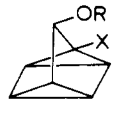
Communications to the Editor

Lithiation of Cyclopropylcarbinols

Sir:

Cyclopropanes, which do not contain activating substituents (R—C═O, -CN, -NC, -C≡CR), are metalated quite sluggishly even by potassium reagents.[1-3] We report herein that this behavior is changed if a C—OH group is appended to the cyclopropane ring. When the bridged cyclopropylcarbinols I-VII (R = X = H) were treated with isopropyllithium (2.5 equiv, ether-pentane (1:1), 24 h), D_2O quench gave the deuterated alcohols I-VII (R = H; X = D) in the yields shown in parentheses.



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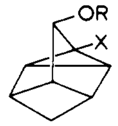

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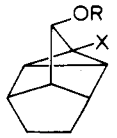

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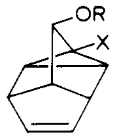

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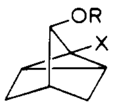

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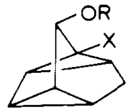

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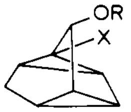

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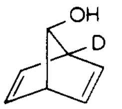
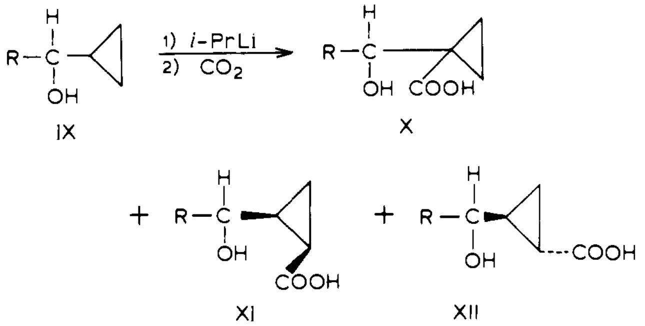


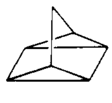
VIII

The position of deuterium was determined in the case of I (R = H; X = D) through conversion ([Rh(norbornadiene)Cl]$_2$, $CDCl_3$, 25 °C, 3 h) into 1-deuterio-7-norbornadienol (VIII) whose ^1H NMR spectrum could be analyzed unequivocally. Mass spectrometry of I (R = CH_3; X = D) indicated the ratio of d_1:d_2 to be ~5:1. The results suggest that initially the lithium derivatives I-VII (R = Li; X = Li) are formed. Treatment of I-VII (R = Li; X = Li) with 1,2-dibromoethane yielded the corresponding bromohydrins I-VII (R = H; X = Br; ~60%). Assignment of structure was possible in the cases of I (conversion into 1-bromo-7-norbornadienol), II (^1H NMR), and IV (comparison with authentic material[4]). With other electrophiles (CH_3I, CO_2, $ClCO_2Et$), I (R = Li; X = Li) was converted into the appropriate derivatives I (R, X, %): H, CH_3, 80; H, CO_2H, 20; CO_2Et, CO_2Et, 80.

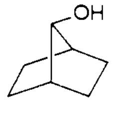
Open-chain cyclopropylcarbinols IX yielded three types of lithium derivatives (*i*-PrLi, pentane, 25 °C, 24 h). Carboxylation of the reaction mixtures gave mixtures of hydroxycarboxylic acids X-XII (~55%) which were methylated with diazomethane and separated by GLC of their methyl esters. The results are given in Table I.



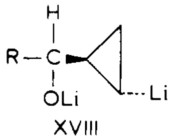
Quadricyclane (XIII), 7-norbornanol (XIV), and *n*-heptylcyclopropane could not be lithiated. It is also noted that in II (R = X = H) lithiation of the cyclobutane bridgehead does not compete with lithiation of the cyclopropane bridgehead. From this it is concluded that both C—H bonds of sufficiently high s character and a coordinating ligand (OLi) must be present at suitable positions of a molecule for lithiation to occur. In earlier work[9] we have shown that enhanced reactivity toward organolithium reagents was observed whenever the substrates used could yield the cyclic moieties XV and XVI.[10] Accordingly organolithiums of type XVI (X = OLi) are held responsible for the formation of XI and four-membered rings XVII (X = OLi)[10] are proposed to account for the reactivity of I-VII (R = X = H) and for the formation of X from IX.[11,12]



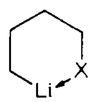
XIII



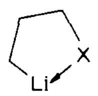
XIV



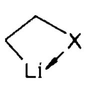
XVIII



XV



XVI



XVII

X = OLi, OR, NR_2, SR

Intramolecular coordination of lithium within a four-membered ring is established as a stabilizing factor[15] of aryllithium compounds, which promotes lithiation of arenes carrying a suitable donor group.[1,16] It has also been invoked to account for the stereochemical integrity of (*E*)-2-(alkoxy)-1-(arylthio)vinyllithium,[17] the stability of (Z)-2-ethoxyvinyllithium,[18] and the metalation of 3-methoxynortricyclene by alkylpotassium and alkylsodium reagents.[2] The mixtures of X and XI formed from IX show that XVI (X = OLi) is slightly preferred over XVII (X = OLi). This preference is enhanced by bulky substituents which lead to unfavorable eclipsing along the CC backbone of XVII. The formation of XII is ascribed to the organolithium XVIII.[10,19] To account for the activating effect of oxygen, we tentatively propose that

Table I. Proportions of Hydroxycarboxylic Acids Obtained from Cyclopropylcarbinols

R in IX	X	XI	XII
CH_3 (61)[a]	18[b]	73[c]	9[d]
c-C_3H_5 (84)[a]	21[e]	74[f]	5[e]
i-C_3H_7 (68)[a]		100[e]	
t-C_4H_9 (70)[a]		100[e]	

[a] Percentage of one deuterium atom incorporated into IX by quenching with D_2O (instead of carboxylation). [b] Structure proven by NMR and by conversion into known[5] 1-acetyl-1-carbomethoxycyclopropane. [c] Methyl ester thermally converted into 2-oxo-3-oxa-*exo*-4-methylbicyclo[3.1.0]hexane, prepared independently from dimethylsulfoxonium methylide and β-angelicalactone.[6,7] [d] Converted into known[8] *trans*-1-acetyl-2-carbomethoxycyclopropane. [e] Structure assigned by analogy of spectroscopic data with those of similar compounds. [f] Mixture of diastereomers yielding upon methylation and thermolysis a 93:7 mixture of *exo*- and *endo*-2-oxo-3-oxa-4-cyclopropylbicyclo[3.1.0]hexane.

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(in the heterogeneous reaction mixtures) aggregates of lithium cyclopropylcarboxide are involved in the formation of XVIII, one unit of the aggregate serving to anchor it to the isopropyllithium hexamer, another one providing a trans C—H bond for lithiation.

Finally, we note that synthons containing nucleophilic carbon are important tools of organic synthesis. The lithiation of cyclopropylcarbinols—themselves valuable synthons owing to the large number of ways in which they can be prepared and subjected to further transformation[20]—holds promise of providing a new kind of such species.[21-23]

References and Notes

(1) Cf. J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69,** 693 (1969).
(2) J. Hartmann and M. Schlosser, *Helv. Chim. Acta*, **59,** 453 (1976).
(3) In bicyclo[1.1.0]butanes C(1)–H is lithiated rather easily owing to increased s character: G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85,** 2022 (1963); G. Szeimies, F. Philipp, D. Baumgärtel, and J. Harnisch, *Tetrahedron Lett.*, 2135 (1977).
(4) G. W. Klumpp, W. G. J. Rietman, and J. J. Vrielink, *J. Am. Chem. Soc.*, **92,** 5266 (1970).
(5) T. Saegusa, I. Murase, and Y. Ito, *Bull. Chem. Soc. Jpn.*, **45,** 1884 (1972).
(6) Cf. T. Durst, *Adv. Org. Chem.*, **6,** 285 (1969).
(7) Y. Bahurel, F. Collonges, A. Menet, F. Pautet, A. Poncet, and G. Descotes, *Bull. Soc. Chim. Fr.*, 2209 (1971).
(8) T. Saegusa, K. Yonezawa, I. Murase, T. Konoike, S. Tomita, and Y. Ito, *J. Org. Chem.*, **38,** 2319 (1973).
(9) A. H. Veefkind, F. Bickelhaupt, and G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **88,** 1058 (1969); A. H. Veefkind, J. v. d. Schaaf, F. Bickelhaupt, and G. W. Klumpp, *Chem. Commun.*, 722 (1971); M. Kool and G. W. Klumpp, *Tetrahedron Lett.*, 1873 (1978).
(10) These are simplified representations. In the organolithium aggregates formed by the transformations, the donor group X may be coordinated to a single lithium; carbon, however, is involved in electron-deficient bonding to three lithium atoms. Cf. R. Zerger, W. Rhine, and G. Stucky, *J. Am. Chem. Soc.*, **96,** 6048 (1974).
(11) Retention of configuration in carboxylation of cyclopropyllithium reagents is known: D. E. Applequist and A. H. Paterson, *J. Am. Chem. Soc.*, **83,** 862 (1961); H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **86,** 3283 (1964).
(12) Species containing XVII (X = OLi) are β-lithium lithium alkoxides, which are known to eliminate lithium oxide[13] if not kept at −78 °C.[14] In the present cases, such elimination does not take place owing to the strain inherent in the olefins to be formed.
(13) J. K. Crandall and L.-H. C. Lin, *J. Am. Chem. Soc.*, **89,** 4526, 4527 (1967); J. J. Eisch and J. E. Galle, *ibid.*, **98,** 4646 (1976).
(14) J. Barluenga, F. J. Fananas, M. Yus, and G. Asensio, *Tetrahedron Lett.*, 2015 (1978).
(15) P. Beak and B. Siegel, *J. Am. Chem. Soc.*, **96,** 6803 (1974).
(16) Cf. H. Gilman and J. W. Morton, Jr., *Org. React.*, **8,** 258 (1954); D. A. Shirley, J. R. Johnson, Jr., and J. D. Hendrix, *J. Organomet. Chem.*, **11,** 209 (1968); H. O. House, T. M. Bare, and W. E. Hanners, *J. Org. Chem.*, **34,** 2209 (1969); A. C. Ranada, R. S. Mali, S. R. Bhide, and S. R. Mehta, *Synthesis*, 123 (1976); D. W. Slocum and C. A. Jennings, *J. Org. Chem.*, **41,** 3653 (1976).
(17) I. Vlattas, L. Della Vecchia, and A. Ong Lee, *J. Am. Chem. Soc.*, **98,** 2008 (1976).
(18) K. S. Y. Lau and M. Schlosser, *J. Org. Chem.*, **43,** 1595 (1978).
(19) That XII is not formed from an organolithium containing XVI (X = OLi) is suggested by the following observation: treatment of the lithium derivative of IX (R = *i*-Pr) with 1,2-dibromoethane yielded a single bromide, which upon bromine–lithium exchange (*i*-PrLi) followed by carboxylation gave XI (R = *i*-Pr) stereospecifically (see also ref 11).
(20) Cf. J. M. Conia, *Angew. Chem.*, **80,** 578 (1968); W. Kirmse, "Carbene, Carbenoide und Carbenanaloge", Verlag Chemie, Weinheim/Bergstr., Germany, 1969; S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem.*, **80,** 592 (1968); S. W. Staley, in "Selective Organic Transformations", Vol. II, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, London, Sydney, Toronto, 1972, p 309; J. M. Conia and M. J. Robson, *Angew. Chem.*, **87,** 505 (1975); E. Proksch and A. de Meijere, *ibid.*, **88,** 802 (1976).
(21) Concerning the use of cyclopropyllithiums as synthons, see J. P. Marino and L. J. Browne, *Tetrahedron Lett.*, 3245 (1976); P. A. Wender and M. P. Filosa, *J. Org. Chem.*, **41,** 3490 (1976).
(22) Part of this work has been carried out with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) via the Netherlands Foundation for Chemical Research (S.O.N.).
(23) NOTE ADDED IN PROOF. Referring to a recent paper (W. A. Beavers, S. E. Wilson, Bernard Gordon III, R. B. Bates, and A. R. Romano, *Tetrahedron Lett.*, 1675 (1979), J. Stapersma has suggested that cyclopropyllithiums, which on carboxylation yield X, may also undergo 1,2-hydrogen shift leading to XVIII.

G. W. Klumpp,* M. Kool, M. Schakel
R. F. Schmitz, C. Boutkan
Scheikundig Laboratorium der Vrije Universiteit
Amsterdam, The Netherlands

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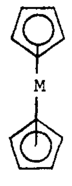
Bis(borabenzene)iron. Nucleophilic and Electrophilic Substitution in Borabenzene–Iron Complexes

Sir:

Metallocene (**1**) and bis(arene)-metal (**2**) systems are among the most familiar organometallic compounds. Bis(borabenzene)-transition metal derivatives (**3**) are formally similar, since the borabenzene moiety behaves as a 6-π-electron ligand.[1] Bis(1-substituted borabenzene)cobalt compounds were first prepared by Herberich in 1970 via a ring expansion of cobaltocene with boron halides.[2] Subsequently, it was found that the reaction of alkali metal salts of 1-substituted borabenzene anions with appropriate metal halides gave 1-substituted borabenzene–metal derivatives.[3,4] Although substantial data are now available for 1-substituted complexes,[5] the parent system $M(C_5BH_6)_2$ has not previously been prepared.[6] We now report on bis(borabenzene)iron (**4**) prepared by a novel route.



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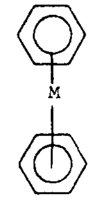

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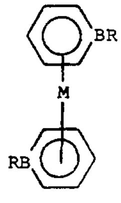
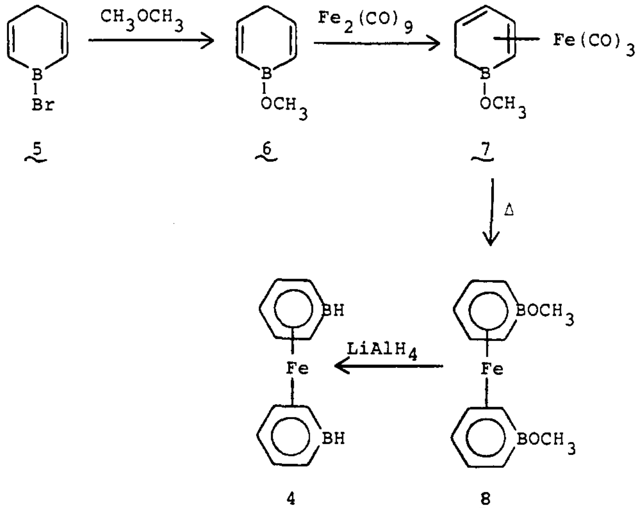


3



Addition of 1-bromo-1,4-dihydroborabenzene[3] (**5**) to excess dimethyl ether gave a nearly quantitative conversion into the corresponding methoxyborane **6**: ^{1}H NMR[7] δ 2.49 (m, 2 H), 2.86 (s, 3 H), 5.95 (dt, J = 12, 1.5 Hz, 2 H), 6.90 (br d, J = 12 Hz, 2 H); ^{11}B NMR δ 38.1; mass spectra m/e 108. Heating **6** to 100 °C for 12 h with an excess of $Fe_2(CO)_9$ gave the conjugated diene–$Fe(CO)_3$ complex **7** as a very air-sensitive yellow oil: ^{1}H NMR δ 0.72 (d, J = 17 Hz, exo H_6),[8] 1.20 (dd, J = 17, 6 Hz, endo H_6),[8] 1.94 (d, J = 9.5 Hz, H_2), 2.81 (dd, J = 7, 6 Hz, H_5), 3.25 (s, OCH_3), 4.75 (dd, J = 7, 5.5 Hz, H_4), 5.45 (dd, J = 9.5, 5.5 Hz, H_3); ^{11}B NMR δ 38.8; mass spectra m/e 248. In contrast to previously reported boradiene–metal complexes, the lack of any change in the ^{11}B chemical shift between **6** and **7** indicates there is no metal–boron bonding.[8,9] Heating **7** to 165 °C for 12 h gave bis(1-methoxyborabenzene)iron (**8**). Alternatively, **8** was obtained in higher yield directly from heating **6** with $Fe_2(CO)_9$ at 165 °C. Bis(1-methoxyborabenzene)iron (**8**) was obtained as a red oil: ^{1}H NMR δ 3.77 (s, OCH_3), 3.91 (d, J = 11 Hz, $H_{2,6}$), 4.38 (t, J = 7 Hz, H_4), 4.89 (dd, J = 7, 11 Hz, $H_{3,5}$); ^{11}B NMR δ 23.6; mass spectra m/e 270 (base peak, M^+ for $C_{12}H_{16}{}^{11}B_2{}^{56}Fe$).

The B–OCH_3 group undergoes facile nucleophilic dis-

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