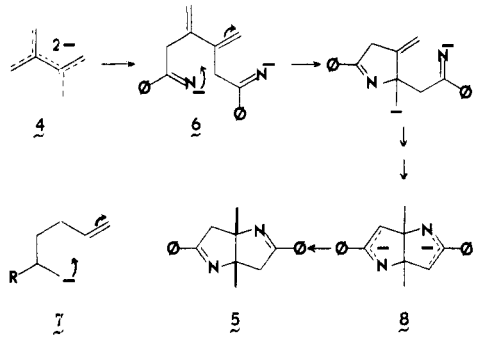
nism is consistent with the finding that pyridine is formed with an H_2O quench as well as with an NH_4Cl–H_2O quench.

When the 2,3-dimethylenebutadiene dianion (**4**)[6] was reacted with benzonitrile, the product, from its spectral and other properties, was **5**; especially helpful in ruling out structures with cyclobutane rings was the large value (14 Hz) for the geminal coupling constant in the methylene groups.

5 is presumably formed via a mechanism like that depicted. Intermediate **6** cannot intramolecularly transfer



a proton via a five- or six-membered-ring transition state but can undergo the intramolecular addition shown via a five-membered-ring transition state; precedent for this comes from the reaction depicted for **7**, itself formed by adding *n*- or *tert*-butyllithium to 1,5-hexadiene.[1b] That **8** is a reasonable last intermediate was shown by quenching with D_2O, giving slightly less than two 2 deuteriums in **5** in the methylene positions only and in a 2:1 exo to endo ratio (^1H NMR).

Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. ^1H NMR spectra were recorded on CCl_4 solutions with a Varian T-60 spectrometer and ^{13}C NMR spectra on $DCCl_3$ solutions with a Bruker WH-90 spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane.

2,6-Diphenyl-4-methylpyridine (2a). To an argon-filled, septum-capped, round-bottom flask at −78 °C containing 1.34 mL (13.2 mmol) of benzonitrile was added dropwise a solution of 6.59 mmol of $1{\cdot}2Li^+{\cdot}2(CH_3)_2NCH_2CH_2N(CH_3)_2$[1b] in 10 mL of THF. After 45 min, the mixture was warmed to room temperature, quenched with 2 mL of H_2O, poured over NH_4Cl–ice–water, made basic with $NaHCO_3$, and extracted with ether. After the extract was dried over $MgSO_4$ and the solvent evaporated, TLC on silica gel with CH_2Cl_2 gave **2a**[2] (1.38 g, 85%; R_f 0.9) and 2-methyl-4-phenyl-2-buten-4-one[7] (52 mg, 5%; R_f 0.6).

2,6-Di-*tert*-butyl-4-methylpyridine (2b). In a similar reaction with the sterically hindered trimethylacetonitrile, even after refluxing for 4 h, considerable unreacted nitrile was recovered; 0.40 g of the desired pyridine, **2b**, mp 40–41 °C,[3] was obtained (30% yield based on starting nitrile).

2,6-Di-(2-pyridyl)-4-methylpyridine (2c). After a reaction similar to that for **2a** above but employing 2-cyanopyridine, extraction was done with $HCCl_3$ rather than ether. ^1H NMR indicated the desired product to be present in 18% yield in the crude dark oil. Dissolving the oil in 10 mL of $HCCl_3$ and adding 20 mL of pentane caused a tar to separate, and chromatographing the solution above the tar on basic alumina, eluting with 80:20 pentane/$HCCl_3$, gave as a first fraction a solid which on recrystallization from pentane gave 97 mg (6%) of **2c**: mp 97–100 °C; ^1H NMR 2.55 (s, 3 H), 7.2 (ddd, 2 H, J = 8, 4.5, 2 Hz), 7.7 (ddd, 2 H, J = 8, 8, 2 Hz), 8.3 (s, 2 H), 8.6 (m, 4 H).

Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.36; H, 5.29; N, 16.86.

***cis*-3,7-Diphenyl-1,5-dimethyl-2,6-diazabicyclo[3.3.0]-octa-2,6-diene (5).** After benzonitrile was reacted similarly with dianion **4**[6] and quenched with 1 mL of H_2O, the solution was washed with NaCl, the solvents evaporated, and the residue flash distilled (170 °C, 1 mm) and recrystallized from $HCCl_3$/pentane to give 0.86 g (45%) **5**: mp 139–141 °C; ^1H NMR 1.5 (s, 6 H), 3.1 (d, 2 H, J = 17 Hz), 3.6 (d, 2 H, J = 17 Hz), 7.4 (m, 6 H), 7.8 (m, 4 H); ^{13}C NMR, 21 (q), 47 (t), 80 (s), 126 (d), 126.5 (d), 128.5 (d), 132.5 (s), 167 (s); MS molecular ion m/e 288; UV λ_{max} (EtOH) 248 nm (ϵ 11200); IR 1580 (m), 1615 (s) cm^{-1}.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.72; H, 6.87; N, 9.64.

When the quench was with 1 mL of D_2O, the product had a molecular ion peak at m/e 290 in the mass spectrum and the ^1H NMR changed only at δ 3.1 (br s, 1.3, endo H) and 3.6 (br s, 0.7, exo H).

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Registry No. **1**, 41792-83-0; **2a**, 53531-57-0; **2b**, 38222-83-2; **2c**, 72036-41-0; **4**, 69780-62-7; **5**, 72036-42-1; benzonitrile, 100-47-0; trimethylacetonitrile, 630-18-2; 2-cyanopyridine, 100-70-9.

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Synthesis of Oxidized Metabolites of Dibenz[*a*,*c*]anthracene

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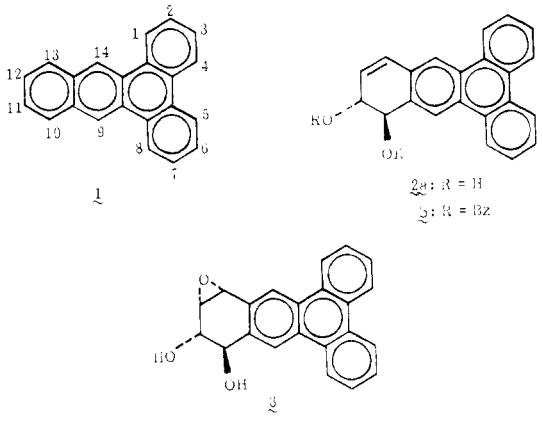
Dibenz[*a*,*c*]anthracene (**1**) is a weak tumor initiator.[1] It undergoes metabolic transformation in rodent embryo cells to a reactive metabolite(s) which binds covalently to the nucleic acids and proteins of the host cells.[2] Incubation of **1** with rat liver homogenates affords a single metabolite tentatively identified as the 10,11-dihydrodiol **2a** on the



basis of its UV absorption spectrum and its conversion on treatment with acid into 10- and 11-hydroxy-**1**.[3] Since there is now good evidence that many carcinogenic hydrocarbons undergo enzymatic activation to diol epoxide derivatives (via arene oxide and trans dihydro diol intermediates) which react covalently with DNA and RNA,[4,5]

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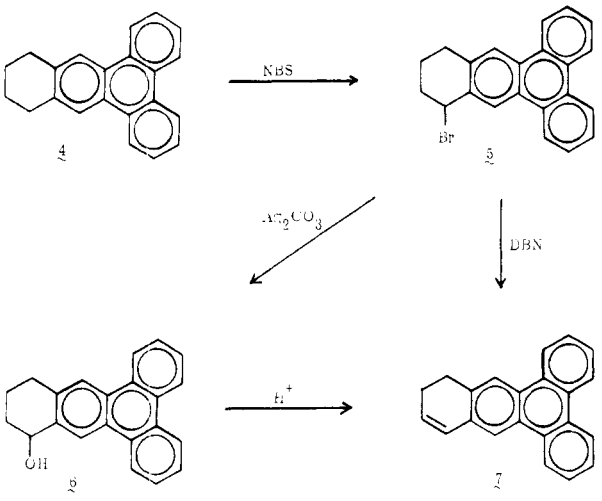
Scheme I



it is conceivable that the reactive form of **1** which binds to nucleic acids in vivo is **3**.[6] In order to test this hypothesis and to make **2a** and **3** available for studies of their mutagenic, carcinogenic, and other biological properties, we undertook their synthesis.

Results

Dihydroarenes are key intermediates in the synthesis of the dihydro diols of polycyclic hydrocarbons.[4b] Synthesis of 10,11-dihydro-**1** (**7**) was accomplished both by the conventional synthetic route[4b] from triphenylene reported by Sims[3] and by a shorter route from **1** itself (Scheme I). The latter method involved initial catalytic hydrogenation of **1** over a platinum catalyst under mild conditions, to afford 10,11,12,13-tetrahydro-**1** (**4**).[7] Several methods for the partial dehydrogenation of **4** to **7** were investigated. Direct dehydrogenation with DDQ[8] afforded **7** in moderate but variable yield, and substantial further conversion to **1** also took place. Reaction of **4** with lead tetraacetate failed to furnish **7**, despite the fact that analogous reaction of 7,8,9,10-tetrahydrobenzo[*a*]pyrene provides the most convenient route to 7,8-dihydrobenzo[*a*]pyrene.[4b,9] Bromination of **4** with NBS gave the bromo derivative **5**. Although direct dehydrobromination of **5** afforded **7** in low yield (20–30%), reaction of **5** with silver carbonate gave the alcohol **6**, acid-catalyzed dehydration of which gave **7** in 60% overall yield.

The olefin **7** was utilized to synthesize the trans dihydro diol **2a** via the sequence of Prévost reaction, dehydrogenation with DDQ (or NBS bromination–dehydrobromination), and methanolysis employed in the synthesis of analogous dihydro diols.[4b] The integrated proton NMR spectrum of **2a**, obtained as a white solid (mp 210–212 °C dec), was in complete agreement with the assigned structure. The coupling constant of the carbinol protons ($J_{10,11}$ = 9.5 Hz) was intermediate between the extreme values of 2.0 and 12.7 Hz anticipated for the pure diaxial and diequatorial conformers, respectively.[10] Therefore, **2a** exists in solution, like other nonbay-region vicinal dihydro diols, as an equilibrium mixture of conformers favoring the diequatorial form.[10]

Epoxidation of **2a** with *m*-chloroperbenzoic acid afforded stereospecifically the anti isomeric diol epoxide derivative **3**, the NMR spectrum of which was in full agreement with the assigned structure and with the spectra of other structurally related diol epoxide derivatives.[4b,10-12] While the synthetic **2** and **3** are racemic, it is likely that only a single enantiomer is formed metabolically.[4,13]

The UV spectrum of racemic **2a** matched that of the dihydro diol isolated as a metabolite of **1**,[3] confirming the tentative structural assignment of the latter.[14] Compound **3** is found to be moderately active as an inhibitor of infectivity of the ϕX174 DNA virus in *E. Coli* spheroplasts.[15] Tests of tumorigenic activity indicate **2a** and **3** to be only weakly tumorigenic on mouse skin;[16] their mutagenicity is currently under investigation.

Experimental Section

General Methods. Dibenz[*a*,*c*]anthracene was synthesized by the method previously described.[17] *m*-Chloroperbenzoic acid (Aldrich) was purified by washing with pH 7.5 phosphate buffer and drying under reduced pressure. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; Arapahoe) and *N*-bromosuccinimide (NBS; Aldrich) were purified by recrystallization from benzene and water, respectively. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN; Aldrich) was used as supplied. Benzene, THF, triethylamine, and Me_2SO were distilled from $LiAlH_4$ prior to use. NMR spectra were obtained on Varian T-60 or Bruker HX-270 spectrometers with tetramethylsilane as the internal standard. Melting points are uncorrected. All new compounds (**2a**, **2b**, **3**, and **9**) gave satisfactory microanalysis for C and H within ±0.3%, which were submitted for review.

10-Oxo-10,11,12,13-tetrahydrodibenz[*a*,*c*]anthracene (8). This compound was synthesized from triphenylene by the method of Buu-Hoi et al.:[18] mp 189–190 °C (lit.[3] mp 186 °C); NMR ($CDCl_3$) δ 2.07–2.47 (m, 2, H_{12}), 2.60–2.93 (m, 2, H_{11}), 2.96–3.13 (m, 2, H_{13}), 7.40–7.83 (m, 4, $H_{2,3,6,7}$), 8.37 (s, 1, H_{14}), 8.37–8.87 (m, 4, $H_{1,4,5,8}$), 9.27 (s, 1, H_9).

10,11,12,13-Tetrahydrodibenz[*a*,*c*]anthracene (4). This compound was prepared by catalytic hydrogenation of **1** as described previously:[7] mp 201–203 °C (lit.[7] mp 201–203 °C); NMR (CCl_4) δ 1.65–2.10 (m, 4, $H_{11,12}$), 2.73–3.17 (m, 4, $H_{10,13}$), 7.30–7.63 (m, 4, $H_{2,3,6,7}$), 8.15 (s, 2, $H_{9,14}$), 8.27–8.63 (m, 4, $H_{1,4,5,8}$).

10,11-Dihydrodibenz[*a*,*c*]anthracene (7). Method A. Reduction of **8** (10 g, 34 mmol) in methanol (50 mL) with $NaBH_4$ (2.6 g) at ambient temperature for 2 h afforded **6** (9.8 g, 98%): mp 154–156 °C (lit.[3] mp 155–156 °C); NMR ($CDCl_3$) δ 1.6–2.3 (m, 4, $H_{11,12}$), 2.5–3.2 (m, 2, H_{13}), 4.88 (m, 1, H_{10}), 7.35–7.65 (m,

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4, $H_{2,3,6,7}$), 8.15–8.80 (m, 6, $H_{1,4,5,8,9,14}$).

Method B. Bromination of **4** (507 mg, 1.8 mmol) with NBS (385 mg, 2.16 mmol) was conducted in the presence of dibenzoyl peroxide (20 mg) in refluxing CCl_4 (100 mL) under N_2 for 45 min. Succinimide was filtered off and the solvent evaporated to yield crude **5** as a yellowish oil; the NMR spectrum of **5** exhibited a characteristic bromomethine peak at σ 5.66. A suspension of **5** (758 mg) and equal weights of Ag_2CO_3 in aqueous dioxane (50:50) was heated at reflux for 1 h.[19] Conventional workup afforded **6** (408 mg, 60%), the physical properties of which were identical with those of **6** obtained by method A.

Dehydrobromination[4b] of **5** by stirring with DBN (0.6 mL) in THF (60 mL) at 0 °C overnight also furnished **7** (25% yield).

Dehydration of **6** with *p*-tosic acid in refluxing benzene for 1 h gave **7** (98%): mp 167–169 °C (lit.[3] mp 168–169 °C); NMR ($CDCl_3$) δ 2.28–2.67 (m, 2, H_{11}), 3.00 (d, 2, $J_{10,11}$ = 8 Hz, H_{10}), 5.92–6.25 (m, 1, H_{12}), 6.62 (d, 1, $J_{12,13}$ = 10 Hz, H_{13}), 7.41–7.73 (m, 4, $H_{2,3,6,7}$), 8.17 (s, 1, H_{14}), 8.25 (s, 1, H_9), 8.40–8.80 (m, 4, $H_{1,4,5,8}$).

Method C. A solution of **4** (500 mg, 1.9 mmol) in benzene (150 mL) was heated with DDQ (410 mg) at reflux for 10 min. NMR analysis of the crude product isolated by conventional workup showed the presence of **4** (83%), **7** (8%), and **1** (8%). The presence of **7** was confirmed by Prévost reaction to provide the corresponding *trans*-dibenzoate ester identical with that from authentic **7**.

Prévost Reaction of 7. A solution of silver benzoate (8.7 g, 38 mmol) and I_2 (4.8 g, 19 mmol) in dry benzene (200 mL) was refluxed for 30 min. A solution of **7** (5.3 g, 19 mmol) in benzene (150 mL) was added, and the resulting solution was stirred at reflux for 24 h under N_2. Workup in the usual manner[4b,5b] afforded the crude product which was purified by chromatography on Florisil. Elution with benzene gave *trans*-10,11-bis(benzoyloxy)-10,11,12,13-tetrahydro-1 (**9**) as a white solid (7.98 g, 80%): mp 180–181 °C; NMR ($CDCl_3$) δ 2.26–2.66 (m, 2, H_{12}), 3.07–3.46 (m, 2, H_{13}), 5.50–5.86 (m, 1, H_{11}), 6.73 (d, 1, $J_{10,11}$ = 5.5 Hz, H_{10}), 7.0–8.65 (m, 20, aromatic).

***trans*-10,11-Bis(benzoyloxy)-10,11-dihydrodibenz[*a*,*c*]anthracene (2b). NBS Method.** To a solution of **9** (3.02 g, 5.78 mmol) from the previous reaction in CCl_4 (50 mL) was added NBS (1.09 g, 6.1 mmol) and benzoyl peroxide (10 mg), and the resulting suspension was heated at reflux under N_2 for 35 min. The insoluble succinimide was filtered off and the solvent evaporated. The residue was dissolved in THF (20 mL), the solution was cooled to 0 °C, and DBN (15 mmol) was added. The resulting solution was stirred at 0 °C overnight and worked up conventionally. Chromatography on Florisil eluted with benzene furnished **2b** (1.02 g, 34%) as a colorless solid: mp 183–184 °C; NMR ($CDCl_3$) δ 5.99 (dd, 1, H_{11}), 6.21 (dd, 1, H_{12}), 6.80 (d, 1, H_{10}), 6.98 (d, 1, H_{13}), 7.15–8.80 (m, 20, aromatic), $J_{10,11}$ = 6 Hz, $J_{11,12}$ = 4 Hz, $J_{12,13}$ = 10 Hz.

DDQ Method. A solution of the dibenzoate ester (2.0 g, 3.8 mmol) and DDQ (1.09 g, 4.8 mmol) in dioxane (150 mL) was refluxed under N_2 for 96 h. Chromatography on a column of neutral alumina eluted with benzene gave **2b** (1.37 g, 69%).

(±)-*trans*-10,11-Dihydroxy-10,11-dihydrodibenz[*a*,*c*]anthracene (2a). To a solution of **2b** (1.1 g, 2.1 mmol) in THF (35 mL) was added a solution of $NaOCH_3$ (232 mg, 4.3 mmol) in methanol (20 mL) and the resulting solution stirred at 60 °C for 20 min. Conventional workup gave **2a** (567 mg, 86%) as a white solid: mp 210–212 °C dec; NMR (Me_2SO-d_6) δ 4.36 (ddd, 1, H_{11}), 4.80 (d, 1, H_{10}), 6.03 (dd, 1, H_{12}), 6.70 (dd, 1, H_{13}), 7.55–7.88 (m, 4, $H_{2,3,6,7}$), 7.42–7.86 (m, 6), $H_{1,4,5,8,9,14}$, $J_{10,11}$ = 9.5 Hz, $J_{11,12}$ = 2 Hz, $J_{12,13}$ = 10 Hz, $J_{11,13}$ = 2 Hz.

(±)-*trans*-10,11-Dihydroxy-*anti*-12,13-epoxy-10,11,12,13-tetrahydrodibenz[*a*,*c*]anthracene (3). A solution of **2a** (88 mg, 0.28 mmol) and *m*-chloroperbenzoic acid (487 mg) in 40 mL of dry THF was stirred at room temperature under N_2 for 1.5 h. The solution was chilled and partitioned between ethyl acetate–ether (1:1) and cold 10% aqueous NaOH solution as rapidly as possible. The organic layer was washed with cold water, dried, and evaporated, avoiding heating.[20] Trituration of the residue with ether provided **3** (52 mg, 56%) as a white solid: mp 167–169 °C dec; NMR Me_2SO-d_6, D_2O δ 3.77 (apparent d, 1, H_{12}), 3.93 (apparent d, 1, H_{11}), 4.34 (d, 1, H_{13}), 4.79 (d, 1, H_{10}), 7.5–7.9 (m, 4, $H_{2,3,6,7}$), 8.57–9.07 (m, 6, $H_{1,4,5,8,9,14}$), $J_{10,11}$ = 9 Hz, $J_{11,12} \simeq$ 1 Hz, $J_{12,13}$ = 4.5 Hz.

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Registry No. **1**, 215-58-7; (±)-**2a**, 72100-19-7; (±)-**2b**, 72100-20-0; (±)-**3**, 72150-71-1; **4**, 25486-89-9; **5**, 72100-21-1; **6**, 39081-07-7; **7**, 39081-08-8; **8**, 39081-06-6; (±)-**9**, 72100-22-2; triphenylene, 217-59-4; silver benzoate, 532-31-0.

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(20) Like other diol epoxides, **3** is thermally and acid sensitive and tends to decompose on attempted chromatography.

Reduction of α,β-Diarylacrylonitriles by Sodium Borohydride

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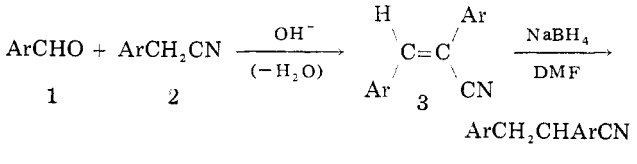
The ready accessibility of α,β-diarylacrylonitriles and their highly selective rapid reduction by $NaBH_4$ provides an excellent synthesis of α,β-diarylpropionitriles. The conversion of 23 combinations of aromatic aldehydes and arylacetonitriles by the two-step sequence to the corresponding substituted propanenitriles is reported. We recommend this sequence as the method of choice for the syntheses of these compounds since both condensation and reduction processes occur in very high yield (80–90%). Furthermore, anhydrous conditions are not necessary, reaction times are short, and workups are simple. We have also examined the kinetics of the reduction reaction in this series for 11 cases.

Corey and others[2] have recently reported the use of magnesium in methanol and $NaBH_3CN$[3] on a millimole scale, for related reductions. The rates of $NaBH_4$ reduction of α-phenylcinnamates by competition runs were reported.[4] Refluxing THF,[5] employed for three α-cyanostilbene reductions, was unnecessary for our compounds. We employed DMF as the solvent and obtained fast reactions at ambient or lower temperatures.

Direct measurement of the progress of conversion of **3** to **4** was readily monitored by infrared analysis.[6] Removal



1 2 3 4

of aliquots at various time intervals showed a decrease in absorbance at 2215 cm^{-1} (conjugated CN) as a corre-

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