phase was dried over magnesium sulfate and concentrated to a red oil. The oil was chromatographed on Celite[8] and the product, eluted with 10% ether–benzene, was recrystallized from ether–petroleum ether (bp 30–60°) to give 1.23 g (63%) of **4** as pink crystals: mp 111–113°; λ_{max} 218, 275 mμ (ϵ 22,500, 10,500); ir 2.9, 3.02, 6.5, 6.67, 8.15, 8.5 μ.

Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.34; H, 5.11; Cl, 18.14; N, 7.16. Found: C, 61.80; H, 5.46; Cl, 18.29; N, 7.34.

2,7-Dimethyl-5-hydroxyindole (**5**).—4-Chloro-5-hydroxy-2,7-dimethylindole (**4**) (392 mg, 2 mmol) and 40 ml of 0.1 *N* aqueous sodium hydroxide were shaken in a Parr low pressure hydrogenation apparatus with 500 mg of 10% palladium-on-charcoal catalyst, at an initial hydrogen pressure of 30 psi, until hydrogen uptake ceased. The reaction mixture was filtered, and the filtrate was acidified with dilute hydrochloric acid and then extracted with ethyl acetate. The combined extracts were dried over magnesium sulfate and concentrated to an oil, which was chromatographed on silica gel. The product was eluted with 5% ether–benzene. Recrystallization from methylene chloride–petroleum ether (bp 30–60°) gave near-white crystals, 58 mg (18%), mp 145–147°, undepressed on admixture of this substance with authentic **5**[1] and identical in ultraviolet and infrared spectrum.

***t*-Butyl 4-Chloro-2,7-dimethyl-5-methoxyindole-3-carboxylate.**—To a stirred solution of 15.5 g (0.0523 mol) of *t*-butyl 4-chloro-5-hydroxy-2,7-dimethylindole (**3**) in 96.3 ml of ethyl alcohol and 193 ml of 2 *N* sodium hydroxide solution was added dropwise over 1 hr 31.6 g (23.4 ml, 0.251 mol) of dimethyl sulfate. The mixture was heated at reflux temperature for 1.5 hr, cooled, diluted with water, and filtered, to give 13.1 g (80%) of product, mp 175–180°. A sample was recrystallized from ether to give crystals: mp 182–184° (gas evol); λ_{max} 221, 285 (shoulder), 285 mμ (ϵ 40,000, 17,100, 11,800); ir 3.05, 3.35, 6.00, 6.25, 6.85, 8.25, 8.6, 9.25 μ.

Anal. Calcd for $C_{16}H_{20}ClNO_3$: C, 62.03; H, 6.50; Cl, 11.47; N, 4.51. Found: C, 61.94; H, 6.65; Cl, 11.18; N, 4.32.

4-Chloro-2,7-dimethyl-5-methoxyindole (**6**).—A solution of 8.2 g (0.0266 mol) of *t*-butyl 4-chloro-2,7-dimethyl-5-methoxyindole-3-carboxylate and 600 mg of *p*-toluenesulfonic acid monohydrate in 900 ml of toluene was heated at reflux for 1 hr. The solution was cooled, filtered, and evaporated to dryness. The residue was chromatographed on silica gel, and elution of product with benzene gave 4.13 g (74.5%) of product melting at 132–136°. A sample was recrystallized from ether–petroleum ether (bp 30–60°) to give crystals: mp 139–140°; λ_{max} 221, 278 mμ (ϵ 28,800, 10,300); ir 2.9, 3.44, 6.26, 7.3 μ.

Anal. Calcd for $C_{11}H_{12}ClNO$: C, 62.99; H, 5.76; Cl, 16.92; N, 6.67. Found: C, 62.81; H, 5.64; Cl, 16.65; N, 6.98.

2,7-Dimethyl-5-methoxyindole (**7**).—4-Chloro-2,7-dimethyl-5-methoxyindole (**6**) (419.4 mg, 2 mmol), 392 mg (4 mmol) of potassium acetate and 480 mg of 10% palladium-on-charcoal in 50 ml of ethyl alcohol was shaken in a Parr low pressure hydrogenation apparatus at an initial hydrogen pressure of 30 psi until hydrogen uptake ceased. The reaction mixture was filtered and concentrated. The residue was partitioned between methylene chloride and water. The organic phase was separated, and washed several times with water, dried, and evaporated. The residue was crystallized from ether–petroleum ether (bp 30–60°) to give 257 mg (73.5%) of crystals, mp 73–75°, undepressed on admixture of this substance with authentic 2,7-dimethyl-5-methylindole (**7**), prepared as described below, and identical in ultraviolet and infrared spectrum.

2,7-Dimethyl-5-methoxyindole (**7**).—To a stirred solution of 26.4 g (0.163 mol) of 2,7-dimethyl-5-hydroxyindole (**5**),[1] 297 ml of ethanol and 595 ml of 2 *N* sodium hydroxide solution was added dropwise, under nitrogen, 73.3 ml of dimethyl sulfate (0.785 mol) over a period of 1 hr. The reaction mixture was then heated at reflux for 1 hr, cooled, diluted with water, and extracted with ethyl acetate. The combined extracts were washed with saline, dried over magnesium sulfate, and concentrated. The residue was dissolved in benzene and passed through a magnesia–silica column using benzene as the eluting solvent. The initial 1200 ml of eluate was evaporated to give 23 g (78%) of yellow oil, which crystallized on standing. A sample was recrystallized from ether–petroleum ether (30–60°) to give near white crystals: mp 76–77°; λ_{max} 215, 272 mμ (ϵ 19,200, 8570); ir 3.0, 3.45, 6.25, 6.73, 8.36, 9.55 μ.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.10; H, 7.31; N, 7.67.

Registry No.—**1**, 19832-87-2; **3**, 23386-23-4; **4**, 23386-24-5; **6**, 23386-25-6; **7**, 23386-26-7; *t*-butyl 4-chloro-2,7-dimethyl-5-methoxyindole-3-carboxylate, 23386-27-8.

Acknowledgment.—We are indebted to Mr. L. Brancone and his staff for the microanalyses and to Mr. W. Fulmor and his associates for the spectral data.

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[8] Celite is the trademark of the Johns–Manville Corp. for diatomaceous earth.

Reductive Cleavage of Ferrocene Derivatives

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Ferrocene (**1**) and a number of ferrocene derivatives have been subjected to reduction by solutions of metals in amines.[1] As part of our research in ferrocene chemistry, we were interested in studying factors influencing the ease of reduction of substituted ferrocenes and in identifying the isomers of substituted cyclopentadienes obtainable by reductive cleavage of 1,1′-dialkylferrocenes. We subjected three symmetrically substituted dialkylferrocenes, 1,1′-dimethyl-, (**2**), 1,1′-diethyl- (**3**), and 1,1′-dibenzylferrocene (**4**), and two ferrocenophanes, [3]ferrocenophane (**5**) and [3][3]-1,3-ferrocenophane (**6**), as well as **1**, to reduction by Li in propylamine (Scheme I). We assumed originally that reduction of each dialkyl compound would lead to three alkylcyclopentadienes and that these could be identified as 1-, 5-, or 7-substituted norbornene derivatives by preparing Diels–Alder adducts with maleic anhydride. However, we found no 7-substituted norbornenes and, in the case of 1,1′-dibenzylferrocene, only the 1-benzylnorbornene derivative, which arises from 2-benzylcyclopentadiene, was found. After reduction and quenching, **1** gave cyclopentadiene which was converted into N-phenyl-5-norbornene-2,3-dicarboximide (**7**) by treatment with maleic anhydride and then acetyl chloride, followed by aniline. Similarly, **2** gave a mixture of 2- and 3-methylcyclopentadienes which were characterized as 1- and 5-methyl-N-phenyl-5-norbornene-2,3-dicarboximides (**8** and **9**). The reduction of **3** and subsequent treatment of the reaction product with maleic anhydride led to 1-ethyl-5-norbornene-2,3-dicarboxylic anhydride (**10**), the corresponding dicarboxylic acid (**11**), and a lactonic acid, mp 157.5–158°, which proved to be 5-ethyl-5-hydroxynorbornane-2,3-dicarboxylic acid γ-lactone (**12**) indicating the formation of 2- and 3-ethylcyclopentadiene only. The preparation of 5-ethyl-5-norbornene-2,3-dicarboxylic acid (**13**), mp 156°, has been reported,[2] but, since its structure was not proved and since the

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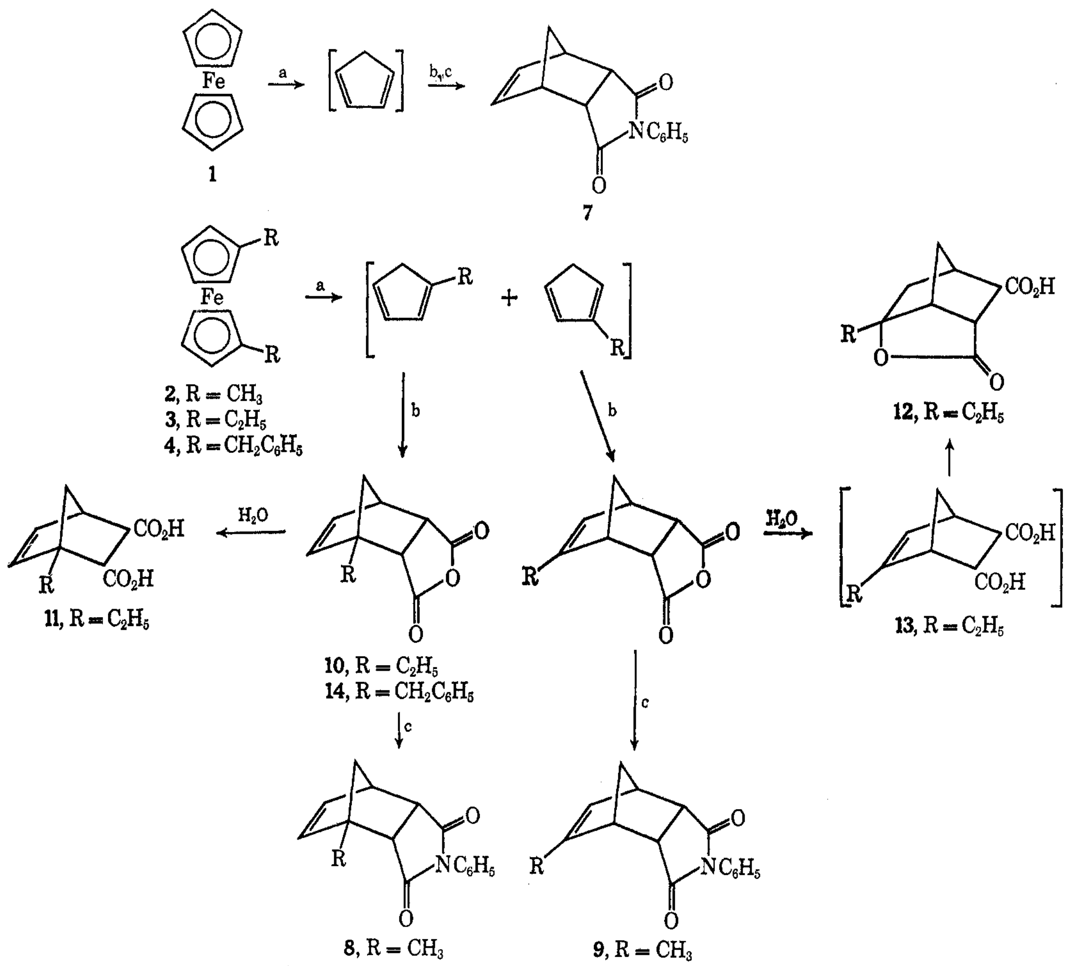
[1] (a) D. S. Trifan and L. Nichols, *J. Amer. Chem. Soc.*, **79**, 2746 (1957). (b) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 4604 (1961). (c) A. N. Nesmeyanov, *et al.*, *Dokl. Akad. Nauk SSSR*, **160**, 137 (1965); **177**, 586 (1967). (d) G. W. Watt and L. J. Baye, *J. Inorg. Nucl. Chem.*, **26**, 2099 (1964). (e) D. W. Slocum and W. E. Jones, *J. Organometal. Chem.*, **15**, 262 (1968).

[2] K. Alder and H.-J. Ache, *Chem. Ber.*, **95**, 503 (1962).

SCHEME I



a, Li + propylamine, then H_2O
b, maleic anhydride
c, aniline, then acetic anhydride + potassium acetate

diacid obtained from 5-methyl-5-norbornene-2,3-dicarboxylic anhydride also undergoes spontaneous lactone formation,[3] we believe that the reported diacid **13**[2] was in fact the lactonic acid **12**.

When our reduction procedure was applied to **4**, only one product, 1-benzyl-5-norbornene-2,3-dicarboxylic anhydride (**14**), could be isolated after treatment with maleic anhydride, indicating that 2-benzylcyclopentadiene was the only isomer formed.

Yields of norbornene derivatives in the cases in which two isomers were formed were quite low since significant losses occurred in the difficult separation and purification steps. More important to us was the degree of degradation of the variously substituted ferrocenes and our experiments indicate that steric effects play a major role in the ease with which reduction occurs. Thus, **1** and **2** were degraded to the extent of 77 and 70% respectively, while **3** (34%) and **4** (45%) proved to be more resistant to reduction. The reduction of **5** was evidenced in the reaction mixture by evolution of heat and deposition of metallic iron, but no well-defined monomeric addition products with maleic anhydride, N-phenylmaleimide, or tetracyanoethylene could be isolated. Based on starting material recovered (67%), **5** is somewhat more resistant to reduction than any of the simple dialkylferrocenes studied. In contrast, no reaction was observed when the reduction was tried with **6**, similar to results reported by Schlögl[4] and Ellis,[5] and this compound was recovered quantitatively from the reaction mixture.

The failure of **6** to react could be due to the constricting effect[6] of the two bridging groups which tend to displace the rings from their equilibrium separation distance toward one another, effectively trapping the iron in a strained hydrocarbon cage. This results in a large reduction potential, probably associated with steric constriction of the transition state for such a process. We expect that [*m*][*n*]ferrocenophanes where *m* and *n* are greater than 3 should be more easily reduced and experiments are planned to explore this idea.

Experimental Section[7]

Ferrocene and Ferrocene Derivatives.—Ferrocene and 1,1′-dimethylferrocene were obtained from Arapahoe Chemical Co. and were purified by column chromatography or sublimation

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[3] V. A. Mironov, E. V. Sololev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

[4] Karl Schlögl, Annual Summary Report No. 3, March 1963, U. S. Air Force Contract No. 61 (052)-383, Air Force Materials Laboratory.

[5] A. F. Ellis, Ph.D. Dissertation, Part II, University of Illinois, Urbana, Ill., 1963.

[6] N. D. Jones, R. E. Marsh, and J. H. Richards, *Acta Crystallogr.*, **19**, 330 (1965).

[7] Melting points were taken on a Kofler hot stage and are uncorrected. Nmr spectra were determined in $CDCl_3$ on a Varian A-60 instrument with tetramethylsilane as an internal reference, and infrared spectra were recorded using a Beckman IR-4 spectrophotometer. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

prior to use. 1,1′-Diethyl-[8] and 1,1′-dibenzylferrocene,[8] [3]ferrocenophane,[9] and [3][3]-1,3-ferrocenophane[9] were prepared by reported procedures.

Reductive Cleavage Reactions.—The usual procedure was to stir 3–5 g of the ferrocene derivative in 30 ml of *n*-propylamine with 1.0–1.6 g of Li wire cut into two or three pieces. Except in the case of **6**, each reaction mixture darkened and boiled spontaneously after a few minutes. Stirring was continued for several hours at room temperature; then the mixtures were diluted with benzene and poured into ice–water. The aqueous layer was added slowly to ice–water containing excess HCl and extracted twice more with benzene. The combined benzene solutions were dried ($MgSO_4$), treated with maleic anhydride, and slowly distilled to dryness on a steam bath to give a mixture of the Diels–Alder adduct and starting material. Separation and purification were accomplished in two different ways as described in the following paragraphs.

N-Phenyl-5-norbornene-2,3-dicarboximide (7) from Ferrocene (1).—The crude product obtained from **1** (3.00 g, 16.1 mmol), 1.63 g of Li, and 2.7 g of maleic anhydride was taken up in acetyl chloride, refluxed for 1 hr, and evaporated; the residue was dissolved in a small volume of benzene and then treated with 2.6 ml of aniline. After 1 hr at room temperature, the mixture was evaporated and the residue was heated for 0.5 hr on the steam bath with 30 ml of acetic anhydride and 2.9 g of anhydrous sodium acetate. This suspension was diluted with benzene, washed thoroughly with water, dried ($MgSO_4$), concentrated, and chromatographed on silica gel. The first fraction eluted with benzene was rechromatographed on Al_2O_3 and gave 0.70 g of **1** (23.3%) and 2.43 g of **7**. Following fractions after rechromatographing (Al_2O_3) yielded 2.19 g of **7**; the total yield of **7** was 4.62 g (59.8%). Recrystallization from methylene chloride–hexane gave pure **7** as white needles: mp 142.5–144.5° (lit.[10] mp 144°); ir (mull) 5.63, 5.82 μ (C=O); nmr τ 8.67–8.21 (m, 2, CH_2), 6.69–6.42 (m, 4, CH), 3.83–3.61 (m, 2, CH=CH), 2.98–2.40 (m, 5, C_6H_5).

1- and 5-Methyl-N-phenyl-5-norbornene-2,3-dicarboximide (8 and 9) from 1,1′-Dimethylferrocene (2).—From **2** (3.46 g, 16.2 mmol), 1.55 g of Li, and 3.0 g of maleic anhydride by the procedure described for **1** was obtained 8.78 g of a thin red oil which was chromatographed on SiO_2. Elution with hexane yielded starting material (1.03 g, 29.7%), with 1:1 hexane–benzene, N-phenylmaleimide, and with benzene, a mixture of **8** and **9**, whose separation required rechromatographing (Al_2O_3) several times followed by recrystallization from methylene chloride–hexane or hexane alone before reasonably pure materials could be isolated. Isomer **8** was isolated: mp 168–180° (lit.[11] mp 179–180°); ir ($CHCl_3$) 5.54, 5.77 μ (C=O); nmr τ 8.38 (m, 5, CH_2 and CH_3), 6.95–6.33 (m, 3, CH), 4.03–3.60 (m, 2, CH=CH), 2.99–2.34 (m, 5, C_6H_5) (lit.[11] τ 8.40, 3.93). The 5-methyl isomer, **9**, was isolated in approximately the same purity: mp 116–122.5° (lit.[11] mp 128–129.5°); ir ($CHCl_3$) 5.54, 5.76 μ (C=O); nmr τ 8.67–8.06 (m, 5, CH_2 and CH_3), 6.76–6.40 (m, 4, CH), 4.22 (m, 1, C=CH), 3.00–2.33 (m, 5, C_6H_5) (lit.[11] τ 8.18, 4.24).

1-Ethyl-5-norborene-2,3-dicarboxylic Anhydride (10), 1-Ethyl-5-norbornene-2,3-dicarboxylic Acid (11), and 5-Ethyl-5-hydroxynorbornane-2,3-dicarboxylic Acid γ-Lactone (12) from 1,1′-Diethylferrocene (3).—Compound **3** (4.55 g, 18.8 mmol), 1.30 g of Li, and 3.0 g of maleic anhydride were allowed to react by the usual procedure to give the crude maleic anhydride adduct which was heated for 2 hr on the steam bath with 75 ml of 2 *N* Na_2CO_3 solution and then extracted three times with 100 ml of methylene chloride. From these extracts was recovered 3.01 g (66.2%) of starting material (chromatographed on Al_2O_3, eluted with hexane). After acidification with 4 *N* HCl, the clear aqueous solution was concentrated under vacuum and extracted three times with 100 ml of methylene chloride to give 5.01 g of crude products. These were separated by fractional crystallization from cyclohexane, cyclohexane–hexane, and methylene chloride–hexane into three components, **10**, **11**, and **12**. Characteristics of **10** follow: mp 64–66° (hexane) (lit.[12] mp 65–66°); ir ($CHCl_3$) 5.37, 5.61 μ (C=O); nmr τ 8.96 (t, 3, CH_3CH_2), 8.67–7.66 (m, 4, CH_3CH_2 and ring CH_2), 6.78–6.13 (m, 3, CH), 3.97–3.60 (m, 2, CH=CH). Those of **11** follow: mp 126–128.5° (methylene chloride–hexane or H_2O) (lit. mp 131–132°,[12] 136° [2]); ir ($CHCl_3$) 5.80 μ (C=O); nmr τ 9.25–7.90 (m, 7, CH_3CH_2 and ring CH_2; discernible are a triplet and quartet from the ethyl group, J = 7.3 Hz), 6.99–6.33 (m, 3, CH), 4.06–3.63 (m, 2, CH=CH), chemical shift variable with concentration (s, 2, OH); equiv wt (titration) 107, calcd 105. Those of **12** follow: mp 157.5–158°; ir (mull) 5.62 (C=O, lactone), 5.80 μ (C=O, acid); nmr (Na salt in D_2O) τ 9.07 (t, 3, CH_3CH_2), 8.65–7.93 (m, 6, CH_2), 7.60–6.84 (m, 4, CH).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71; mol wt, 210. Found: C, 62.48; H, 6.53; mol wt (titration), 205.

1-Benzyl-5-norbornene-2,3-dicarboxylic Anhydride (14) from 1,1′-Dibenzylferrocene (4).—Compound **4** (3.08 g, 8.4 mmol) and 0.92 g of Li wire were stirred for 7.5 hr in 30 ml of propylamine and subjected to the standard work-up. The resulting dried benzene solution containing benzylcyclopentadiene was treated with 1.5 g of maleic anhydride, concentrated on the steam bath, extracted five times with 50 ml of water (which yielded 0.57 g of maleic acid) and evaporated to dryness. The residue was heated 3.5 hr at 107° with 50 ml of 2 *N* Na_2CO_3 solution and the resulting suspension was extracted thoroughly with methylene chloride from which was recovered 1.63 g of **4** (52.9%). The alkaline solution was acidified with 2 *N* HCl and extracted with methylene chloride to give 2.14 g of crude acid (46.7%, calcd for benzylnorbornenedicarboxylic acid).

This acid was converted into its anhydride by refluxing for 1 hr with 25 ml of acetyl chloride. The solution was evaporated to dryness and the residue was extracted several times with hot hexane. The concentrated extracts, upon cooling, gave white crystals which were purified by recrystallization from ethyl acetate: mp 121–122.5° (lit.[13] mp 123°); ir ($CHCl_3$) 5.34, 5.58 μ (C=O); nmr τ 8.75–8.17 (m, 2, ring CH_2), 6.89–6.42 (m, 5, CH and benzyl CH_2), 3.88–3.60 (m, 2, CH=CH), 2.72 (s, 5, C_6H_5).

Attempted cleavage of [3]Ferrocenophane (5) and [3][3]-1,3-Ferrocenophane (6).—Attempted cleavage of **5** gave an intractable mixture whereas **6**, when subjected to similar reaction conditions, remained unchanged.

Registry No.—**1**, 102-54-5; **2**, 1291-47-0; **3**, 1273-97-8; **4**, 12114-61-3; **5**, 12402-44-7.

Acknowledgment.—We thank Mr. J. L. Pflug and Mrs. Antoinette Austin for assistance in taking spectra.

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Quantitative Deuteration of a Grignard Reagent. The Preparation of 2-Butene 2-d_1

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In connection with a recent study of a photocycloaddition reaction,[1] a sample of 2-butene-2-d_1 was desired in which the label was introduced not only specifically but quantitatively. Quenching of the appropriate Grignard reagent appeared a good method of preparation; however, in our hands other prepartions had given less than quantitative introduction of label.[2] Also, Pocker and Exner,[3] in a careful study, had noted that phenyl- and benzyllithium and magnesium com-

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[2] R. A. Caldwell and G. W. Sovocool, unpublished work.

[3] Y. Pocker and J. H. Exner, *J. Amer. Chem. Soc.*, **90**, 6764 (1968).