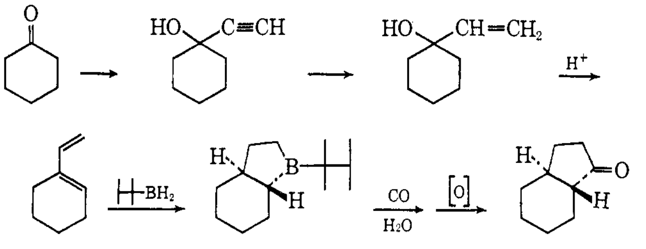
As far as we can ascertain, the yields are very high based on the amount of cyclic organoborane produced in the cyclic hydroboration. For example, we realized only a 46% yield of 3-methylcyclopentanone from isoprene. However, we have previously observed that conjugated dienes such as 1,3-butadiene and isoprene undergo considerable initial attack at an internal position.[4] This would lead to the formation of polymer rather than to the desired cyclic species. Indeed, distillation of the crude hydroboration mixture gave a yield of only 54% of distillate, identified as 1-thexyl-3-methylboracyclopentane (bp 55° (4 mm), n^{20}D 1.4429) from its analysis and infrared and pmr spectra. Carbonylation of the distilled cyclic species gave an 86% yield of 3-methylcyclopentanone based on the cyclic borane.

The results suggest that the ketones realized correspond to the structures of the cyclic organoboranes actually present in the reaction mixtures. However, one minor anomaly should be pointed out. The yield of 21% 2,5-dimethylcyclopentanone from the organoborane produced in the cyclic hydroboration of 1,5-hexadiene is considerably greater than the yield of 2,5-hexanediol obtained in the oxidation of the intermediate. Possibly this indicates some isomerization of the organoborane intermediate during the carbonylation stage. This discrepancy is under investigation.

Finally, to test the utility of this procedure for complex synthetic problems, we undertook to use it for the stereospecific synthesis of the thermodynamically unfavorable *trans*-1-hydrindanone[5] (III) by the following procedure.[6]



III

No difficulty was encountered in obtaining a 60% isolated yield of *trans*-1-hydrindanone, as follows. A 300-ml flask equipped with a septum inlet, a condenser, a stirring bar, and a mercury-sealed outlet was flushed with nitrogen. Into the flask was introduced 50 ml of dry THF, followed by the simultaneous slow addition at 20 to 25°,[7] over a period of 3 hr, of 28.2 ml of 1.77 *M* thexylborane[2] (50 mmoles) and 5.95 g (55 mmoles) of 1-vinylcyclohexene[6] in 25 ml of THF. After stirring at room temperature for 5 hr to complete the cyclization,[7] 1.8 ml (100 mmoles) of water was added, and the mixture was transferred into a 250-ml autoclave under nitrogen and carbonylated at 1000 psi[8] and 50°. Although absorption was complete in 1 hr, the reaction was allowed to proceed for 3 hr. The reaction mixture was transferred to a glass flask and oxidized in the usual manner with 20 ml of 3 *M* sodium acetate and 20 ml of 30% hydrogen peroxide; the temperature was maintained between 30 and 50°. The reaction mixture was maintained at 50° for 1 hr to complete the oxidation, cooled, and saturated with potassium carbonate, and the product was isolated. Distillation of a 45-mmole aliquot yielded 3.7 g (60%) of *trans*-1-hydrindanone, bp 40–43° (0.5 mm), n^{20}D 1.4782, oxime mp 145–146° (lit.[9] mp 146°).

It is evident that this procedure should be capable of wide ramification in synthesizing ring compounds, including the presence of functional substituents,[2] and in making possible the stereospecific construction of additional rings onto a basic framework. We continue to explore the potentialities of this new synthesis.

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Received August 3, 1967

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[4] G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

[5] H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 31 (1963).

[6] In applying this procedure our work was facilitated by a generous gift of 1-vinylcyclohexene, prepared as indicated, from C. A. Brown.

[7] For the other experiments in Table I a temperature of 0–5° was used, together with a much shorter reaction time after mixture of the reagents. In the present case the cyclization stage, resulting in the formation of the rigid bicyclic, is evidently slow, making the higher temperature and longer reaction time desirable.

[8] As was pointed out earlier[2] these thexyl derivatives react only sluggishly with carbon monoxide at atmospheric pressure.

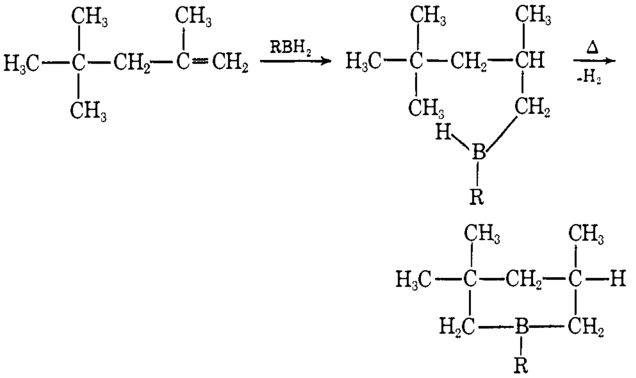
[9] W. Hückel, M. Sachs, J. Yantschulewitsch, and F. Nerdel, *Ann.* **518**, 155 (1935).

[10] Postdoctorate research associate on a grant supported by the National Institutes of Health (ROI-GM 10937).

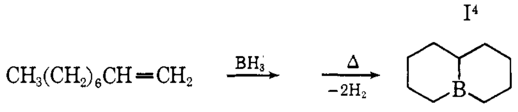
Carbonylation of Perhydro-9b-boraphenalene to Form Perhydro-9b-phenalenol. A New General Synthesis of Polycyclic Derivatives

Sir:

The remarkably easy addition of the boron–hydrogen bond to carbon–carbon double and triple bonds,[1] the less easy but still facile substitution of carbon–hydrogen bonds by boron–hydrogen bonds,[2] and the ready isomerization of organoboranes[3] all combine to give the organic chemist an unparalleled opportunity to utilize the unique characteristics of boron to bring together widely separated portions of a carbon structure into a more compact cyclic or polycyclic entity. Some representative examples follow.



I[4]



II[5]

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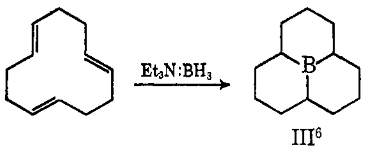
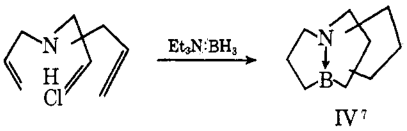
[1] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[2] R. Köster, *Angew. Chem. Intern. Ed. Engl.*, **3**, 174 (1964).

[3] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1433 (1966); **89**, 561 (1967).



III[6]

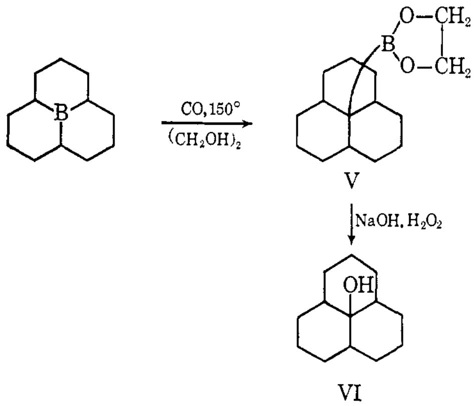


IV[7]

It is evident that if the boron atom in these "stitched together" structures could be replaced by carbon, we should have a major new approach to the synthesis of complex carbon structures.

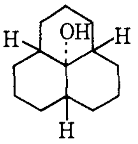
We selected perhydro-9b-boraphenalene (III) as a critical test of this possibility. In this molecule the boron atom is imbedded in the center of a relatively rigid, symmetrical circle of carbon atoms. We reasoned that if the carbonylation reaction could be made to operate here, there was little question but that the reaction should be generally applicable for the synthesis of relatively complex polycyclic structures.

Perhydro-9b-boraphenalene[6] proved to be inert to carbon monoxide at atmospheric pressure in the presence of ethylene glycol[8] even at 150°. On the other hand, carbonylation at 50° and 1000 psi[9] followed by heating for 1 hr at 150° to facilitate migration of the groups from boron to carbon[8] resulted in the formation of essentially a single product, identified as the ethylene glycol ester of the boronic acid V in a yield of 90%, mp 100–101° from pentane. Oxidation with alkaline hydrogen peroxide produced the corresponding tertiary alcohol, characterized as the hitherto unknown perhydro-9b-phenalenol (VI), in an over-all yield of 70%.



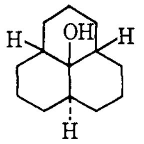
VI

The assignment of the perhydro-9b-phenalenol structure VI is based on the following evidence. (1) The product, mp 78–78.5° from pentane, was isomerically pure by capillary glpc. (2) It gave the correct analysis *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.41; H, 11.27. It formed a *p*-nitrobenzoate, mp 149–151°. (3) The molecular weight by mass spectrometry was 194. (4) Its pmr indicated that the substance is a tertiary alcohol with no straight-chain substituents or unsaturation (presence of a sharp peak at 1.2 ppm which disappeared upon shaking with D_2O and shifted upfield upon dilution, with absence of peaks for α hydrogens, methyl hydrogens, or olefinic hydrogens). (5) The presence of a hydroxyl group is also indicated by its infrared spectrum (absorptions at 3600 and 3450 cm^{-1} in CCl_4). (6) When VI was treated with 6 *M* sulfuric acid at room temperature, two olefins in a ratio of 70:30 were formed. Hydrogenation of the two olefins yielded a saturated hydrocarbon identical in all respects with a sample of all-*trans*-perhydrophenalene.[10]



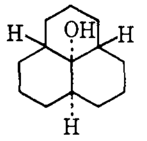
all-*trans*

VII



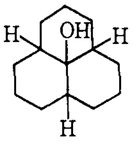
cis, cis, trans

VIII



cis, trans, trans

IX



all-*cis*

X

Of the four possible isomeric strucures, VII–X, we are inclined to assign the *cis,cis,trans* structure VIII to our product on the following evidence. In addition to the sharp peak for the hydroxylic hydrogen, the spectrum of VI revealed relatively broad, partially resolved peaks at 1.45 and 1.32 ppm, with much smaller shoulders centered at 2.0, 1.8, 1.6, and 1.1 ppm. It has been generally observed[11] for decalins, perhydroanthracenes, and their alcohols that those compounds which have *trans* ring fusions show essentially doublet-like spectra and those with *cis* ring fusions show essentially singlet-like spectra. The pmr data reported by Mousseron, *et al.*,[12] also point to the same conclusion. The pmr spectrum of *trans*-9-decalol shows two peaks at 1.45 and 1.25 ppm and that of *cis*-9-decalol shows a single peak at 1.38 ppm in addition to peaks for the hydroxylic hydrogen. The pmr data thus support either the all-*trans* structure VII or the *cis,cis,trans* structure VIII, excluding the all-*cis* structure X. The pmr spectrum of the *p*-nitrobenzoate of VI shows a well-separated doublet-like peak for β hydrogens centered at 2.87 ppm. Its area, however, amounts only to two hydrogens, arguing against the all-*trans* structure VII. The third β hydrogen, whose peak appears at around 2.1 ppm as a broad shoulder, must have a considerably different environment. The fact that the two hydrogens exhibit the larger shift favors the *cis,cis,trans* structure VIII[13,14] over the *cis,trans,trans* structure IX.

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(4) H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1443 (1966).

(5) R. Köster and G. Rotermund, *Angew. Chem.*, **72**, 563 (1960).

(6) G. W. Rotermund and R. Köster, *Ann.*, **686**, 153 (1965). We found it necessary to heat our product for 3–6 hr at 200° in order to realize a material with properties ($n^{35}\text{D}$ 1.5095) corresponding to those described for the more stable, all-*cis* isomer ($n^{35}\text{D}$ 1.5100).

(7) N. N. Greenwood, J. H. Morris, and J. C. Wright, *J. Chem. Soc.*, 4753 (1964).

(8) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 2737 (1967).

(9) H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967).

(10) A. Schneider, R. W. Warren, and E. J. Janoski, *ibid.*, **86**, 5365 (1964). We are indebted to Dr. Schneider for an authentic sample of all-*trans*-perhydrophenalene.

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 399; J. I. Musher and R. E. Richards, *Proc. Chem. Soc.*, 230 (1958); R. L. Clarke, *J. Am. Chem. Soc.*, **83**, 965 (1961).

(12) M. Mousseron, M. Mousseron-Canet, G. Philippe, and J. Wylde, *Compt. Rend.*, **256**, 51 (1963). The pmr spectra of *cis*- and *trans*-9-decalols were kindly provided by Professor Mousseron.

(13) The accumulated evidence that the carbonylation reaction proceeds with retention raises a question about Köster's proposed assignment of the all-*cis* configuration to the borane III. This is under reexamination.

(14) Dr. M. G. B. Drew of the University of California, Berkeley, has informed us that the X-ray analysis of the ethylene glycol ester of the boronic acid V indicates that it is the *cis,cis,trans* isomer.

Thus the results support the conclusion that the carbonylation of perhydro-9b-boraphenalene proceeds cleanly to product perhydro-9b-phenalenol. This represents the first member of a new class of derivatives, characterized by having the central carbon atom carrying a functional group supported by three rings with common sides, which we propose to call "tercyclanols,"[15] etc. Even more important, this development establishes the practicality of this new approach to the synthesis of complex polycyclic derivatives. Certainly the simple formation of three carbon–carbon bonds in a single operation offers major promise for the synthesis of new, interesting structures. We continue to explore the potentialities of this new synthesis.

[15] We are exploring the chemistry of these unusual derivatives (work in progress with W. C. Dickason).

[16] Postdoctorate research associate on a grant supported by the National Institutes of Health (ROI-GM 10937).

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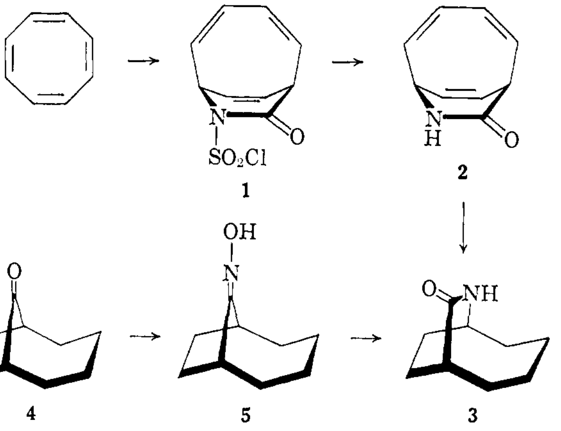
A Synthesis of the Azabullvalene System[1]

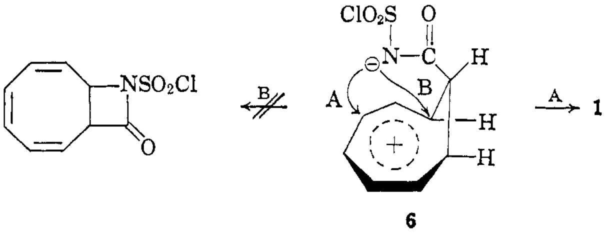
Sir:

Characterization of molecules with fluctuating bonds has advanced rapidly in recent years due chiefly to the capability of nmr spectroscopy to study fast reactions which produce no net chemical change.[2] A unique member of this class of molecules is bullvalene wherein fast and reversible valence isomerization results in complete scrambling of all the carbon atoms (1,209,600 interconvertible permutations).[3,4] In this communication, we wish to describe an exceptionally facile synthetic entry into the azabullvalene (azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene) system. The subsequent report[5] deals with the intriguing temperature-dependent nmr spectrum of a monomethoxy derivative.

First, slow addition of chlorosulfonyl isocyanate to cyclooctatetraene[6] in the absence of solvent at 50° led in 73% yield to an N-(chlorosulfonyl) lactam (**1**), mp 85–86.5°.[7,8] Reduction of **1** proceeded smoothly (98% yield) with thiophenol and pyridine in acetone at 0°[9] with loss of the chlorosulfonyl group to produce C_9H_9NO (**2**), mp 139–140°.[7] The structure of this lactam (**2**) was deduced from its spectral parameters[10] [$\nu_{\max}^{\mathrm{CHCl_3}}$ 1685 cm^{-1}, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 266 mμ (ϵ 3100), very little change upon addition of acid, $\delta_{\max}^{\mathrm{CDCl_3}}$ 3.63 (multiplet, 1 H, >CHC(=O)–), 4.07 (multiplet, 1 H, >CHNH–), 5.93 (multiplet, 6 H, vinyl protons), and 8.07 (broad singlet, 1 H, >NH)[11]] and by its catalytic reduction with the absorption of six atoms of hydrogen to **3**, mp 157°.[7,12] Independent synthesis of **3** was effected from the known bicyclo[4.2.1]nonan-9-one (**4**).[13] Oximation of the carbonyl group and subsequent Beckmann rearrangement of the resulting oxime **5** produced **3** in very low yield as the sole characterizable product.



With the secure establishment of structure **2** comes the realization that the formation of **1** represents a unique example of 1,4 cycloaddition to cyclooctatetraene.[14] Likewise, it appears to be the first example of conjugate addition for the chlorosulfonyl isocyanate reagent.[15] A possible mechanistic rationale for the



6

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[1] Unsaturated Heterocyclic Systems. XXXII. For paper XXXI, see L. A. Paquette and D. E. Kuhla, *Tetrahedron Letters*, in press.

[2] For a recent review, consult G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem. Intern. Ed., Engl.*, **4**, 752 (1965).

[3] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[4] G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

[5] L. A. Paquette, T. J. Barton, and E. B. Whipple, *J. Am. Chem. Soc.*, **89**, 5481 (1967).

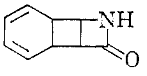
[6] We wish to thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

[7] Satisfactory elemental analyses were obtained for all new compounds.

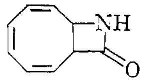
[8] On one occasion the chlorosulfonyl isocyanate–cyclooctatetraene mixture exploded violently ~1 hr after the completion of addition. Due to the approximate time of the explosion (3 AM), no witnesses were present; however, the extensive distribution of broken glass and black tar in the laboratory suggests that proper safety precautions should be enforced in the execution of this experiment.

[9] R. Graf, *Ann.*, **661**, 111 (1963).

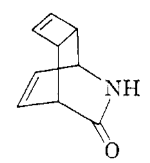
[10] These data effectively removed the following logical alternative structures from consideration.



i



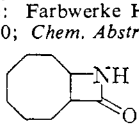
ii



iii

[11] A satisfying nmr parallel is found in the spectra of the 2-pyridone photodimers: L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, **85**, 765 (1963).

[12] The possible formation of ii under these conditions was further denied by the independent synthesis of iv (mp 76°) from chlorosulfonyl isocyanate and cyclooctene: Farbwerke Hoechst A.-G., Netherlands Patent Application 6,504,300; *Chem. Abstr.*, **64**, 8135 (1966).



iv

[13] C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960). We are indebted to Professor Gutsche for a generous sample of ketone **4**.

[14] To our knowledge, only four examples (all radical in nature) of 1,4 addition to cyclooctatetraene are known: α-cyanoisopropyl radicals, J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963); difluoramino radicals, T. S. Cantrell, *J. Org. Chem.*, **32**, 911 (1967); cyanonitrene, A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965); dinitrogen tetroxide (as ·NO$_2$), H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *ibid.*, **89**, 3005 (1967).

[15] The addition of chlorosulfonyl isocyanate to derivatives of 1,3-butadiene reportedly results in open-chain amide formation: H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 1875 (1963).