

mmol), triethylamine (0.6 g, 6 mmol), and butyl vinyl ether (1.0 g, 10 mmol) in 2 mL of DMF was added. The tube was closed and heated for 18 h at 95 °C in an oil bath. After cooling, 75 mL of diethyl ether (containing naphthalene as internal standard) and 25 mL of water were added. The organic layer was then subjected to GLC-MS analysis.

Reaction of 4-Nitrophenyl Triflate with Butyl Vinyl Ether in Acetonitrile (Table II). A solution containing 4-nitrophenyl triflate (1.36 g, 5 mmol), butyl vinyl ether (1.0 g, 10 mmol), triethylamine (0.6 g, 6 mmol), palladium acetate (11.2 mg, 0.05 mmol), and naphthalene (internal standard, 0.5 g) in 15 mL of acetonitrile was prepared. Aliquots (3-mL) of this solution were added to Pyrex tubes containing the appropriate tetrabutylammonium salts (1 mmol). The closed tubes were heated in an oil bath at 100 °C. Samples were removed after 4 and 20 h, partitioned between diethyl ether and water, and analyzed by GLC-MS.

Reaction of Phenyl Triflate with Butyl Vinyl Ether. Phenyl triflate¹² (0.45 g, 2 mmol), triethylamine (0.24 g, 2.4 mmol), butyl vinyl ether (0.4 g, 4 mmol), palladium acetate (4.5 mg, 0.02 mmol), and, if present, lithium chloride (85 mg, 2 mmol) were dissolved in 1.5 mL of DMF. After heating at 100 °C for 18 h, the products were quantified as above.

Acknowledgment. We thank the Swedish Natural Science Research Council for financial support.

Novel Synthesis of Dihydrofurans from the Addition of Enolate Dianion Derivatives to (η^4 -Diene)Co(CO)₃BF₄

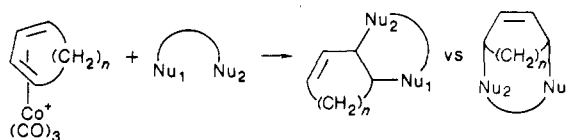
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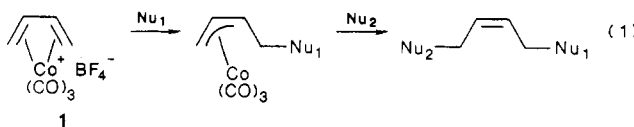
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Despite the long-standing existence of transition-metal complexes of 1,3-dienes¹ and the commercial importance of metal-catalyzed additions, oligomerizations, and telomerizations of dienes,² the reactivity of diene-metal complexes has been surprisingly little studied. Our interest in this subject has been stimulated by recent reports of the contrasting regioselectivity observed in additions of nucleophiles to (η^4 -diene)Mo³ and -Pd⁴ species (terminal attack) compared to the -Fe(CO)₃ counterparts⁵ (internal attack). In our initial studies of nucleophilic reactions of (η^4 -butadiene)Co(CO)₃BF₄ (1) we demonstrated the regioselective attack at the diene terminus by a variety of carbon and heteroatomic agents,⁶ the potential for regioselective 1,4-difunctionalization of dienes via addition

Scheme I



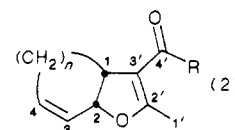
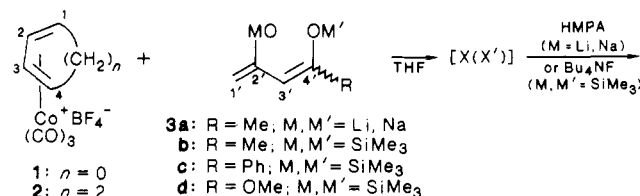
of a second nucleophile to the intermediate allyl complex (eq 1),⁶ and we provided a theoretical model to account for the role of the metal fragment in determining regioselectivity.⁷



The ability of the (η^4 -diene)Co(CO)₃⁺ complexes to serve as olefin dication equivalents has led us to consider annelation schemes based on their reactions with bis nucleophiles (Scheme I). On the basis of the established behavior of dianions of β -dicarbonyl compounds⁸ and the related 1,3-bis(siloxy) dienes⁹ as 2,4-carbon-centered bis nucleophiles, we anticipated the possibility of forming cyclopentanone (via 1,2-addition to the diene) or cycloheptenone (via 1,4-addition) derivatives. Herein we report the unexpected, but synthetically useful, results of such reactions.

Results and Discussion

When a suspension of complex 1 in THF was treated with 1 equiv of pentanedione dianion 3a at -78 °C, a new complex X formed which persisted at room temperature (IR: 2080 and 1995 cm⁻¹) along with Co(CO)₄⁻. Addition of HMPA to this mixture caused gradual disappearance of X and formation of a single isolable organic product (12% purified yield), which was identified as 2-vinyl-4-acetyl-5-methyl-2,3-dihydrofuran (4a) (eq 2) on the basis of its spectral characteristics, NMR homonuclear decoupling experiments, and comparison with known compounds.



4: n = 0
 5: n = 2
 a, R = Me; b, R = Ph; c, R = OMe

We were pleased to find that such dihydrofuran derivatives could be prepared generally and much more efficiently when 1 was combined at 20 °C with the corre-

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Table I. Dihydrofuran and Tetrahydrobenzofurans from Reactions of (η^3 -Diene)Co(CO)₃BF₄ with 2,4-Bis(siloxy) Dienes

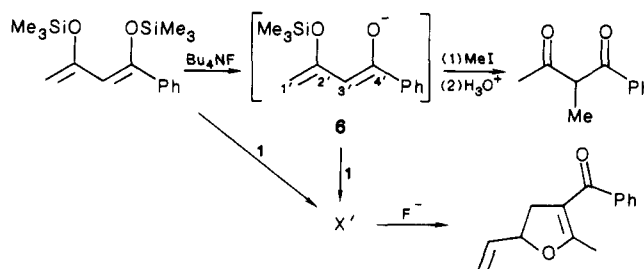
diene complex	nucleophile	product	yield, ^a %
			76
			55
			72
			68
			52
			60

^a Isolated, purified product.

sponding bis(trimethylsiloxy) dienes **3b-d** as the nucleophilic partners followed by treatment of the intermediate complexes X' (IR: ca. 2045, 1990 cm⁻¹) with Bu₄NF (Table I). (η^4 -1,3-Cyclohexadiene)Co(CO)₃BF₄ (**2**) reacted similarly producing previously little known 4,5,8,9-tetrahydrobenzofurans. The cis stereochemistry, established by the H₈,H₉ coupling constants of 8–9 Hz,¹⁰ in combination with the electronically saturated cobalt atom, may be explained by a process involving nucleophilic attack on the diene face opposite to the cobalt in both bond-forming steps. The preparation of acyldihydrofurans and -tetrahydrobenzofurans by this method appears to be amongst the most general and efficient available.¹³

The observation of overall 1,2-addition to the coordinated diene involving the carbon (C3') and oxygen (O2') of the nucleophiles was quite unexpected since electrophilic addition to both enolate dianions⁸ and bis(siloxy) dienes⁹ previously had always been observed to occur initially at the terminal carbon (C1') and secondarily at the internal one (C3'). A key to the order of bond formation presumably lies in the identity of the intermediates X and X'. Unfortunately, while IR monitoring of the reactions in-

Scheme II



dicates formation of the expected neutral Co(CO)₃ complex (op. cit.), in situ ¹H NMR spectral studies have thus far been inconclusive. However, hydrolysis (dilute HCl) of X' from **1** + **3c** afforded primarily 1-phenyl-2-(3-butenyl)-1,3-butanedione, demonstrating that the initial bond formation is between C3' of the siloxy diene and C1 (terminal) of the diene complex.

In the case of the bis(siloxy) dienes, attack by C3' could potentially be accounted for by initial F⁻ (from BF₄⁻)-induced desilylation¹⁶ of O4' to produce the fully conjugated diene-enolates, e.g., **6**, which are known to be attacked by electrophiles at C3'.¹⁷ Indeed, treatment of **3c** with Bu₄NF (1 equiv, THF, 20 °C) produced a species which upon addition of CH₃I forms the C3'-methylated derivative and which upon addition of complex **1** gave the same intermediate X' (by NMR) as in the direct reaction with the bis(siloxy) diene (Scheme II). However, no reaction was observed when bis(siloxy) diene **3c**, methyl iodide, and Bu₄NBF₄ were stirred together (THF, 20 °C, >12 h), a result which argues against the involvement of BF₄⁻-promoted desilylation of **3** → **6** during the reactions of **3** with complexes **1** and **2**.

The occurrence of C3' rather than the usual C1' attack product in the reaction of **1** with the enolate dianion is equally surprising. Two admittedly speculative, but interesting, possibilities include (a) initial O2'/C2 polar coupling followed by C3'/C1 connection and (b) initial electron transfer from dianion to complex followed by coupling of the enolate radical anion (via C3') to C1 of the 19e⁻ diene complex and then O2'/C2 polar coupling as in Scheme II. Experiments to further probe these mechanistic possibilities are in progress.

Experimental Section

General. Solvents and common reagents were obtained commercially and used as received or purified as follows: tetrahydrofuran was distilled under nitrogen from sodium/benzophenone; diisopropyl amine and trimethylsilyl chloride were distilled from calcium hydride. The following were prepared by the literature procedures: (butadiene)tricarbonylcobalt tetrafluoroborate,⁶ (cyclohexadiene)tricarbonylcobalt tetrafluoroborate,⁶ 1,3-bis(trimethylsiloxy)-1-methyl-1,3-butadiene (from 2,4-pentanedione), and 1,3-bis(trimethylsiloxy)-1-methoxy-1,3-butadiene (from methyl acetoacetate).^{8b} Thin-layer chromatography was carried out on 0.2-mm silica gel coated plastic sheets with F-254 indicator (EM); preparative TLC was conducted on 2 mm silica gel coated 20 × 20 cm glass plates with F-254 indicator (EM). Analytical and preparative gas chromatography was carried out on a Hewlett Packard 5790 instrument using 1/8 in. × 6 ft and 1/4 in. × 6 ft columns packed with OV 101. IR spectra were recorded on a Perkin-Elmer Model 1420 spectrophotometer. ¹H and ¹³C NMR spectra were obtained on a Varian XL-300 NMR spectrometer; resonances are reported relative to Me₄Si standard.

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(10) Vicinal coupling constants of 5–9 Hz have been observed in several related cis-fused bicyclic compounds (ref 11). The corresponding trans isomers exhibit coupling constants of 20–24 Hz (ref 12).

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(13) 4-Acyldihydrofurans previously have been prepared in variable yields by oxidative coupling of β -dicarbonyl compounds with olefins and dienes (ref 14) and acid-catalyzed cyclization of unsaturated β -dicarbonyls (ref 15). Only one 4,5,8,9-tetrahydrobenzofuran derivative appears to have been made previously (ref 11c).

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Low-resolution mass spectra were obtained on a Hewlett-Packard 5985 spectrometer; high-resolution mass spectra were recorded on a Kratos MS 25 RF instrument. All reactions were carried out under a dry nitrogen atmosphere.

Reaction of (Butadiene)Co(CO)₃BF₄ (1) with Pentanedione Dianion. A 100-mL three-neck flask was equipped with a solid addition tube, a pressure-equalizing dropping funnel, a magnetic stir bar, and a nitrogen inlet and then charged with 10 mL of THF. To the solid addition tube was added 200 mg (0.7 mmol) of (butadiene)tricarbonylcobalt tetrafluoroborate. A freshly prepared THF solution (10 mL) of 2,4-pentanedione dianion (from treatment of 0.70 mmol of 2,4-pentanedione with 0.70 mmol of sodium hydride followed by 0.70 mmol of butyllithium) was then added to the dropping funnel. The dianion solution and the cobalt complex were added to the flask slowly and simultaneously over a period of 1 h at -78 °C. The solution was stirred for 30 min more at -78 °C then allowed to warm to 25 °C. Then 0.5 mL of HMPA was added and stirred for 5 h. The reaction mixture was poured into 10 mL of water, acidified with 1.5 M HCl, and extracted thrice with 30-mL portions of the pentane. The combined organic extracts were washed with saturated sodium chloride and dried with MgSO₄. Evaporation of the pentane afforded crude 2-vinyl-4-acetyl-5-methyl-2,3-dihydrofuran (**4a**), which was purified by preparative GC (14 mg, 12%). ¹H NMR (CDCl₃): δ 5.92 (m, 1 H, CH=), 5.25 (m, 2 H, CH₂=), 5.05 (m, 1 H, CH-O), 3.12 (apparent t, *J* = 14, 7 Hz, 1 H, CH_{2A}), 2.72 (dd, *J* = 14, 6 Hz, 1 H, CH_{2B}), 2.23 (s, 3 H, COCH₃), 2.19 (s, 3 H, CH₃). Irradiation of the signal at δ 5.92 caused collapse of the δ 5.25 signal to two broad singlets at δ 5.29 and 5.21 and partial collapse of δ 5.05 to a broad triplet; irradiation of the δ 5.05 absorption caused collapse of the δ 3.12 and 2.72 peaks to two doublets, *J* = 14 Hz, respectively, and partial collapse of the δ 5.92 resonance; irradiation of the δ 3.12 signal caused collapse of the δ 2.72 resonance to a doublet, *J* = 6 Hz; irradiation of the δ 2.72 signal caused collapse of the δ 3.12 resonance to a doublet, *J* = 7 Hz. ¹³C NMR (CDCl₃): δ 194.5 (C=O), 167.4 (=CH₃), 136.8 (CH=), 116.8 (CH₂=), 111.9 (CC(O)CH₃), 82.5 (CHO), 36.3 (CH₃), 29.3 (COCH₃), 14.9 (CH₃). IR (CCl₄): 1670, 1620, 1600 cm⁻¹. MS: calcd for C₉H₁₂O₂ 152.0837, found 152.0859.

1,3-Bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (3c). 1-(Trimethylsilyloxy)-1-phenyl-1-buten-3-one^{9b} (5 g, 21 mmol) was added to a 50-mL THF solution containing 25 mmol of freshly prepared lithium diisopropyl amide at -78 °C. After being stirred for 1 h the mixture was quenched with 21 mmol of chlorotrimethylsilane, and the THF was removed under reduced pressure. The resulting residue was washed with cold, dry hexane and the hexane washings were combined and concentrated. 1,3-Bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene was isolated by fractional distillation, bp 102–105 °C (0.2 mm), in 90% yield. ¹H NMR (CDCl₃): δ 7.52–7.3 (5 H, m), 5.51 (1 H, s), 4.98 (1 H, s), 4.52 (1 H, s), 0.27 (9 H, s, OSi(CH₃)₃), 0.15 (9 H, s, OSi(CH₃)₃). IR (neat): 3080, 2980, 2920, 1638, 1610 cm⁻¹. MS (70 eV): *m/e* 306 (M⁺), 233 (M⁺ - Si(CH₃)₃), 73 (Si(CH₃)₃⁺).

1,3-Bis(trimethylsilyloxy)-1-methyl-1,3-butadiene (3b). With the same procedure from 1-(trimethylsilyloxy)-1-methyl-1-buten-3-one,¹⁸ **3b** was obtained in 95% yield (*E* + *Z*), bp 43–45 °C (0.3 mm). ¹H NMR (CDCl₃): δ 5.19 (1 H, s), 4.75 (1 H, s), 4.72 (1 H, s), 4.31 (1 H, s), 4.13 (1 H, s), 4.09 (1 H, s), 2.00 (3 H, s), 1.84 (3 H, s), 0.23 (9 H, s), 0.21 (9 H, s), 0.20 (9 H, s), 0.19 (9 H, s). IR (neat): 2950, 2910, 1645, 1600 cm⁻¹. MS (70 eV): *m/e* 244 (M⁺), 229 (M⁺ - CH₃), 155 (M⁺ - OSi(CH₃)₃), 73 ((CH₃)₃Si⁺).

General Procedure for the Preparation of Dihydrofurans and Tetrahydrobenzofurans from (Diene)tricarbonylcobalt Tetrafluoroborate and Bis(1,3-trimethylsilyloxy)-1,3-butadienes. To 20 mL of a stirred THF suspension containing 0.70 mmol of the cobalt complex at -78 °C was added 0.70 mmol of the bis(silyloxy) diene by syringe. The mixture was allowed to warm to room temperature over a period of 3–5 h, at which time it was homogeneous and exhibited IR bands at ca. 2045 and 1990 cm⁻¹. A solution of Bu₄NF in THF (2.10 mmol) was then added and stirring continued at 20 °C for 6–12 h. The mixture was then poured into 50 mL of water, acidified with dilute hydrochloric acid, and extracted thrice with 50-mL portions of CH₂Cl₂. The

combined organic extracts were washed with saturated NaCl solution and dried over MgSO₄. The products were isolated and purified by preparative TLC (1:1 EtOAc/hexane) or GC.

4b. ¹H NMR (CDCl₃): δ 7.3–7.6 (5 H, m, Ph), 6.00 (1 H, m, CH₂=CH), 5.30 (2 H, m, CH₂, vinyl), 5.09 (1 H, m, CH-O), 3.28 (1 H, m, C3-H), 2.93 (1 H, m, C3H'), 1.84 (3 H, s, CH₃). Irradiation of δ 6.00 caused the signal at δ 5.30 to collapse to two singlets at δ 5.33 and 5.24 and the signal at δ 5.09 to collapse to a broad triplet; irradiation of δ 5.09 caused collapse of δ 6.00 to dd, *J* = 9, 15 Hz, and collapse of δ 5.30 to two doublets, *J* = 15, 9 Hz, respectively, and collapse of δ 3.28 and 2.93 to two doublets, *J* = 14 Hz; irradiation of δ 3.28 caused collapse of δ 2.93 to a doublet, *J* = 7.5 Hz; irradiation of δ 2.93 caused collapse of δ 3.28 to a d, *J* = 6 Hz. ¹³C NMR (CDCl₃): δ 136.6 (CH₂=CH), 133.1 (Ar), 131.0 (Ar), 128.46 (Ar), 127.82 (Ar), 117.1 (CH₂=CH), 82.8 (CH₂C-O), 37.0 (CH₂), 15.4 (CH₃); C=O, C4 and C5 not observed. MS: calcd for C₁₄H₁₄O₂ 214.1007, found 214.0994. IR (neat): 1715, 1670, 1600 (br) cm⁻¹.

4c. ¹H NMR (CDCl₃): δ 5.87 (1 H, m, CH₂=CH), 5.30 (2 H, m, CH₂=CH), 4.84 (1 H, q, *J* = 7 Hz, H-2), 3.68 (3 H, s, OCH₃), 3.26 (1 H, m, H-3), 3.03 (1 H, m, H-3), 2.20 (3 H, s, CH₃). Irradiation of δ 5.87 caused δ 5.30 to collapse to two singlets at δ 5.24 and 5.35, and δ 4.84 collapsed to a triplet, *J* = 7 Hz. ¹³C NMR (CDCl₃): δ 167 (C=O), 136.9 (CH₂=CH), 129.5 (C4), 128.4 (C5), 116.7 (CH₂=CH), 82.6 (CH₂CHO), 50.8 (OCH₃), 35.5 (C3), 14.0 (CH₃). IR (neat): 1710, 1645 cm⁻¹. MS: calcd for C₉H₁₂O₃ 168.0786, found 168.0793.

5a. ¹H NMR (CDCl₃): δ 6.20 (m, 1 H, CH₂CH=), 5.92 (m, 1 H, CH=CH), 4.7 (m, 1 H, CH-O), 3.05 (m, 1 H, CH₂CH-CH), 2.27 (s, 3 H, COCH₃), 2.22 (s, 3 H, CH₃), 1.91–2.00 (m, 4 H, CH₂'s). Irradiation of the δ 6.20 absorption caused collapse of the δ 5.92 signal to a broad singlet; irradiation at δ 5.92 caused collapse of the δ 6.2 absorption to a broad triplet and collapse of δ 4.7 to a doublet, *J* = 8.3 Hz, indicating *J*_{8,9} = 8.3 Hz. ¹³C NMR (CDCl₃): δ 194 (C=O), 168.1 (-C-CH₃), 134.7 (CH=CH), 122.9 (CH₂C-H=CH), 119.5 (C=CCOCH₃), 78.2 (CH-O), 40.8 (CH-CH₂), 29.4 (COCH₃), 25.2 (CH₂-CH), 23.5 (CH₂CH₂), 15.8 (vinyl CH₃). IR (CCl₄): 1670, 1642, 1619, 1590 cm⁻¹. MS: calcd for C₁₁H₁₄O₂ 178.0994, found 178.0965.

5b. ¹H NMR (CDCl₃): δ 7.4–7.6 (5 H, m, Ph), 6.21 (1 H, m, CH₂CH=CH), 5.91 (1 H, m, CH₂CH=CH), 4.85 (1 H, dd, *J* = 9, 1 Hz, CH-O), 3.40 (1 H, m, CH₂CH), 2.05 (1 H, m, H-4), 1.9 (1 H, m, H-4), 1.71 (3 H, s, CH₃), 1.45 (2 H, m, H-5). IR (neat): 1720 w, 1670, 1600 (br) cm⁻¹; MS: calcd for C₁₆H₁₆O₂ 240.1145, found 240.1150.

5c. ¹H NMR (CDCl₃): δ 6.15 (1 H, m, H-6), 5.80 (1 H, m, H-7), 4.82 (1 H, dd, *J* = 9, 1 Hz, H-8), 3.71 (3 H, s, OCH₃), 3.0 (1 H, m, H-9), 2.19 (3 H, s, CH₃), 2.1 (1 H, m, H-4), 1.85 (1 H, m, H-4), 1.2 (2 H, m, H-5); identical with the literature spectrum.^{11c}

Hydrolysis of Adduct from 1 + 3c. To a 10-mL THF suspension of 0.20 g (0.70 mmol) of **1** was added 0.215 g of **3c** (0.70 mmol) at -78 °C. The solution was allowed to warm to 25 °C over a period of 1 h. After 3 h at 20 °C the solution was homogeneous and showed IR bands at 2060 and 1995 cm⁻¹ (M-CO). The solution was then quenched with 1.5 M HCl and stirred for 3 h more, then poured into 25 mL water, and extracted three times with 25 mL of ether. The combined ether layers were washed with saturated NaCl solution and dried over MgSO₄. Removal of the ether under reduced pressure afforded 0.10 g (70%) of 1-phenyl-2-(3-butenyl)-1,3-butanedione as a mixture of keto and enol tautomers. ¹H NMR (CDCl₃): δ 7.9–7.4 (m, phenyl), 5.9–5.7 (m, =CH), 5.4–5.2 (m, =CH₂), 5.1–4.9 (m, =CH₂), 4.49 (apparent t, *J* = 7 Hz, C(=O)CH, keto), 3.0 (dd, *J* = 6, 7 Hz, C(1)H₂, enol), 2.2–2.0 (m, CH₂), 2.15 (s, CH₃), 2.0 (s, CH₃). IR (neat): 3070 (=C-H), 2940, 2760 (C-H), 1720, 1680 (C=O), 1645 (w, C=C) cm⁻¹. MS (70 eV): *m/e* (relative intensity) 216 (0.9, M⁺), 162 (35, M⁺ - CH₂=CHCH=CH₂), 161 (15.1, M⁺ - CH₂=CHCH₂), 105 (100, C₆H₅CO⁺), 77 (36.1, C₆H₅⁺).

Desilylation of 3c and Trapping with CH₃I and 1. To a THF solution (10 mL) containing 0.67 g (2.1 mmol) of 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene and 0.31 g (2.1 mmol) of methyl iodide at -78 °C was added 2.1 mL Bu₄NF (1 M THF) over a period of 30 min. The solution was allowed to warm to 25 °C and stirred for 2 h. The mixture was then poured into 50 mL of water, acidified with 1.5 M HCl, extracted thrice with 30-mL portions of methylene chloride, washed with saturated sodium

chloride, and dried with $MgSO_4$. The methylene chloride was removed at reduced pressure and the residue washed with several portions of ether, leaving behind a white solid (Bu_4NI). The ethereal solution upon evaporation afforded 0.36 g (97%) 3-methyl-1-phenyl-2,4-pentanedione. 1H NMR ($CDCl_3$): δ 7.4-8.1 (m, 5 H, Ar), 4.5 (q, 1 H, $CHCH_3$), 2.2 (s, 3 H, $COCH_3$), 1.5 (d, 3 H, $CHCH_3$).

Bis(siloxy) diene **3c** (0.035 mmol) in 0.5 mL of $THF-d_8$ was treated first with Bu_4NF (0.035 mmol) at 20 °C followed by addition of complex **1** (0.035 mmol) at -78 °C. After warming to 20 °C over a period of 1 h the solution was homogeneous (orange), and its 1H NMR spectrum was identical with that obtained directly from **1** and **3c** (vide infra).

In Situ NMR of 1 + 3c Reaction. To a $THF-d_8$ suspension (0.5 mL) of 0.035 mmol of (butadiene)tricarbonyl cobalt tetrafluoroborate was added an equimolar quantity of 1,3-bis(trimethylsiloxy)-1-phenyl-1,3-butadiene at -78 °C. The mixture was allowed to warm to 20 °C over a period of 3 h, at which time the solution was homogeneous. 1H NMR ($THF-d_8$) δ 8.0 (m), 7.51 (m), 6.32 (m), 5.17 (d, $J = 16$ Hz), 5.05 (d, $J = 9$ Hz), 2.04 (s), 1.94 (s), 1.28 (s), 0.90 (s), 0.20 (s), 0.18 (s), 0.11 (s), 0.06 (s), 0.02 (s), -0.095 (s), -0.15 (s). Irradiation at δ 6.32 caused collapse of the signals at δ 5.17 and 5.05 to singlets, suggesting the presence of an uncoordinated vinyl group.

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Metal-Ammonia Reduction of α -Tetralone. Competition between Ring Reduction, Carbonyl Reduction, and Dimer Formation

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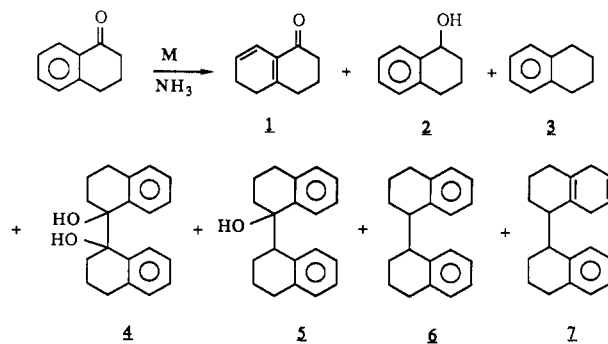
The metal-ammonia reduction of cyclic ketones has received considerable attention,¹ and the mechanistic aspects of this reaction have been somewhat controversial.^{1c,d} The incorporation of additional unsaturation present in aryl ketones provides greater complexity since, in principle, reduction may occur either at the carbonyl group or in the aromatic ring. In fact the reduction of aryl ketones to alcohols and/or hydrocarbons has been known for some time, but nuclear reduction was first observed in 1973 by Narisada and Watanabe.² We now report our results with the metal-ammonia reduction of α -tetralone that provide mechanistic insight into this complex process.

We have found that the reaction of α -tetralone with alkali metal (especially lithium) in ammonia can produce as many as seven different products (1-7) including the previously unknown nuclear reduction product **1**.³ Moreover, the reaction shows considerable sensitivity to conditions as illustrated in Table I.

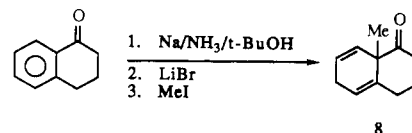
(1) For reviews, see: (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972. (b) Rautenstrauch, V.; Willhalm, B.; Thommen, W.; Burger, U. *Helv. Chim. Acta* 1981, 64, 2109. (c) Huffman, J. W. *Acc. Chem. Res.* 1983, 16, 399. (d) Pradhan, S. K. *Tetrahedron* 1986, 42, 6351.

(2) Narisada, M.; Watanabe, F. *J. Org. Chem.* 1973, 38, 3887.

(3) Products were isolated by silica gel chromatography. New compounds (1, 3, and 5) were identified by GC/MS and NMR.



Previously, Hall et al.⁴ reported the conversion of α -tetralone to tetralin in high yield, while Narisada and Watanabe carried out the reductive methylation² affording the methyl dihydro product **8** in 60% yield. In neither case, however, was any significant amount of dimerization observed. As indicated in Table I, reduction with Li at



-78 °C provides dimeric products as the major outcome (54-84%), whereas higher temperatures (-33 °C) or the use of Na reduces dimer formation to a trace (0-2%). The method of addition was important (i.e., α -tetralone vs metal added last; methods A and B), especially at -78 °C where dimeric products increased ca. 25% when α -tetralone was added last. The method of quench was also important, as noted by Hall et al.,⁴ especially for Li at -33 °C where direct quench with NH_4Cl gives 98% tetralin and inverse quench into aqueous NH_4Cl affords the alcohol as the major product (70%).

We feel that Scheme I provides a plausible explanation for these results. The initially formed radical anion may form a dimeric ion pair of the type suggested by Huffman^{1c,5,6} (or some other aggregate) or accept a second electron, resulting in a dianion. The presence of the aromatic ring is quite important here since the ketyl dimer should be less important (relative to aliphatic ketones) due to greater charge delocalization, and the dianion should be more stable.⁷ Hence we suggest the ion pair dimer as the major route to dimeric products. This is consistent with the metal effect since such dimers are expected to be more important for Li than Na.⁵ The effect of temperature may result from greater solvation of the ion dimer at lower temperature⁶ making it more resistant to protonation.^{10,11} Adding α -tetralone last also leads to more dimer. Since at the early stage of the reaction this means excess metal, and presumably more dianions, perhaps path A of Scheme I represents the actual mode of ion dimer formation.

(4) Hall, S. S.; Lipsky, S. D.; McEnroe, F. J.; Bartels, A. P. *J. Org. Chem.* 1971, 36, 2588.

(5) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* 1964, 86, 2538.

(6) Hirota, N. *J. Am. Chem. Soc.* 1967, 89, 32.

(7) The dianion is expected to be accessible under these conditions since the half-wave potentials for the formation of the monoanion/dianion from acetophenone, for example, are -1.99 V/-2.46 V (vs SCE),⁸ and the reduction potentials in ammonia (at -50 °C) are -2.99 V for Li and -2.59 V for Na.⁹

(8) Meites, L. *Polarographic Techniques*, 2nd ed.; Wiley-Interscience: New York, 1965.

(9) Wilds, A. L.; Nelson, N. A. *J. Am. Chem. Soc.* 1953, 75, 5360.

(10) *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1.

(11) A reviewer has suggested that dimerization might be more common at lower temperature since it is an entropically disfavored pathway.