References and Notes

(1) M. M. Runde, E. W. Scott, and J. R. Johnson, *J. Am. Chem. Soc.*, **52**, 1284 (1930); T. Reichstein, *Chem. Ber.*, **63**, 749 (1930).

(2) (a) S. Divald, M. C. Chun, and M. M. Joullié, *Tetrahedron Lett.*, 777 (1970). (b) S. Divald, Ph.D. Dissertation, University of Pennsylvania, 1969, and references cited therein. (c) T. M. Cresp and M. V. Sargent, *Aust. J. Chem.*, **27**, 905 (1974); F. Yamamoto, H. Morita, and S. Oae, *Heterocycles*, **3**, 1 (1975); S. Divald, M. C. Chun, and M. M. Joullié, *J. Org. Chem.*, **41**, 2835 (1976). 2-Furylmethyltrimethylammonium iodide was caused to react with cyanide, under special conditions, to yield a mixture of **2** (27%) and **3** (5%): E. L. Eliel and P. E. Peckham, *J. Am. Chem. Soc.*, **76**, 1209 (1950).

(3) (a) W. Herz and J. L. Rodgers, *J. Am. Chem. Soc.*, **73**, 4921 (1951); (b) W. Herz, *ibid.*, **75**, 483 (1953); W. Orth, L. Rappen, and G. Busse, U.S. Patent 3 523 952 (1970).

(4) Prepared by methylation of 2-dimethylaminomethyl-*N*-methylpyrrole[3a] using a suitable reagent.

(5) This fact raises the question as to whether other reported reactions of N-substituted pyrrolylmethylammonium salts actually produced only the "unrearranged" (or "normal") nitrile: see ref 3a; W. Herz and R. L. Settine, *J. Org. Chem.*, **24**, 201 (1959).

(6) Carbon–carbon bond cleavages of this type are not unprecedented in pyrrole chemistry; see, e.g., W. M. Quattlebaum, Jr., and A. H. Corwin, *J. Am. Chem. Soc.*, **64**, 922 (1942).

(7) Azafulvalenium ions may be implicated in various aspects of pyrrole chemistry,[8a,8c] and two examples of isolable salts from NH pyrroles have been reported.[8b,8c]

(8) (a) E.g., R. M. Silverstein, E. E. Ryskiewicz, C. Willard, and R. C. Koehler, *J. Org. Chem.*, **20**, 668 (1955); D. Klamann, P. Weyerstahl, and H. Dujmovits, *Justus Liebigs Ann. Chem.*, **714**, 76 (1968); (b) P. E. Sonnet, *J. Heterocycl. Chem.*, **7**, 1101 (1970), and references cited therein; (c) K. Hafner and K. Pfeiffer, *Tetrahedron Lett.*, 4311 (1968).


Carbon–Carbon Reductive Cleavage during Metal–Ammonia Reaction

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The majority of metal–ammonia reactions (Birch reductions) do not involve carbon–carbon bond cleavage.[2] We have recently observed that the photodimers **1**[3] and **2**[4] are selectively cleaved to hydrocarbons **3**[5] and **4**,[6] respectively, on
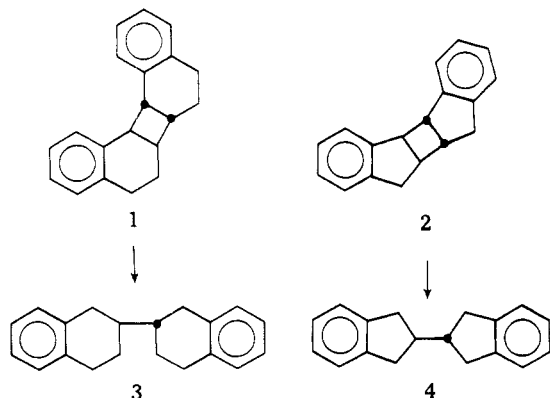
treatment with lithium or sodium in ether–ammonia. Hydrocarbons **1** and **2** react rapidly and a permanent blue color is not observed until after addition of 2 equiv of metal.

In contrast, hydrocarbons **5**[7] and **6**,[4] isomers of **1** and **2**, respectively, are totally inert to the lithium–ammonia cleavage reaction under comparable conditions. We attribute this spectacular difference in reactivity to a combination of steric strain and contiguous benzylic positions in **1** and **2**. We have

recently obtained an x-ray crystallographic analysis[3] of hydrocarbon **1**, which shows that the four-membered ring is planar and has an elongated bond (1.579 Å). Interestingly, it is this bond which is cleaved during the lithium–ammonia reduction. We have also determined that **7**[8a] is inert to Na–
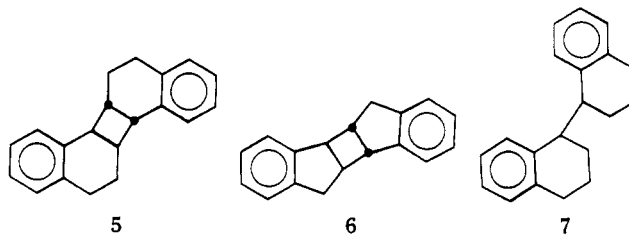

NH₃ reductive cleavage. Comparison of structures **1**, **5**, and **7** suggests that relief of steric strain is involved in the reductive cleavage of **1**.

We offer the rationalization shown in Scheme I as an ex-

Scheme I
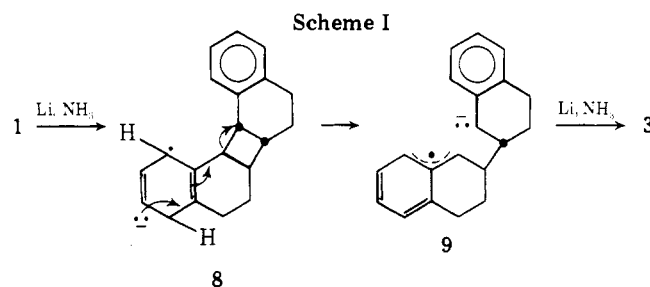
planation for the process and feel that while relief of steric strain is important, the availability of a benzylic position to stabilize the anion in structure **9** is an essential factor. Base-induced cleavage of **1** and **2** without the assistance of a reductive process is unlikely, since these hydrocarbons are stable to strong anhydrous base.[8b]

Recent reviews provide a few examples of carbon–carbon reductive cleavage.[2] The major structural features responsible for this effect are vicinal benzylic positions and/or relief of strain, as implied above. Whereas 1,2-diarylethanes appear to be stable to reduction,[9] tri- and tetraarylethanes are known to cleave.[10] If **10** is considered to be a diarylethane, it should
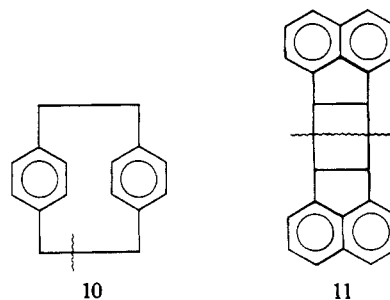
be stable. However, cleavage of the carbon–carbon bond as shown indicates that relief of steric strain must be essential.[11] Cleavage of the cyclobutane ring of **11** with sodium to the radical anion of acenaphthalene has been established by ESR studies.[12]

It is of interest that while hydrocarbon **7** is unaffected by the Li–NH₃ reaction, the diol **12**[13] is cleaved to tetralin in
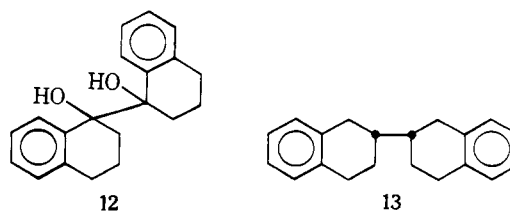
approximately 25% yield. However, the cleavage of **12** could result from a retro-pinacol reaction,[2b] and hence this may be an unfair comparison. Nevertheless, it serves as a good reminder that predictions of reductive cleavage must be made cautiously.

While the reductive cleavage described for **1** and **2** is useful in distinguishing head-to-head and head-to-tail dimers of the type shown by **1, 2, 5,** and **6,** it is also useful as a stereospecific synthesis of β,β'-linked hydrocarbon types illustrated by **3** and **4,** which are otherwise difficult to obtain as pure hydrocarbons. Since a single product was obtained in the preparation of **3,** we assume that the positions β to the aromatic rings of **1** are not involved. This permits the stereochemical assignment shown for **3,** mp 84–85 °C,[5] and hence suggests the meso configuration for hydrocarbon **13,** mp 118–119 °C.[14]

Experimental Section

Li–NH₃ Reductive Cleavage of *cis,anti,cis*-5,6,6a,-6b,7,8,12b,12c-Octahydrodibenzo[*a,i*]biphenylene (1) to 1,1′,-2,2′,3,3′,4,4′-Octahydro-2,2′-binaphthyl (3). To a solution of 2.0 g (7.2 × 10⁻³ mol) of **1,**[3] mp 71–72 °C, in 10 ml of dry ether and 50 ml of ammonia was added 0.11 g (1.57 × 10⁻² g-atom) of lithium in small pieces. After addition, the blue color persisted. After 1 h, the reaction was quenched with anhydrous ammonium chloride, ammonia was allowed to evaporate, and 200 ml of water was added to the residue. The reaction mixture was extracted (ether, 3 × 100 ml) and the organic layer was washed with 50-ml portions of 10% sulfuric acid, Claisen's alkali,[16] and water. The ether layer was dried (MgSO₄) and concentrated to give 1.95 g of a crystalline product, mp 73–78 °C. GC analysis[17a] of the product showed less than 2% of unreacted **1** and a major peak corresponding to **3.**[5b] Recrystallization of the crude product from isohexane gave 1.2 g (60% yield) of white needles, mp 84.5–85 °C. A second crop of 0.5 g of less pure material was obtained by concentration of the mother liquor. The total yield was 85%. The product had an identical ¹H NMR spectrum and undepressed melting point on mixing with a known sample of **3.**[5b]

Li–NH₃ Reductive Cleavage of 4bβ,4cα,9,9aα,9bβ,10-Hexahydrocyclobuta[1,2-*a*:4,3-*a′*]diindene (2) to 2,2′-Biindanyl (4). To a solution of 1.0 g (4.3 × 10⁻³ mol) of the photodimer **2,**[4] mp 110 °C, in 10 ml of ether and 50 ml of ammonia was added 0.65 g (9.3 × 10⁻³ g-atom) of lithium. The reaction and product isolation was carried out as described above to give 1.0 g of a solid. GC analysis[17b] of this solid showed a major peak and no unreacted **2.** Recrystallization of the product from acetone gave 0.8 g (80% yield) of white crystals of **4:** mp 165–167 °C (lit.[6a] mp 165–166.5 °C); ¹H NMR (CDCl₃) δ 7.10 (m, 8, ArH), 3.20–2.90 (m, 4, ArCH₂), 2.83–2.30 (m, 6, ArCH₂CH); mass spectrum (70 eV) *m/e* 234.

Hydrogenation of 1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-binaphthyl-1,1′-diol (12) to 1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-binaphthyl (7). A solution of 15 g (0.051 mol) of the pinacol **12**[13] in 500 ml of acetic acid and 1.5 g of 10% Pd/C was shaken in a Parr hydrogenation vessel under a 50-psig hydrogen atmosphere at 60–70 °C for 43 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude hydrogenation product was purified by chromatography on basic alumina using isohexane. The combined hydrocarbon fractions were distilled using a Kugelrohr apparatus at 160–170 °C (0.2 mm) to give 3.5 g (0.013 mol, 26% yield) of a clear, colorless oil:[8a,17c] ¹H NMR (CDCl₃) δ 7.31–6.86 (m, 8, ArH), 3.72–3.20 (m, 2, ArCH), 2.65 (t, 4, ArCH₂), *J* = 4 Hz, and 2.13–1.04 (m, 8, ArCH₂CH₂CH₂); mass spectrum (70 eV) *m/e* 262.

Reaction of 12 with Sodium–Ammonia. A solution of 0.8 g (0.0027 mol) of **12,** mp 185–189 °C (lit.[13] mp 191 °C), in 50 ml of THF was added to a solution of 50 ml of ammonia and 0.5 g (0.22 g-atom) of sodium. After 1 h, the reaction was quenched by addition of solid ammonium chloride and the products isolated as previously described. The resulting oil was analyzed by GC[17c] and shown to contain 25% tetralin.

Registry No.—**1,** 42182-84-3; **2,** 23358-17-0; **3,** 61158-73-4; **4,** 39060-95-2; **7,** 1154-13-8; **12,** 3073-53-8; tetralin, 119-64-2; lithium, 7439-93-2; ammonia, 7664-41-7; sodium, 7440-23-5.

References and Notes

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(2) (a) R. L. Augustine, Ed., "Reduction", Marcel Dekker, New York, N.Y., 1968; (b) A. J. Birch and G. Subba Rao, *Adv. Org. Chem.,* **8,** 1–65 (1972).
(3) J. E. Burks, Jr., D. van der Helm, T. K. Dobbs, L. L. Ansell, P. H. Ruehle, and E. J. Eisenbraun, *Acta Crystallogr.,* submitted.
(4) (a) W. Metzner and D. Windisch, *Justus Liebigs Ann. Chem.,* **730,** 111 (1970); (b) J. Bowyer and Q. N. Porter, *Aust. J. Chem.,* **19,** 1455 (1966).
(5) (a) L. Reggel, H. W. Sternberg, and I. Wender, *Nature (London),* **190,** 81 (1961); (b) E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, and W. P. Duncan, *J. Org. Chem.,* **35,** 1265 (1970).
(6) (a) W. Lüttke and J. Grussdorf, *Chem. Ber.,* **98,** 140 (1965); (b) F. Fichter and H. Stenzl, *Helv. Chim. Acta,* **22,** 425 (1939).
(7) (a) J. Dekker and T. G. Dekker, *J. S. Afr. Chem. Inst.,* **28,** 122 (1975); (b) Alternate synthesis, this laboratory.
(8) (a) Unpublished work, this laboratory. We assume to have a mixture of meso and *dl* isomers. (b) Hydrocarbons **1** and **2** were separately treated with potassium *tert*-butoxide in anhydrous dimethyl sulfoxide at room temperature for 2.5 h and recovered unchanged.
(9) C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.,* **56,** 1133 (1934).
(10) Reference 2a, p 106.
(11) J. L. Marshall and T. K. Folsom, *Tetrahedron Lett.,* 757 (1971).
(12) von F. Gerson and B. Weidmann, *Helv. Chim. Acta,* **49,** 1837 (1966).
(13) E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.,* 1104 (1935).
(14) (a) W. Hückel and M. Wartini, *Justus Liebigs Ann. Chem.,* **686,** 40 (1965); (b) R. C. Bansal, Ph.D. Thesis, Oklahoma State University, 1966; (c) P. Markov, D. Lasarov, and C. Ivanov, *Justus Liebigs Ann. Chem.,* **704,** 126 (1967).
(15) ¹H NMR spectra were obtained on a XL-100 Varian instrument. GC analyses for the hydrocarbons were obtained with a Hewlett-Packard Model 5750 apparatus fitted with a hydrogen-flame detector using helium as carrier gas. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and were uncorrected.
(16) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 153.
(17) (a) An 8 ft × 0.25 in. column of 80–100 mesh Chromosorb G coated with 7% UC W-98 at 230 °C was used; (b) ref 17a at 190 °C; (c) a 6 ft × 0.25 in. column of 80–100 mesh, AW-DMCS-treated Chromosorb G coated with 3.5% *N,N′*-bis(*p*-methoxybenzylidine)-α,α′-bitoluidine at 220 °C was used.


Reactions of Enones with the New Organocuprates, LiCu₂(CH₃)₃, Li₂Cu₃(CH₃)₅, and Li₂Cu(CH₃)₃

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It has been reported that a mixture of (CH₃)Li and LiCu(CH₃)₂ provides unusually stereoselective methylation of 4-*tert*-butylcyclohexanone compared to CH₃Li alone.[1] It was suggested that a highly reactive cuprate having the stoichiometry Li₂Cu(CH₃)₃ or Li₃Cu(CH₃)₄ is formed when CH₃Li and LiCu(CH₃)₂ are allowed to react and that reaction of these species with the ketone would explain the observed results. We have recently obtained direct evidence for the existence of LiCu₂(CH₃)₃ and Li₂Cu(CH₃)₃ in both dimethyl ether and tetrahydrofuran and indirect evidence for the species Li₂Cu₃(CH₃)₅ and Li₂Cu(CH₃)₃ in diethyl ether by low-temperature NMR.[2] All of the cuprates appear to be single species in solution except Li₂Cu(CH₃)₃ which has been shown to exist as an equilibrium mixture. Since LiCu(CH₃)₂ has proven to be an excellent conjugate methylating agent for α,β-unsaturated carbonyl compounds, it was considered to be important to evaluate these new cuprates as conjugate methylating agents.

$$\text{LiCu(CH}_3)_2 + \text{CH}_3\text{Li} \rightleftharpoons \text{Li}_2\text{Cu(CH}_3)_3 \qquad (1)$$
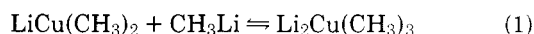
Six enones (I–VI) were chosen to react with LiCu(CH₃)₂, LiCu₂(CH₃)₃, and Li₂Cu(CH₃)₃ in THF and LiCu(CH₃)₂, Li₂Cu₃(CH₃)₅, and Li₂Cu(CH₃)₃ in Et₂O solvent. The results of these reactions are shown in Tables I and II. In THF solvent