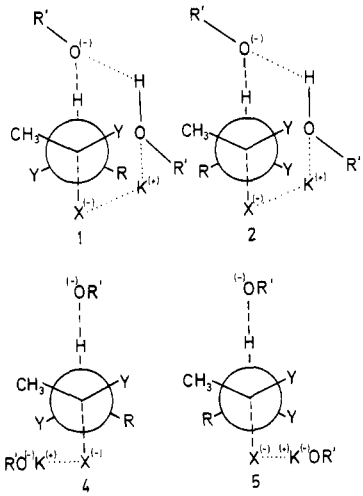
Table I. Geometrical Orientation in Base-Promoted Dehydrochlorination of 2,2,3-Trichlorobutane[a] at 35 °C

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**.

(5) Závada, J.; Pánková, M.; Bartsch, R. A.; Cho, B. R. *Collect. Czech. Chem. Commun.* **1981**, *46*, 850.
(6) Závada, J.; Pánková, M.; Vitek, A. *Collect. Czech. Chem. Commun.*, in press.

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.

(7) Scharf, H. D.; Laux, F. *Synthesis*, **1970**, 582.

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]

(1) Dipple, A. "Chemical Carcinogens"; Searle, C. E., Ed.; American Chemical Society: Washington, DC, 1976; ACS Monogr. No 173, p 245.

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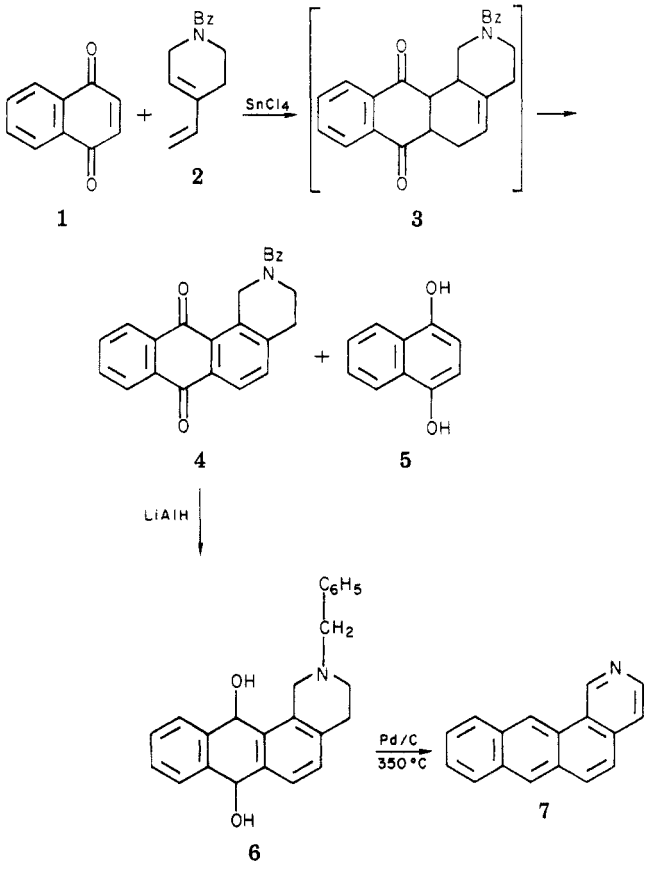
The strategy involved construction of the ring system via a Diels–Alder reaction of 1,4-naphthoquinone (1) with *N*-benzoyl-4-vinyl-1,2,5,6-tetrahydropyridine (2). A similar approach was described by Manning et al.,[2] who carried out the Diels–Alder reaction of 1 with styrene to give benz[*a*]anthracene-7,12-dione, analogous to 4. Key intermediate 3 would be capable of facile conversion to the target compound 7. The diene 2 was synthesized from commercially available *N*-benzoyl-4-piperidone by a Grignard reaction followed by dehydraton.[3]



Finkelstein and Perchonock[3] observed that 2 was quite unreactive and required highly active dienophiles, e.g., dimethyl acetylenedicarboxylate in order to form condensation products. The attempt to condense 2 with 1,4-naphthoquinone (1) confirmed this observation. No condensation product could be detected under noncatalyzed Diels–Alder conditions, and starting materials were recovered unchanged. Different Lewis acids ($AlCl_3$,[4] $SnCl_4$[5]) were used in attempts to catalyze the reaction, varying the temperature (0–25 °C) and the time (1–48 h). Again no product resulted. Only when equimolar amounts of $SnCl_4$ were added to the quinone and diene was reaction observed. Of the two major components isolated, one, an insoluble white solid, was identified as 1,4-dihydroxynaphthalene (5). A second component, purified by silica gel chromatography, was the partially dehydrogenated Diels–Alder adduct 4. Under the required reaction conditions, oxidation–reduction occurred between 1 and Diels–Alder product 3 to give hydroquine 5 and partially aromatized Diels–Alder adduct 4.

Reaction conditions were modified to use the diene 2 (1.0 equiv), the quinone 1 (3 equiv), and anhydrous stannic chloride (3 equiv), affording a 55% yield of crystalline adduct 4. Structure 4 was assigned on the basis of spectral and chemical evidence.

Adduct 4 was reduced by using lithium aluminum hydride (6 equiv). The resulting diol (6) was used without further purification. Aromatization was effected by treatment of the diol 6 with 10% Pd/C at 350 °C. Purification of compound 7 by silica gel chromatography gave an overall yield of 18% from the Diels–Alder adduct (4) of 2-azabenz[*a*]anthracene 7.[6,7]

Experimental Section[7]

***N*-Benzoyl-2-aza-1,2,3,4-tetrahydrobenz[*a*]anthracene-7,12-dione (4).** A mixture of 62.3 g (0.39 mol) of 1,4-napthoquinone (1) and 28.0 g (0.13 mol) of *N*-benzoyl-4-vinyl-1,2,3,6-tetrahydropyridine (2) in 1.6 L of toluene was refluxed for 0.5 h in a flask equipped with a Dean–Stark trap and then allowed to cool. Anhydrous stannic chloride (99.0 g, 0.39 mol) was added. The mixture was refluxed for 2 h and then poured into 2 L of ice–water. The solid was filtered and washed with toluene. The filtrate was extracted with toluene, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel with CH_2Cl_2/EtOAc (8/2) as a elutant. Recrystallization from EtOAc yielded 26.2 g (55%) of 4 as golden crystals: mp 204–205 °C; IR (Nujol mull) 1660, 630 cm^{-1}; NMR ($CDCl_3$) δ 3.07 (2 H, br t, H-4), 3.91 (2 H, br s, H-3), 5.36 (2 H, br s, H-1), 7.59 (6 H, m, benzoyl, H-5), 7.73 (2 H, m, H-9, H-10), 8.22 (3 H, m, H-6, H-8, H-11); UV (CH_2Cl_2) λ_{max} 220 nm (ϵ 42 400), 258 (123 500), 277 (47 100), 336 (19 300); mass spectrum, *m/e* (relative intensity) 367 (M^+, 40), 105 (100). Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81. Found: C, 78.37; H, 4.89; N, 3.84.

***N*-Benzyl-2-aza-1,2,3,4-tetrahydrobenz[*a*]anthracene-7,12-diol (6).** To 5.5 g (0.02 mol) of quinone (4) in 300 mL of dry tetrahydrofuran, under an inert atmosphere, was slowly added 3.7 g (0.09 mol) of lithium aluminum hydride. After the initial vigorous reaction, the mixture was refluxed for 18 h. The cooled mixture was carefully poured into 400 mL of saturated sodium carbonate solution, extracted with dichloromethane, washed with water, dried ($MgSO_4$), and evaporated to give 4.7 g of an oily solid. The diol 6 was used without further purification due to its instability.

2-Azabenz[*a*]anthracene (7). A mixture of 5.30 g (0.015 mol) of the crude diol 6 and 0.53 g of 10% palladium on carbon was heated under an inert atmosphere from 200 to 340 °C in a fluidized sand bath over 2.5 h and then cooled. The mixture was refluxed in absolute ethanol, filtered, and evaporated. The residue was chromatographed on silica gel with hexane/EtOAc (1/1) as the eluant to give 0.53 g (18% from the Diels–Alder adduct 4 of gold solid 7:[6] mp 162–163°C; IR (Nujol mull) 1212, 970 cm^{-1}; NMR ($CDCl_3$) δ 7.62 (4 H, m, H-8, H-9, H-10, H-11), 8.09 (3 H, m, H-4, H-5, H-6), 8.40 (1 H, s, H-12), 8.74 (1 H, d, J = 5 Hz, H-3), 9.26 (1 H, s, H-7), 10.14 (1 H, s, H-1); UV (MeOH) λ_{max} 203 nm (ϵ 32 200), 219 (37 600), 260 (60 800), 270 (8100), 278 (42 100), 284 (41 100), 290 (35 400), 298 (21 400), 327 (7700), 343 (7800), 360 (4800), 397 (600); mass spectrum, *m/e* (relative intensity) 229 (M^+, 100). Anal. Calcd for $C_{17}H_{11}N{\cdot}0.25H_2O$: C, 87.34; H, 4.96; N, 5.99. Found: C, 87.30; H, 5.09; N, 5.93.

Acknowledgment. This work was supported by Contract No. N01-CP-85612 from the National Cancer Institute.

Registry No. 1, 130-15-4; 2, 76513-40-1; 4, 80641-39-0; 6, 80641-40-3; 7, 25082-33-1.

(2) Manning, W. B.; Tomaszewski, J. E.; Muschik, G. M.; Sato, R. L. *J. Org. Chem.* **1977**, *42*, 3465.
(3) Finkelstein, J. A.; Perchonock, C. D. *Tetrahedron Lett.* **1980**, 3323.
(4) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436.
(5) Lou, J. S.; Reusch, W. *J. Org. Chem.* **1980**, *45*, 5012.

(6) 2-Azabenz[*a*]anthracene is presently available as a reference material from Dr. David G. Longfellow, Assistant Chief, Chemical and Physical Carcinogenesis Branch, Division of Cancer Cause and Prevention, National Cancer Institute, Landow Building, Room 8C-33, Bethesda, MD 20205.

(7) Melting points (uncorrected) were obtained in capillary tubes by using a Mel-Temp apparatus. NMR spectra were recorded on Varian Associates EM 390 spectrometer. All chemical shifts are reported in parts per million (δ) downfield from $(Me)_4Si$ as the internal standard. IR spectra were recorded on a Perkin-Elmer 137 spectrometer. UV spectra were determined on a Perkin-Elmer 552 spectrometer. Mass spectra were done on a LKB-900 mas spectrometer.