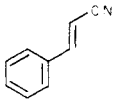
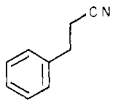
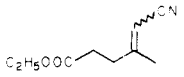
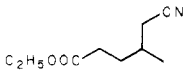
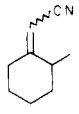
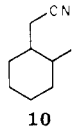
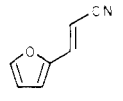
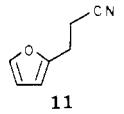
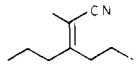
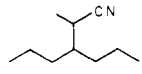
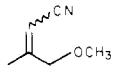
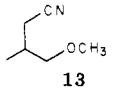
Table I. Reductions with Copper Hydride Complex[a]

substrate	product	yield, %
	 7	99
	 8	32
	 9	70
	 10	92
	 11	51
	 12	83
	 13	29

[a] See Experimental Section for details.

to 0 °C under a nitrogen atmosphere was added 7.4 mL (26.0 mmol) of Vitride[12] (3.5 M solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene). The resulting dark solution was stirred at 0 °C for 30 min and brought to −78 °C. 2-Butanol (2.3 mL, 26.0 mmol) was cautiously introduced via syringe, followed by a solution of the ene nitrile (1.3 mmol) in dry tetrahydrofuran (5 mL). After 2 h at this temperature, the reaction mixture was maintained at room temperature for a minimum of 4 h before being treated with saturated ammonium chloride solution (6 mL). The product was extracted into dichloromethane and the organic phase was dried, filtered, and evaporated. Silica gel chromatographic purification of the residue (elution with ether–hexane, 1:1) afforded the dihydro product in the yields (nonoptimized) cited in Table I.

As concerns characterization, **7** is a commercially available commodity,[14] whereas **8** and **10** were previously reported by Profitt, Watt, and Corey.[6] The furan derivative **11** has also been described earlier.[15]

For **9**: ν_{max} (neat) 2930, 2210, 1460, 1430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.18 (m, 2 H), 0.89 (br s, 4 H), 0.60–0.20 (m, 5 H); *m/e* calcd 109.0891, obsd 109.0895.

For **12**: ν_{max} (neat) 2960, 2870, 2220, 1455, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–1.10 (m, 13 H), 0.90 (m, 6 H); *m/e* calcd 153.1517, obsd 153.1522.

For **13**: ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 3 H), 3.5–3.2 (m, 1 H), 2.40 (d, J = 5 Hz, 2 H), 1.08 (d, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 75.6, 59.1, 31.1, 21.4, 16.3 ppm (nitrile carbon shift not recorded); *m/e* calcd 113.0841, obsd 113.0844.

Acknowledgment. This investigation was made possible by a grant from the National Institutes of Health (AI-11490).

Registry No. **3**, 72017-14-2; **7**, 645-59-0; **8**, 52162-21-7; **9**, 72017-15-3; **10**, 53154-06-6; **11**, 21446-61-7; **12**, 72017-16-4; **13**, 21589-41-3; (*E*)-3-phenyl-2-propenenitrile, 1885-38-7; ethyl 4-(cyanomethylene)pentanoic acid, 72017-17-5; 3-cyclopropyl-2-butenenitrile, 822-95-7; (2-methylcyclohexylidene)acetonitrile, 53153-81-4; (*E*)-3-(2-furanyl)-2-propenenitrile, 6125-63-9; 2-methyl-3-propyl-2-hexenenitrile, 72017-18-6; 4-methoxy-3-methyl-2-butenenitrile, 72017-19-7.

(14) Available from the Aldrich Chemical Co.
(15) Sorm, F.; Brandejs, J. *Collect. Czech. Chem. Commun.* **1947**, *12*, 444.

Reactions of Dianions with Nitriles. A New Pyridine Synthesis

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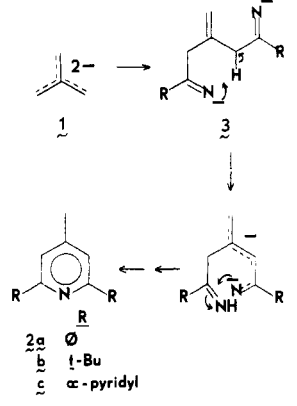
The 2-methyleneallyl dianion (**1**) has previously been reacted with many electrophiles[1] but not with nitriles. When we added dianion **1** in THF–pentane to 2 equiv of benzonitrile at −78 °C and warmed the mixture to 25 °C, 2,6-diphenyl-4-methylpyridine[2] (**2a**) was formed in 85% yield. Similar reactions with trimethylacetonitrile and



α-cyanopyridine gave 2,6-di-*tert*-butyl-4-methylpyridine[3] (**2b**, 30%) and 2,6-di-(2-pyridyl)-4-methylpyridine (**2c**, 18%), respectively; the former is a sterically hindered base, and the latter is an excellent tridentate ligand.[4] With acetonitrile (and probably other nitriles with α-hydrogens), however, no product of this type was detected, presumably due to rapid proton abstraction by the dianion. Other nitriles which gave no product of this type (perhaps due to rapid electron transfer[5]) were 2-cyanophenanthroline and 2,6-dicyanopyridine.

A possible mechanism for the formation of pyridines **2** is shown; a key step is intramolecular proton transfer in **3** via a six-membered-ring transition state. This mecha-

(1) (a) J. Klein and A. Medlik, *J. Chem. Soc., Chem. Commun.*, 275 (1973); (b) J. J. Bahl, R. B. Bates, W. A. Beavers, and N. S. Mills, *J. Org. Chem.*, **41**, 1620 (1976); (c) R. B. Bates, W. A. Beavers, B. Gordon III, and N. S. Mills, *ibid.*, **44**, 3800 (1979).
(2) M. Y. Kornilov, L. M. Shulezhko, and A. I. Tolmachev, *Theor. Exp. Chem. (Engl. Transl.)*, **10**, 397 (1975).
(3) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, **41**, 3034 (1976).
(4) **2c** is a new compound, but its coordinating properties should closely resemble those of the well-known but not readily available compound lacking the methyl group (F. A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, p 723). Indeed, oxidation and decarboxylation of **2c** might provide a competitive route to the latter.
(5) S. L. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967); H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971).

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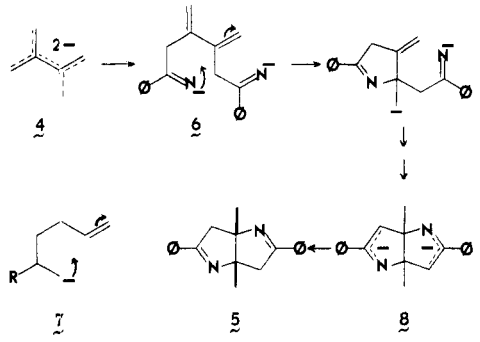
nism is consistent with the finding that pyridine is formed with an H_2O quench as well as with an NH_4Cl–H_2O quench.

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).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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.

(6) J. J. Bahl, R. B. Bates, and B. Gordon III, *J. Org. Chem.*, **44**, 2290 (1979).

(7) J. M. Watson, J. L. Irving, and R. M. Roberts, *J. Am. Chem. Soc.*, **95**, 3348 (1973).

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

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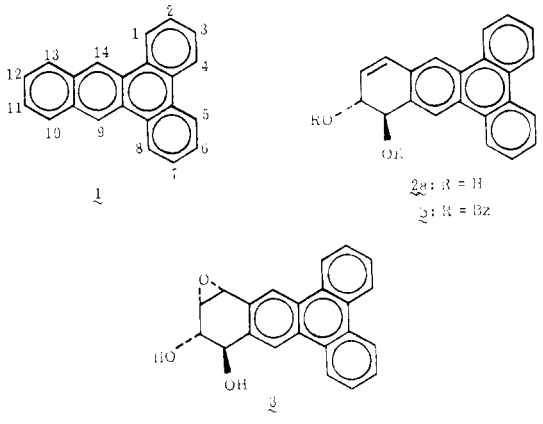
Dibenz[*a*,*c*]anthracene (**1**) is a weak tumor initiator.[1] It undergoes metabolic transformation in rodent embryo cells to a reactive metabolite(s) which binds covalently to the nucleic acids and proteins of the host cells.[2] Incubation of **1** with rat liver homogenates affords a single metabolite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

(1) Scribner, J. D. *J. Natl. Cancer Inst.* **1973**, *50*, 1717. Lijinski, W.; Garcia, H.; Saffiotti, U. *Ibid.* **1970**, *44*, 641.

(2) Duncan, M. E.; Brookes, P.; Dipple, A. *Int. J. Cancer* **1969**, *4*, 813. Duncan, M. E.; Brookes, P. *Ibid.* **1972**, *9*, 349. Kuroki, T.; Heidelberger, C. *Cancer Res.* **1971**, *31*, 2168.

(3) Sims, P. *Biochem. J.* **1972**, *130*, 27; *Biochem. Pharmacol.* **1970**, *19*, 795.

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