	0.50	1.13 ± 0.02
5	*t*-BuOK-*t*-BuOH	1.0	0.94 ± 0.01
6	*t*-BuOK-18-crown-6-*t*-BuOH[c]	0.50	3.79 ± 0.42

[a] [Substrate] = 0.20 M. [b] Standard deviations from the analysis of three or four reaction solutions. [c] [18-Crown-6] = 0.50 M.

those observed for eliminations from 2-alkyl halides and tosylates.[2,3] Thus, the (E)-/(Z)-2,3-dichloro-2-butene ratio (a) decreases sharply when the base–solvent system is changed from MeONa–MeOH (dissociated base) to *t*-BuOK–*t*-BuOH (associated base; compare entries 1, 2 with 3–5), (b) decreases regularly as the base concentration is enhanced for *t*-BuOK–*t*-BuOH (entries 3–5) but remains invariant for similar base concentration changes with MeONa–MeOH (entries 1, 2), (c) increases markedly for *t*-BuOK–18-crown-6–*t*-BuOH (dissociated base) compared with *t*-BuOK–*t*-BuOH (associated base; compare entries 4, 6).

These observations cast serious doubt upon the validity of the solvated ion pair model represented by **1** and **2** for explaining the effects of base association upon geometrical orientation.



Very recently, Závada[5,6] had advanced an alternative explanation for the effect of base association upon geometrical orientation in base-promoted eliminations from 2-alkyl halides and tosylates. In this model, the leaving group is "solvated" by a metal alkoxide ion pair as shown in **4** and **5** (with Y = H). In **5** the metal alkoxide is located in a region of lesser steric interference with the α- and/or β-substituents than in **4** which reduces the transition-state free-energy difference from that found with dissociated bases. Our observations for the effect of base association upon geometrical orientation in eliminations from **3** are consistent with this model if for Y = Cl, the metal alkoxide favors a more polar region of transition-state **5** rather than the less polar environment in **4**.

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Experimental Section

Chemicals. Methanol (Fisher, reagent) was dried by reaction with magnesium turnings and distillation, *tert*-Butyl alcohol (Fisher, reagent) was triply distilled. 18-Crown-6 (Parish) was used as received. 2,2,3-Trichlorobutane (**3**) was prepared by the method of Scharf and Laux.[7] Authentic samples of (Z)- and (E)-2,3-dichloro-2-butene[7] for determining GLC molar responses and for stability studies were prepared from a sealed tube reaction of 1.5 g of **3**, 1.2 g of *t*-BuOK (Aldrich), and 10.5 mL of dry THF for 24 h at 100 °C. The reaction mixture was subjected to preparative GLC (0.25 in. × 10 ft of 20% SE-30 on Chromosorb PAW at 65 °C) on an Antek Model 461 gas chromatograph to produce pure samples of (Z)- and (E)-2,3-dichloro-2-butene.

Control Experiments. When **3** was heated at 50 °C for 48 h in the presence of 2,6-lutidine (sterically hindered base to supress possible acid-catalyzed decomposition) in MeOH, no formation of 2,3-dichloro-2-butene by solvolytic elimination was observed. Solvolysis would be even less favored at lower temperatures or in the less ionizing solvent *t*-BuOH. No product isomerization or degradation was evident when a mixture of (Z)- and (E)-2,3-dichloro-2-butenes was heated at 35 °C for 18 h with 1.0 M *t*-BuOK–*t*-BuOH. However, for similar treatment of a 2,3-dichloro-2-butene mixture with 0.50 M *t*-BuOK–*t*-BuOH containing 0.50 M 18-crown-6, decomposition was detectable after 5 min.

Base–Solvent Solutions. A 1.0 M solution of *t*-BuOK-*t*-BuOH was prepared by the reaction of clean potassium metal with dry *t*-BuOH under nitrogen. A 1.0 M solution of MeONa–MeOH was prepared from the reaction of clean sodium metal and dry MeOH under nitrogen. Solutions with lower base concentrations were prepared by dilution.

Elimination Reactions. Three or four 0.5–1.0-mL samples of the base-solvent solution (0.20 M in **3**) were sealed in nitrogen-flushed, glass ampules and placed in a 35 °C water bath. After overnight reaction (or 5 min with *t*-BuOK–18-crown-6–*t*-BuOH), the contents of the ampules were analyzed by GLC, using a $^1/_8$ in. × 10 ft column of 20% SE-30 on Chromosorb PAW at 55 °C on a Varian Aerograph Model 2400 flame-ionization gas chromatograph with toluene as an internal standard.

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Registry No. **3**, 10403-60-8.

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Synthesis of 2-Azabenz[*a*]anthracene

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Azabenz[*a*]anthracenes have been detected in GC/MS spectra of samples of lake surface sediments, street dust, and suspended urban particulates. They can be regarded as aza derivatives of benz[*a*]anthracene, the parent compound of a series that contains many highly carcinogenic members.[1] As aza derivatives of the carcinogenic benz[*a*]anthracenes, they may be responsible for the mutagenic activity that has been observed in the basic fraction of environmental pollutants.

We report a synthesis of 2-azabenz[*a*]anthracene by a route that is adaptable to the preparation of alkyl derivatives at C-7 and C-12, substitutions that result in high carcinogenicity in the benz[*a*]anthracene series.[1]

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