Table I, Entry 9. The reaction was quenched with 3 g (21 mmol) of iodomethane. The usual workup followed after standing for another day. Chromatography (3 × 60) with toluene provided (subsequent to the hydrocarbons) 1.07 g (100%) of **16e** as oil, identified by ^{1}H NMR comparison with an authentic sample prepared from propiophenone and benzyl chloride according to ref 20: ^{1}H NMR (90 MHz) δ 1.15 (d, J = 6.5 Hz, Me), 2.64 (dd, ^3J = 7.8 Hz, ^2J = 13.6 Hz, 1 benzylic H), 3.15 (dd, ^3J = 6.3 Hz, ^2J = 13.6 Hz, 1 benzylic H), 3.67 (mc, CHCO), 7.07–7.50 (m, Ph, meta and para H of benzoyl), 7.83–7.94 (m, ortho H of benzoyl); IR (film) 1682 cm^{-1}.

Table I, Entry 10. Chromatography (1.5 × 45) with toluene provided (subsequent to the hydrocarbons) 197 mg (94%) of **8** whose benzylic methylene group contained (^{1}H NMR at 250 MHz) about 60% of the theoretical protium content for a deuterium transfer from AH_2-d_4 to 1^{2-}: ^{1}H NMR (250 MHz) δ 3.07 (mc, t-like with apparent $J \sim 8$ Hz, benzylic CH_2), 3.30 (mc, t-like with apparent $J \approx 8$ Hz, benzoylic CH_2), 7.16–1.34 (m, benzylic Ph), 7.40–7.48 (m, meta H of benzoyl), 7.50–7.58 (m, para H of benzoyl), 7.92–7.98 (m, ortho H of benzoyl).

Table I, Entry 11. Chromatography (2.2 × 60) with toluene provided i-PrAH_2, 390 mg (38%) of **11**, and a mixture of (^{1}H NMR) 31 mg (3%) of **11** and 129 mg (12%) of **12**. Elution with ethyl acetate provided 230 mg (46%) of **5**.

***trans*-1,3-Diphenyl-3-(10-isopropyl-9,10-dihydroanthr-9-yl)propan-1-one (11)**: mp 116–117 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.91 (d, J = 6.9 Hz, 2 Me), 2.22–2.35 (m, CH of i-Pr), 3.20 (dd, ^3J = 4.5 Hz, ^2J = 17.6 Hz, 1 H, COCH), 3.45 (dd, ^3J = 8.6 Hz, ^2J = 17.6 Hz, 1 H, COCH), 3.61 (d, J = 5.0 Hz, 10-H), 4.34–4.41 (m, COCCH), 4.59 (d, J = 4.7 Hz, 9-H), 6.92–6.98 (m, 2 ortho H of Ph at saturated C), 7.03–7.54 (m, 14 H, aryl H except 4 ortho H), 7.79 (d, J = 7.4 Hz, 2 ortho H of benzoyl); IR (KBr) 1686 cm^{-1} (C=O). Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.21; H, 6.95.

***cis*-1,3-Diphenyl-3-(10-isopropyl-9,10-dihydroanthr-9-yl)propan-1-one (12)**: not pure, identified by ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.06 (d, J = 6.7 Hz, 1 Me), 1.08 (d, J = 6.5 Hz, 1 Me), 2.00 (mc, CH of i-Pr), 3.35–3.41 (m, 1 H, COCH), 3.43 (d, J = 10.0 Hz, 10-H), 3.55–3.68 (m, 2 H, 9-H, COCH), 4.01-4.08 (m, COCCH), 6.16 (d br, J = 7.8 Hz, 1 H, ortho H of pH at saturated C), 6.72 [td, (t) ^3J = 7.7 Hz, (d) ^4J = 1.3 Hz, 1 H neighboring meta H of Ph], 6.93–7.47 (m, 14 H, aryl H except 3 ortho H and 1 meta H), 7.66 (d, J = 7.3 Hz, ortho H of benzoyl); IR (KBr) 1687 cm^{-1} (C=O).

Table I, Entry 12. Chromatography (3 × 60) with toluene provided 100 mg (15%) of **8**. Elution with CH_2Cl_2 gave 420 mg, and elution with ethyl acetate gave 270 mg of mixtures of many unidentified products.

Table I, Entry 13. A 420-mg (47%) portion of A was removed by filtration. Chromatography (3 × 60) with CH_2Cl_2 of the filtrate gave a mixture of A and AH_2, then 65 mg (4%) of **15a**, and finally 600 mg (81%) of **16a**.

3-(9,10-Dihydroanthr-9-yl)-3-phenylbutan-2-one (15a): mp (MeOH) 119–120 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.96 (s, Me), 2.78–3.00 (m, $COCH_2$), 3.15 (d br, J = 18.5 Hz, 10-H pseudo ax), 3.48–3.57 (m, COCCH), 3.53 (d, J = 18.5 Hz, 10-H pseudo eq), 4.11 (d, J = 6.7 Hz, 9-H pseudo eq), 6.60 (d, J = 7.3 Hz, ortho H of pH at saturated C), 6.82 (d, J = 7.5 Hz, 1 H, 1-H of AH), 6.99–7.36 (m, 10 H, aryl H except 2 ortho H and one 1-H of AH); IR (KBr) 1710 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{22}O$: C, 88.30; H, 6.79. Found: C, 88.01; H, 6.61.

Table I, Entry 14. Chromatography (3 × 25) with toluene provided AH_2; elution with CH_2Cl_2 gave 740 mg (83%) of **15a**.

Table I, Entry 15. A 530-mg (72%) portion of A was removed by filtration. Chromatography (3 × 60) of the filtrate with toluene provided a mixture of A and AH_2 and then 470 mg (78%) of **16b** that soon began to change into **16c**: ^{1}H NMR of **16b** ($CDCl_3$, 60 MHz) δ 1.10 (d, J = 6.4 Hz, Me), 2.47–3.28 (m, $CHCH_2$), 7.18 (s br, Ph), 9.70 (s, CHO).

2-Methyl-3-phenylpropionic acid (16c): oil; lit.[21] mp 36.5 °C; ^{1}H NMR identical with that of an authentic sample prepared from ethyl benzylmethylacetoacetate according to ref 21; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.15 (d, J = 6.6 Hz, Me), 2.38–3.21 (m, $CHCH_2$), 6.99–7.31 (m, Ph), 11.03 (s br, OH); IR (film) 1705 cm^{-1}.

Table I, Entry 16. Chromatography (3 × 60) with CH_2Cl_2 provided AH_2 and 1.23 g (87%) of **15c**.

4-(9,10-Dihydroanthr-9-yl)-4-methylpentan-2-one (15c): mp 71–72 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.90 (s, 2 Me), 2.08 (s, COMe), 2.36 (s, $COCH_2$), 3.74 (d, J = 19.2 Hz, 10-H pseudo eq), 4.15 (d br, J = 19.2 Hz, 10-H pseudo ax), 4.23 (s br, 9-H pseudo eq ?), 7.20 (mc, aryl H); IR (KBr) 1709 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.96. Found: C, 86.10; H, 8.15.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. This support is gratefully acknowledged.

(20) Haller, A.; Bauer, E.; Ramart, P. *Ann. Chim.* **1924**, *2*(10), 269.

(21) Jones, L. W.; Wallis, E. S. *J. Am. Chem. Soc.* **1926**, *48*, 169.

Birch Reduction and Reductive Alkylation of Benzonitriles and Benzamides

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In contrast to literature suggestions, benzonitriles and *N,N*-dialkylbenzamides are excellent substrates for Birch reduction and reductive alkylations. Thus, *o*-methoxybenzonitrile (**1a**) and benzonitrile (**1b**) give 1,4-cyclohexadienes **2a–2d** from alkali-metal reduction in NH_3–THF with *tert*-butyl alcohol (1 equiv), followed by sequential addition of an alkyl halide and excess NH_4Cl. The product of HCN elimination [e.g., diphenylmethane (**3**)] is obtained if NH_4Cl is not added prior to an aqueous workup. Birch reduction of **1a** followed by NH_4Cl quench gives 2-cyano-1-methoxy-1,3-cyclohexadiene (**4**), while benzonitrile (**1b**) gives the dimeric dinitrile **8**, isolated as a 7:5 mixture of diastereoisomers. Hydrogenation of the mixture, **8**, gives chromatographically separable **9a** and **9b**; a single-crystal X-ray diffraction study provided the molecular structure of **9b**. Birch reduction of *N,N*-dimethylbenzamide (**12a**) gives 1,4-cyclohexadiene **13a**, while reductive benzylation gives **13b**. The effect of alkali metal (type and quantity), the availability of a proton source, and variation in reaction temperature on the course of Birch reduction of *N,N*-dimethylbenzamide (**12a**) is reported.

For the past few years, we have been involved with the development of new strategies for chiral 2,4- and 2,5-cyclohexadien-1-one construction.[1] In the course of this work, we have examined the alkali metal in ammonia re-

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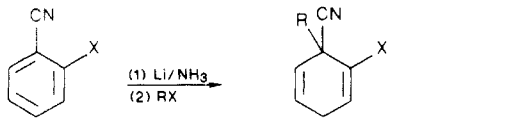
duction of benzonitriles and N,N-disubstituted benzamides and now comment on apparent misconceptions about the suitability of these substrates for Birch reductions and reductive alkylations.

Birch Reduction of Benzonitriles. Benkeser and co-workers have reported that benzonitrile is reduced to cyclohexylmethylamine by lithium in ethylamine.[2] No successful Birch reduction of a benzonitrile to a dihydrobenzonitrile appears to have been reported in the chemical literature.[3] As recently as 1980, it was suggested that, in Birch reductions, "... groups such as NO_2, F, and CN are reducible preferentially to the (benzene) ring ...".[4] We report that Birch reduction of *o*-methoxybenzonitrile (**1a**)

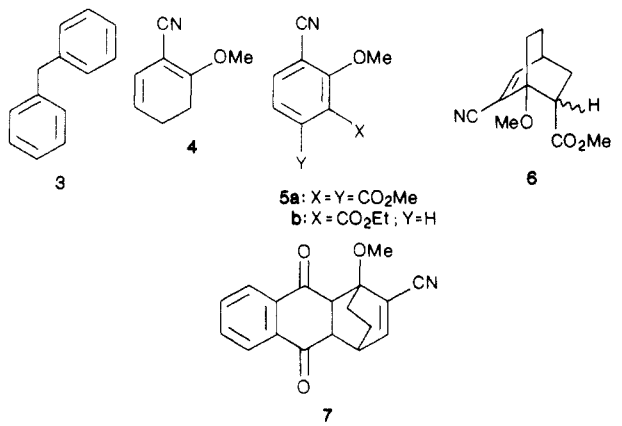


1a: X = OMe
b: X = H

2a: X = OMe; R = $CH_2CH_2CH_2Cl$
b: X = H; R = $CH_2CH_2CH_2Cl$
c: X = H; R = CH_2Ph
d: X = H; R = *m*-$MeOC_6H_4CH_2$

with lithium (2 equiv) in NH_3–THF solution in the presence of *tert*-butyl alcohol (1 equiv), followed by alkylation with 1-bromo-3-chloropropane, gave the 1,4-cyclohexadiene *2a* in 85% isolated yield. Analogous reactivity was observed with benzonitrile (**1b**); 1,4-cyclohexadienes **2b–2d** were obtained by reductive alkylations of **1b** with 1-bromo-3-chloropropane (83% yield), benzyl bromide (76%), and *m*-methoxybenzyl bromide (67%), respectively.

It is essential to quench the alkylation reaction mixture with excess NH_4Cl before evaporative removal of NH_3 and aqueous workup. If NH_4Cl is not added, then the 1,4-cyclohexadiene undergoes elimination of HCN to give an aryl derivative. For example, **1b** was converted to diphenylmethane (**3**) in 90% yield. In certain cases, this aromatic substitution process might be of synthetic interest, especially for the preparation of alkylbenzenes not readily available by more conventional methodology.



3 4 6

5a: X = Y = CO_2Me
b: X = CO_2Et; Y = H

7

(1) (a) Schultz, A. G.; Dittami, J. P. *Tetrahedron Lett.* **1983**, *24*, 1369. (b) Schultz, A. G.; Dittami, J. P.; Lavieri, F. P.; Salowey, C.; Sundararaman, P.; Szymula, M. B. *J. Org. Chem.* **1984**, *49*, 4429. (c) Schultz, A. G.; Sundararaman, P. *Tetrahedron Lett.* **1984**, *25*, 4591. (d) Schultz, A. G.; McCloskey, P. J.; Sundararaman, P. *Tetrahedron Lett.* **1985**, *26*, 1619. (e) Schultz, A. G.; Lavieri, F. P.; Snead, T. E. *J. Org. Chem.* **1985**, *50*, 3086. (f) Schultz, A. G.; Puig, S. *J. Org. Chem.* **1985**, *50*, 915. (g) Schultz, A. G.; Sundararaman, P.; Macielag, M.; Lavieri, F. P.; Welch, M. *Tetrahedron Lett.* **1985**, *26*, 4575. (h) Schultz, A. G.; McCloskey, P. J. *J. Org. Chem.* **1985**, *50*, 5905. (i) Schultz, A. G.; Lavieri, F. P.; Macielag, M. *Tetrahedron Lett.* **1986**, *27*, 1481.

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(3) Kaiser, E. M. *Synthesis* **1972**, 91.

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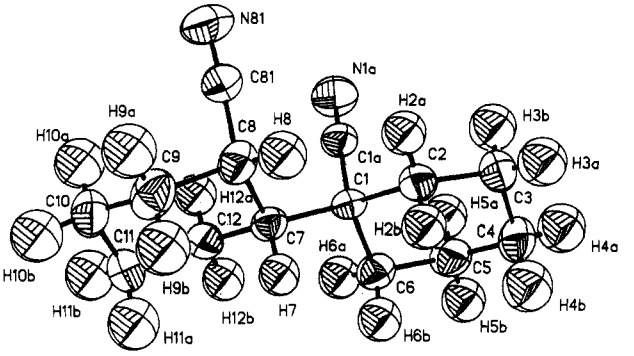
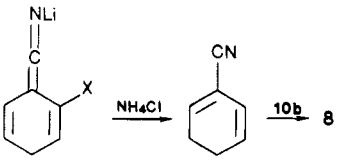


Figure 1. Molecular structure of **9b**.

Scheme I

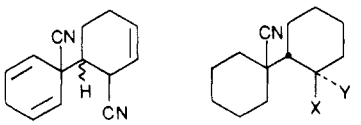


10a: X = OMe
b: X = H

11

When the nitrile-stabilized carbanion, **10a**, generated by Birch reduction of **1a** was treated with NH_4Cl rather than an alkyl halide, 2-cyano-1-methoxy-1,3-cyclohexadiene (**4**) was obtained in 76% isolated yield. Diene **4** is stable to silica gel chromatography, and it successfully undergoes Diels–Alder reactions with a variety of dienophiles. Aryl esters **5a** and **5b** were prepared by cycloadditions of **4** to dimethyl acetylenedicarboxylate and ethyl propiolate, respectively, followed by expulsion of ethylene via cycloreversion. The ethano bridge is retained in the methyl acrylate adduct **6** and the 1,4-naphthoquinone adduct **7**.

Interestingly, 1,3-cyclohexadiene **11** could not be obtained from the Birch reduction of benzonitrile **1b**. Rather, the dimeric dinitrile **8** was isolated as a 7:5 mixture of



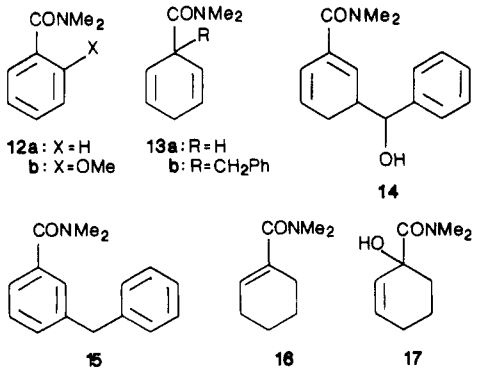
8

9a: X = CN; Y = H
b: X = H; Y = CN

diastereoisomers. Separation of stereoisomers was not possible, but hydrogenation of **8** produced a chromatographically separable mixture of **9a** (mp 104–106 °C) and **9b** (mp 148–150 °C). The structures of these diastereoisomers were determined by combustion analyses, spectral data, and a single-crystal X-ray diffraction study of **9b**. A perspective drawing of **9b** derived from X-ray coordinates is shown in Figure 1.

Presumably **8** is formed by a relatively slow γ-protonation of nitrile-stabilized carbanion **10b** by added NH_4Cl to give **11**; **11** then undergoes a relatively fast Michael addition with **10b** (Scheme I). The analogous γ-protonation of carbanion **10a** produced **4**, from which subsequent Michael addition with residual **10a** is disfavored by virtue of the vinylogous relationship of the methoxy and cyano substituents. On the other hand, alkylation of both **10a** and **10b** occurs predominately (perhaps exclusively) at the α-position.

Birch Reduction of *N,N*-Dimethylbenzamide. The Birch reduction of *N,N*-dimethylbenzamide (**12a**) with sodium in NH_3 in the presence of *tert*-butyl alcohol has been reported to give benzaldehyde and a benzaldehyde–ammonia adduct.[5] Inasmuch as we have previously re-



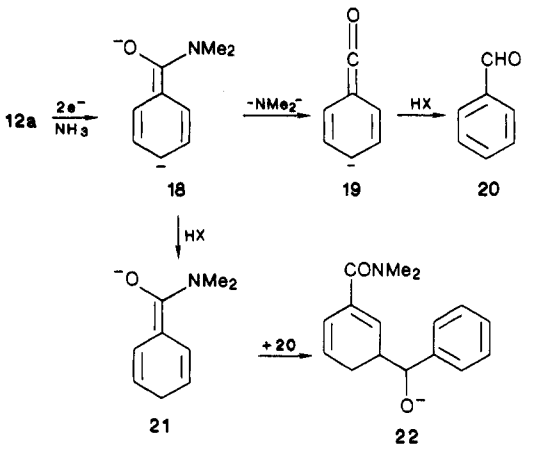
ported the successful reductive alkylation of *o*-methoxybenzamide (**12b**)[1b] and several other *N,N*-dialkylbenzamides,[1] we felt compelled to reinvestigate the literature report. *N,N*-Dimethylbenzamide (**12a**), on Birch reduction with either sodium or potassium as described for reduction of **1a** and **1b**, gave **13a** in excellent yield. Furthermore, reductive alkylation of **12a** with benzyl bromide gave 1,4-cyclohexadiene **13b** in 76% isolated yield. Thus, *N,N*-dimethylbenzamide (**12a**) and related *N,N*-dialkylbenzamides are appropriate substrates for Birch reductions and reductive alkylations.

Investigation of Selected Reaction Parameters for Birch Reduction of *N,N*-Dimethylbenzamide (12a). Birch reductions of **12a** in the presence of *tert*-butyl alcohol in NH_3–THF solution (–78 °C) were performed with potassium, sodium, and lithium.[6a] The highest yield (92%) was obtained with 2.2 equiv of potassium; the yield of **13a** decreased to 81% with sodium and 69% with lithium. As yields of **13a** decreased, increased amounts of benzaldehyde and the previously observed[5] benzaldehyde–ammonia adduct were produced.

The earlier study[5] focused on reductions of **12a** with sodium. For this reason, we examined the effect of reaction temperature and the presence of additives on the sodium in ammonia reduction of **12a**. Exclusion of the cosolvent, THF, had no effect on product distribution, nor did a change in the reaction temperature from –78 to –33 °C. However, the absence of a suitable proton donor,[6b] *tert*-butyl alcohol, resulted in a 31% yield of **13a** at –78 °C and no **13a** at –33 °C.[7] At –78 °C, the "proton donor free" reaction also contained benzaldehyde (29%) and the benzaldehyde–ammonia adduct (30%), but at –33 °C, **13a** and benzaldehyde were replaced by dimeric alcohol **14** (isolated as one diastereoisomer in 29% yield) and products presumably resulting from related condensation reactions. The structure assigned to **14** was confirmed by dehydration to the 3-benzylbenzoic acid derivative **15**.

A markedly reduced yield of **13a** (57%) also resulted when reduction with potassium (2.2 equiv) at –78 °C was carried out in the absence of *tert*-butyl alcohol. Cyclohexadiene **13a** was not observed in reactions conducted at –33 °C with 3.3 equiv of potassium in the absence of *tert*-butyl alcohol. Under these conditions, cyclohexene **16** was produced in 55% isolated yield, along with the novel allylic alcohol **17** (35%). By contrast, reduction with lithium (3.3 equiv, –33 °C, no *tert*-butyl alcohol) gave

Scheme II



benzaldehyde (10%) and benzyl alcohol (62%).

We believe that amide group reduction occurs by the mechanism shown in Scheme II. Two-electron reduction of **12a**, without a protonation step, would generate dianion **18**. Expulsion of dimethylamide ion from **18** produces **19** (an acyl anion),[8] and protonation of **19** at the acyl carbon atom would give benzaldehyde (**20**). On the other hand, protonation of dianion **18** by ammonia would generate **21** and condensation of **21** with benzaldehyde would give **22**. On reaction workup, **21** and **22** would provide **13a** and **14**, respectively.

Dianion formation is favored when lithium rather than sodium or potassium is present as the counterion.[9] Our data are consistent with this principle, in that the greatest propensity for amide group reduction is observed with lithium, while aromatic ring reduction is favored with potassium; the behavior of sodium is intermediate between lithium and potassium. With excess lithium, benzaldehyde is reduced to benzyl alcohol, but with excess potassium, ring reduction continues to afford **16** and **17**.[10]

Conclusion. High yields of 1,4-cyclohexadiene **13a** are obtained from reduction of *N,N*-dimethylbenzamide (**12a**) with potassium, but only with careful attention to the stoichiometry of the reduction. A 2-equiv portion of potassium is sufficient, and 1 equiv of *tert*-butyl alcohol (to discourage formation of dianion **18**) is essential.

Experimental Section

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on Varian XL-200 (200-MHz) and IBM WP-100SY (100-MHz) spectrometers (tetramethylsilane internal standard). ^{13}C NMR spectra were obtained on the IBM WP-100SY spectrometer. Infrared spectra were obtained from either a Perkin-

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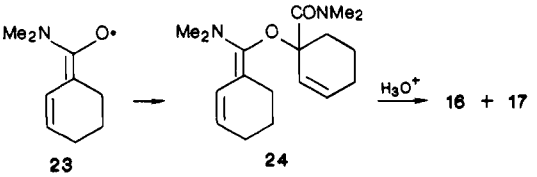
(6) (a) For an earlier demonstration of the effectiveness of lithium, sodium, and potassium on the Birch reduction of benzoic esters, see: Hook, J. M.; Mander, L. N.; Woolias, M. *Tetrahedron Lett.* **1982**, *23*, 1095; (b) A sodium in ammonia reduction of benzoic esters in the presence of 1.5 equiv of water as proton donor has been reported: Rabideau, P. W.; Wetzel, D. M.; Young, M. D. *J. Org. Chem.* **1984**, *49*, 1544.

(7) THF was not used in these reactions.

(8) Seyferth, D.; Weinstein, R. M.; Wang, W.-L. *J. Org. Chem.* **1983**, *48*, 1144.

(9) (a) For an excellent discussion of the dissolving metal reduction, see: House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, 1972; Chapter 3. (b) Szwarc, M. *Acc. Chem. Res.* **1969**, *2*, 87. (c) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268.

(10) Compounds **16** and **17** may be produced by a three-electron reduction of **12a** to give **23**, or an equivalent, followed by *C* to *O* dimerization to give **24**. On workup, **24** would be expected to undergo hydrolysis to **16** and **17**.



Elmer 1376 or 298 spectrophotometer (polystyrene standard). Mass spectra were obtained from a Hewlett-Packard 5987A GC–MS system (methane, chemical ionization gas). Elemental analyses were determined by Spang Microanalytical Laboratories, Eagle Harbor, MI.

General Procedure for the Reductive Alkylation of Benzonitriles and *N,N*-Dimethylbenzamide Derivatives. 6-(3-Chloropropyl)-6-cyano-1-methoxy-1,4-cyclohexadiene (2a). A solution of *o*-methoxybenzonitrile (**1a**; 1.60 g, 12 mmol) in dry THF (12 mL) and *tert*-butyl alcohol (0.88 g, 12 mmol) was cooled to −78 °C. Liquid NH_3 (60 mL, predried over sodium amide and then distilled) was added to the reaction mixture. Lithium (0.20 g, 0.030 mol) was added to the stirred solution in small pieces. 1-Bromo-3-chloropropane (3.78 g, 24 mmol) was added, and the resulting yellow solution was stirred for 1 h at −78 °C. After addition of NH_4Cl (~5 g), the mixture was warmed slowly to room temperature while the ammonia was removed with a stream of nitrogen. Brine (~40 mL) was added, and the mixture was extracted with ether (3 × 40 mL). The combined organic extracts were washed with water (1 × 40 mL) and brine (1 × 40 mL) and dried over anhydrous magnesium sulfate. Removal of solvent in vacuo afforded the crude product as a yellow oil. Flash chromatography (neutral Al_2O_3, hexane–ethyl acetate 6:1) gave **2a** [2.15 g (85%)] as a clear pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.6–2.0 (m, 3 H), 2.24 (m, 1 H), 2.86 (m, 2 H), 3.54 (t, 2 H, J = 7 Hz), 3.64 (s, 3 H), 4.92 (m, 1 H), 5.59 (m, 1 H), 6.03 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.1, 27.2, 35.3, 39.9, 44.2, 54.8, 94.5, 120.8, 123.7, 128.2, 148.8; IR (film) 2235, 1690, 1650, 1450 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 212 (M^+ + 1, 5), 185 (100), 176 (11), 149 (6), 134 (15). An acceptable analysis could not be obtained.

3-(3-Chloropropyl)-3-cyano-1,4-cyclohexadiene (2b) was prepared in 83% yield from **1b** as described for **2a**; flash chromatography (neutral Al_2O_3, hexane–ethyl acetate 7:1) gave **2b** (oil): ^1H NMR ($CDCl_3$) δ 1.76–2.00 (m, 4 H), 2.70 (m, 2 H), 3.56 (t, 2 H, J = 6 Hz), 5.64 (m, 2 H), 6.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.6, 27.2, 36.3, 38.0, 44.2, 121.3, 123.8, 127.9; IR (film) 2225, 1445, 1415 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 182 (M^+ + 1, 10), 155 (100), 146 (5), 119 (30), 104 (15). An acceptable analysis could not be obtained.

3-Benzyl-3-cyano-1,4-cyclohexadiene (2c) was prepared in 73% yield from **1b** as described for **2a** (alkylation reagent benzyl bromide); flash chromatography (silica gel, hexane–ethyl acetate 5:1) gave **2c** (colorless solid). The analytical sample was prepared by recrystallization from hexane–methylene chloride: mp 45–46 °C; ^1H NMR ($CDCl_3$) δ 2.54 (m, 1 H), 2.67 (m, 1 H), 2.99 (s, 2 H), 5.68 (m, 2 H), 5.96 (m, 2 H), 7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.5, 38.0, 47.1, 121.2, 124.1, 127.2, 128.1, 130.5, 134.2; IR (film) 2222, 1490, 1435, 1420 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 196 (M^+ + 1, 2), 169 (12), 91 (100). Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71. Found: C, 86.12; H, 6.77.

3-Cyano-3-(3-methoxybenzyl)-1,4-cyclohexadiene (2d) was prepared in 67% yield from **1b** and 3-methoxybenzyl bromide as described for **2a**; flash chromatography (silica gel, hexane–ethyl acetate 4:1) gave **2d** (oil): ^1H NMR ($CDCl_3$) δ 2.58 (m, 1 H), 2.67 (m, 1 H), 2.98 (s, 2 H), 3.82 (s, 3 H), 5.68 (m, 2 H), 5.96 (m, 2 H), 6.85–6.91 (m, 3 H), 7.27 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.6, 37.9, 47.2, 55.2, 112.8, 116.3, 121.3, 123.0, 124.2, 127.3, 129.2, 135.8, 159.4; IR (film) 2222, 1600, 1580, 1485, 1450, 1435 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 226 (M^+ + 1, 6), 225 (5), 199 (100), 121 (26). An acceptable analysis could not be obtained.

Diphenylmethane (3) was prepared in 90% yield from **1b** by the procedure described for the synthesis of **2a** except that the reaction was quenched by addition of water (40 mL) after evaporation of NH_3; flash chromatography (silica gel, hexane–ethyl acetate 8:1) gave **3**: mp 24–26 °C (lit.[11] mp 24–25 °C); ^1H NMR ($CDCl_3$) δ 3.95 (s, 2 H), 7.20 (m, 10 H); IR ($CHCl_3$) 3080, 3060, 3020, 1490, 1445 cm^{-1}.

General Procedure for the Birch Reduction of Benzonitriles and *N,N*-Dimethylbenzamide Derivatives. 2-Cyano-1-methoxy-1,3-cyclohexadiene (4). A solution of *o*-methoxybenzonitrile (**1a**; 1.60 g, 12 mmol), THF (10 mL), and *tert*-butyl alcohol (0.88 g, 12 mmol) was cooled to −78 °C. Liquid NH_3 (60 mL, predried over sodium amide and then distilled) was added to the reaction mixture. Lithium (0.20 g, 0.030 mol) was added to the stirred solution in small pieces producing a deep blue coloration. 1,3-Pentadiene (freshly distilled) was added until the blue disappeared. Solid ammonium chloride (~2 g) was added rapidly at −78 °C, and stirring was continued for 10 min. The ammonia was removed with a stream of nitrogen, and brine (40 mL) was added to the residue. The mixture was extracted with chloroform (3 × 40 mL), and the combined organic extracts were washed with water (1 × 40 mL) and brine (1 × 40 mL) and dried over anhydrous magnesium sulfate. Removal of solvents in vacuo afforded the crude product as a red oil. Flash chromatography (silica gel, hexane–ethyl acetate 4:1) gave **4** [1.23 g (76%)] as a clear oil: ^1H NMR ($CDCl_3$) δ 2.24–2.38 (m, 2 H), 2.40–2.50 (m, 2 H), 4.00 (s, 3 H), 5.56 (m, 1 H), 5.84 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.2, 25.4, 57.0, 84.2, 111.5, 119.6, 122.6, 169.5; IR (film) 2222, 1635, 1585, 1460, 1370; chemical ionization mass spectrum, m/e (relative intensity) 136 (M^+ + 1, 100). Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71. Found: C, 71.06; H, 6.81.

General Procedure for Preparation of Diels–Alder Adducts Derived from 4. Dimethyl 4-Cyano-3-methoxyphthalate (5a). To a solution of **4** (135 mg, 1 mmol) in dry toluene (5 mL) was added dimethyl acetylenedicarboxylate (142 mg, 1 mmol). The resulting solution was heated at reflux temperature for 24 h. Concentration of the reaction mixture followed by flash chromatography (silica gel, hexane–ethyl acetate 2:1) gave **5a** [202 mg (81%)] as a colorless oil: ^1H NMR ($CDCl_3$) δ 3.90 (s, 3 H), 3.96 (s, 3 H), 4.09 (s, 3 H), 7.73 (d, J = 8 Hz, 1 H), 7.81 (d, J = 8 Hz, 1 H); IR (film) 2238, 1727, 1565, 1455, 1435 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 250 (M^+ + 1, 88), 218 (100). Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45. Found: C, 57.91; H, 4.50.

Ethyl 3-Cyano-2-methoxybenzoate (5b). Reaction of **4** with ethyl propiolate in toluene at reflux temperature for 72 h followed by flash chromatography (silica gel, hexane–ethyl acetate 4:1) afforded **5b** [161 mg (84%)] as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.40 (t, J = 6.5 Hz, 3 H), 4.07 (s, 3 H), 4.42 (q, J = 6.5 Hz, 2 H), 7.28 (t, J = 8 Hz, 1 H), 7.77 (dd, J = 8 Hz, 2 Hz, 1 H), 8.05 (dd, J = 8 Hz, 2 Hz, 1 H); IR (film) 2224, 1728, 1585, 1462, 1415 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 206 (M^+ + 1, 100), 160 (33). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.42; H, 5.50.

2-Carbomethoxy-6-cyano-1-methoxybicyclo[2.2.2]oct-5-ene (6). Reaction of **4** with methyl acrylate (2 mL, neat) at reflux temperature for 128 h afforded a 94:6 mixture of isomers corresponding to structure **6**. Flash chromatography (silica gel, hexane–ethyl acetate 3:1) gave **6** [127 mg (61%)] as a colorless solid. An analytical sample of the major isomer (presumably endo) was prepared by recrystallization from ether: mp 114–115 °C; ^1H NMR ($CDCl_3$) δ 1.48–1.70 (m, 4 H), 1.80 (m, 1 H), 2.00 (m, 1 H), 2.75 (m, 1 H), 3.02 (dd, J = 9 Hz, 4.5 Hz, 1 H), 3.47 (s, 3 H), 3.69 (s, 3 H), 7.16 (d, J = 7 Hz, 1 H); IR ($CHCl_3$) 2220, 1720, 1435 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 222 (M^+ + 1, 74), 190 (100). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.23; H, 6.78.

***endo-cis*-1,4,4a,10a-Tetrahydro-2-cyano-1-methoxy-1,4-ethanoanthracene-5,10-dione (7).** Reaction of **4** with 1,4-naphthoquinone in toluene at reflux temperature for 56 h followed by flash chromatography (silica gel, hexane–ethyl acetate 2:1) gave **7** [177 mg (60%)] as a light tan solid. The analytical sample was prepared by recrystallization from ether: mp 168–172 °C dec; ^1H NMR ($CDCl_3$) δ 1.52–1.72 (m, 2 H), 1.99 (m, 1 H), 2.18 (m, 1 H), 3.32 (m, 1 H), 3.41 (dd, J = 9 Hz, 3 Hz, 1 H), 3.62 (d, overlapping s at 3.58, 4 H, J = 9 Hz), 6.85 (d, J = 7 Hz, 1 H), 7.70–7.80 (m, 2 H), 7.9 (m, 1 H), 7.98 (m, 1 H); IR ($CHCl_3$) 2220, 1660, 1585 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 294 (M^+ + 1, 100), 161 (31), 136 (68). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15. Found: C, 73.72; H, 5.23.

3-Cyano-3-(2-cyanocyclohex-3-enyl)-1,4-cyclohexadiene (8) was prepared as a 7:5 mixture of diastereomers in 49% yield from **1b** as described for **4**; flash chromatography (silica gel, hexane–ethyl acetate 6:1) gave **8** (oil): ^1H NMR ($CDCl_3$) δ 1.50, 1.77 (two m, 1 H), 1.96–2.42 (m, 4 H), 2.80 (m, 2 H), 3.14, 3.44 (two m, 1 H), 5.52-5.74 (m, 2 H), 5.80–6.08 (m, 2 H), 6.12–6.26 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 23.1, 24.1, 25.8, 25.9, 28.2, 28.4, 40.0,

(11) Hartman, W. W.; Phillips, R. *Org. Synth.* **1934**, *14*, 34.

41.1, 44.1, 44.8, 118.2, 119.8, 120.0, 120.2, 120.8, 121.2, 121.6, 123.3, 129.8, 130.6, 130.7, 130.9, 131.2, 131.6; IR (film) 2222, 1445, 1430, 1410 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 211 ($M^+ + 1$, 5), 184 (100), 157 (40).

1-Cyano-1-(2-cyanocyclohexyl)cyclohexane (9a and 9b). A solution of **8** (125 mg, 0.59 mmol) in ethyl acetate (8 mL) containing 5% palladium on carbon (13 mg, 1 mol %) was stirred under an atmosphere of hydrogen at 20 °C for 24 h and then filtered through Celite. Concentration of the reaction mixture followed by flash chromatography (silica gel, hexane–ethyl acetate 4:1) gave **9a** [R_f 0.47; 39.9 mg (31%)] and **9b** [R_f 0.28; 59.8 mg (47%)]. **9a** could be further purified by recrystallization from hexane–methylene chloride: mp 104–106 °C; ^1H NMR ($CDCl_3$) δ 1.10–1.36 (m, 4 H), 1.40–1.94 (m, 11 H), 2.10 (m, 2 H), 2.26 (m, 1 H), 2.38–2.60 (m, 2 H); IR ($CHCl_3$) 2225, 1445 cm^{-1}; mass spectrum, m/e (relative intensity) 216 (M^+, 9), 109 (100). Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32. Found: C, 77.75; H, 9.34.

9b could be further purified by recrystallization from hexane–methylene chloride: mp 148–150 °C; ^1H NMR ($CDCl_3$) δ 1.07–1.40 (m, 3 H), 1.42–2.00 (m, 14 H), 2.05–2.12 (m, 2 H), 3.21 (m, 1 H); IR ($CHCl_3$) 2228, 1448 cm^{-1}; mass spectrum, m/e (relative intensity) 216 (M^+, 15), 109 (100). Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32. Found: C, 77.81; H, 9.32.

3-[(*N*,*N*-Dimethylamino)carbonyl]-1,4-cyclohexadiene (13a) was prepared in 92% yield from the potassium reduction of **12a** as described for **4**; flash chromatography (silica gel, hexane–ethyl acetate 1:1) gave **13a** (oil): ^1H NMR ($CDCl_3$) δ 2.71 (m, 2 H), 2.94 (s, 3 H), 3.08 (s, 3 H), 4.02 (m, 1 H), 5.68 (m, 2 H), 5.90 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.8, 36.1, 37.2, 40.9, 123.0, 126.2, 172.3; IR (film) 1625, 1490, 1440, 1390 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 152 ($M^+ + 1$, 100).

3-Benzyl-3-[(*N*,*N*-dimethylamino)carbonyl]-1,4-cyclohexadiene (13b) was prepared in 76% yield from **12a** as described for **2c**; flash chromatography (silica gel, hexane–ethyl acetate 3:1) gave **13b**. The analytical sample was prepared by recrystallization from hexane: mp 103–104 °C; ^1H NMR ($CDCl_3$) δ 1.83 (m, 1 H), 2.27 (m, 1 H), 2.98 (br s, 6 H), 3.07 (s, 2 H), 5.62 (m, 2 H), 5.68 (m, 2 H), 7.13 (m, 5 H); IR ($CHCl_3$) 1610, 1490, 1450, 1380 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 242 ($M^+ + 1$, 100), 179 (8), 151 (26). Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94. Found: C, 79.82; H, 7.76.

Birch Reduction of *N*,*N*-Dimethylbenzamide with Sodium. 2-[(*N*,*N*-Dimethylamino)carbonyl]-6-(phenylhydroxymethyl)-1,3-cyclohexadiene (14) and 1-Phenyl-*N*,*N*′-bis(phenylmethylene)methanediamine. Liquid NH_3 (120 mL, predried over sodium amide and then distilled) was added to **12a** (1.49 g, 10 mmol) at −78 °C. The solution was warmed gradually to −33 °C, and then potassium (1.29 g, 0.033 mol) was added in small pieces. Solid ammonium chloride (~2 g) was added rapidly, and stirring was continued for 10 min. The ammonia was removed with a stream of nitrogen, and brine (50 mL) was added to the residue. The mixture was extracted with chloroform (3 × 50 mL), and the combined organic extracts were washed with brine (1 × 50 mL) and dried over anhydrous magnesium sulfate. Removal of solvent in vacuo afforded the crude product as a yellow gum. Flash chromatography (silica gel, methylene chloride–ethyl acetate 4:1) gave 1-phenyl-*N*,*N*′-bis(phenylmethylene)methanediamine [278 mg (28%)] and **14** [373 mg (29%)]. 1-Phenyl-*N*,*N*′-bis(phenylmethylene)methanediamine could be further purified by recrystallization from ethanol: mp 103 °C (lit.[5] mp 103–104 °C); ^1H NMR ($CDCl_3$) δ 5.99 (br s, 1 H), 7.29–7.54 (m, 11 H), 7.87 (m, 4 H), 8.60 (br s, 2 H).

14: oil; ^1H NMR ($CDCl_3$) δ 2.39 (m, 2 H), 2.78 (m, 1 H), 2.90 (br s, 6 H), 4.71 (d, J = 7 Hz, 1 H), 5.59 (d, J = 4 Hz, 1 H), 5.97 (m, 2 H), 7.28–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.8, 40.4, 75.2, 122.9, 126.6, 127.0, 127.6, 127.7, 128.4, 133.7, 142.7, 170.9; IR ($CHCl_3$) 3380, 2995, 1610, 1490, 1450, 1395 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 258 ($M^+ + 1$, 74), 240 (100), 152 (62), 107 (67).

***N*,*N*-Dimethyl-3-(phenylmethyl)benzamide (15).** To a solution of **14** (51 mg, 0.20 mmol) in benzene (3 mL) was added phosphorus pentoxide (57 mg, 0.40 mmol) with stirring. The resulting suspension was heated at reflux temperature for 3 h. Brine (10 mL) was added, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and brine (1 × 10 mL) and dried over anhydrous magnesium sulfate. Removal of solvent in vacuo provided the crude product (42 mg) as a yellow oil. Flash chromatography (silica gel, hexane–ethyl acetate 1:1) gave **15** [34 mg (72%)] as a clear viscous oil: ^1H NMR ($CDCl_3$) δ 2.94 (br s, 3 H), 3.09 (br s, 3 H), 4.00 (s, 2 H), 7.10–7.40 (m, 9 H); IR ($CHCl_3$) 2997, 1620, 1495, 1445, 1395 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 240 ($M^+ + 1$, 100), 195 (6). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16. Found: C, 80.12; H, 7.22.

Birch Reduction of *N*,*N*-Dimethylbenzamide with Potassium. 1-[(*N*,*N*-Dimethylamino)carbonyl]-1-cyclohexene (16) and 3-[(*N*,*N*-Dimethylamino)carbonyl]-3-hydroxy-1-cyclohexene (17). Liquid NH_3 (120 mL, predried over sodium amide and then distilled) was added to **12a** (1.49 g, 10 mmol) at −78 °C. The solution was warmed gradually to −33 °C, and then potassium (1.29 g, 0.033 mol) was added in small pieces. Ethanol (1.38 g, 30 mmol) was added via syringe, and stirring was continued for 10 min. The ammonia was removed with a stream of nitrogen, and brine (50 mL) was added to the residue. The mixture was extracted with chloroform (3 × 50 mL), and the combined organic extracts were washed with brine (1 × 50 mL) and dried over anhydrous magnesium sulfate. Removal of solvent in vacuo afforded the crude product as a dark yellow oil. Flash chromatography (silica gel, hexane–ethyl acetate 1:1) gave **16** [841 mg (55%)] and **17** [491 mg (35%)]. **16** could be further purified by Kugelrohr distillation: bp 105–107 °C (1 mm) [lit.[12] bp 110–111 °C (1 mm)]; ^1H NMR ($CDCl_3$) δ 1.66 (m, 4 H), 2.15 (m, 4 H), 2.97 (br s, 6 H), 5.81 (m, 1 H); IR (film) 1610, 1495, 1440, 1390 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 154 ($M^+ + 1$, 100).

17: oil; ^1H NMR ($CDCl_3$) δ 1.64–2.28 (m, 6 H), 3.02 (br s, 3 H), 3.09 (br s, 3 H), 5.08 (br s, 1 H, exchangeable with D_2O), 5.69 (m, 1 H), 6.04 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.2, 24.6, 33.6, 37.9, 38.0, 69.8, 128.1 131.2, 175.5; IR (film) 3360, 3020, 2935, 1620, 1495, 1435 cm^{-1}; chemical ionization mass spectrum, m/e (relative intensity) 170 ($M^+ + 1$, 85), 152 (100), 124 (15). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93. Found: C, 64.04; H, 8.80.

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Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **9b** (6 pages). Ordering information is given on any current masthead page.

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