Acknowledgment. This investigation was supported by Eli Lilly and Co.

121 (1971); U. Weiss, W. B. Whalley, and I. L. Karle, *ibid.*, 16 (1962). and references therein.

(11) Subtle differences of energy content of the two dienes **4** are noted also from a study of equilibration of their nuclear double bonds [E. Wenkert and Z. Kumazawa, *ibid.*, 140 (1968)]. While **4a** remained unfazed, acid-induced isomerization of **4b** led to an equilibrium mixture of **2a**, **4b**, and sandaracopimaradiene.

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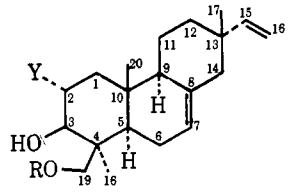
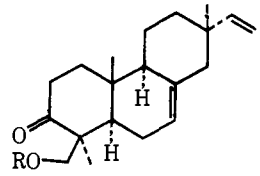
Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. XI. Biosynthesis of the Virescenosides[1]

Sir:

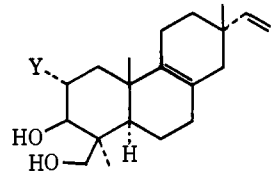
Structure analysis of the metabolites of the mushroom *Oospora Virescens* (Link) Wallr. has shown them to be diterpenic glycosides and the first altrose derivatives in nature.[2] Each metabolite contains one of three isopimaradienic aglycone units [*e.g.*, the virescenosides A, B, and C (**1c**, **1d**, and **2b**, respectively)], the biosynthesis of two of which (**1a** and **1b**) now has been uncovered. This study constitutes the first analysis of terpene biosynthesis by cmr spectroscopy.[3]



1a, R = H; Y = OH
b, R = Y = H
c, R = β-D-altropyranosyl; Y = OH
d, R = β-D-altropyranosyl; Y = H



2a, R = H
b, R = β-D-altropyranosyl



3a, Y = OH
b, Y = H

(1) For the preceding paper see E. Wenkert and B. L. Buckwalter, *J. Amer. Chem. Soc.*, **94**, 4367 (1972).

(2) N. Cagnoli-Bellavita, P. Ceccherelli, M. Ribaldi, Z. Baskevitch, and J. Polonsky, *Gazz. Chim. Ital.*, **97**, 1344, 1625 (1967); J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, and P. Ceccherelli, *Chem. Commun.*, 1404 (1968); J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, and P. Ceccherelli, *Bull. Soc. Chim. Fr.*, 1912 (1970); N. Cagnoli-Bellavita, P. Ceccherelli, M. Ribaldi, J. Polonsky, and Z. Baskevitch, *Gazz. Chim. Ital.*, **99**, 1354 (1969); N. Cagnoli-Bellavita, P. Ceccherelli, R. Mariani, J. Polonsky, and Z. Basekvitch, *Eur. J. Biochem.*, **15**, 356 (1970).

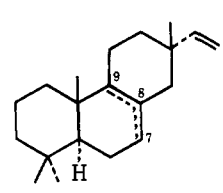
(3) For previous cmr-aided biosynthesis studies see M. Tanabe, H. Seto, and L. F. Johnson, *J. Amer. Chem. Soc.*, **92**, 2157 (1970); M. Tanabe, T. Hamasaki, H. Seto, and L. F. Johnson, *Chem. Commun.*, 1539 (1970); M. Tanabe, T. Hamasaki, D. Thomas, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 273 (1971); A. G. McInnes, D. G. Smith, L. C. Vining, and L. F. Johnson, *Chem. Commun.*, 325 (1971); R. Neuss, C. H. Nash, P. A. Lembe, and J. B. Grutzner, *J. Amer. Chem. Soc.*, **93**, 2337 (1971); R. J. Cushley, D. R. Anderson, S. R. Lipsky, R. J. Sykes, and H. H. Wasserman, *ibid.*, **93**, 6284 (1971). For previous studies of the biosynthesis of diterpenes by other means see B. E. Cross, *Progr. Phytochem.*, **1**, 195 (1968); J. R. Hanson, "The Tetracyclic Diterpenes," Pergamon Press, New York, N. Y., 1968, Chapter 8.

Table I. Cmr Chemical Shifts[a]

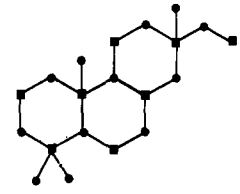
	1a	1b	2a	3a	3b
C-1	43.3	38.0	36.8[b]	42.6	35.4
C-2	69.1	28.0	35.5[b]	69.6	29.2
C-3	85.8	81.3	217.6	85.4	81.0
C-4	43.3	42.1	52.9	43.2	43.0
C-5	51.8[b]	51.4[b]	53.3[c]	51.9	52.1
C-6	23.6	23.2	24.2	21.6	21.6
C-7	121.8	121.7	121.7	32.8	33.1
C-8	135.9	136.0	136.2	125.0	125.1
C-9	52.5[b]	52.1[b]	50.8[c]	134.9	136.7
C-10	37.4[c]	35.2	35.5	38.4	37.4
C-11	21.2	20.6	21.1	19.6	19.1
C-12	36.7	36.3	36.5	35.0	34.9
C-13	37.0[c]	37.0	37.2	35.3	35.1
C-14	46.4	46.1	46.3	42.0	42.0
C-15	150.6	150.6	150.3	146.1	146.2
C-16	110.2	109.7	109.9	111.3	111.1
C-17	22.2	21.7	21.9	28.1	28.3
C-18	24.0	23.0	22.5	23.3	22.9
C-19	66.0	64.8	66.4	65.5	64.7
C-20	17.8	16.4	16.0	21.6	20.6

[a] Chloroform spectra taken at 15.077 MHz on a Fourier transform spectrometer; chemical shifts in parts per million downfield from TMS; $\delta^{TMS} = \delta^{CHCl_3} + 77.6$ ppm. [b,c] Values within any vertical column may be reversed.

The ^{13}C natural abundance nmr spectra of the aglycone alcohols **1a**, **1b**, and **2a** and their double bond isomers **3a** and **3b**, obtained by acid hydrolysis of the glycosides,[2] were recorded and their chemical shifts collated (Table I). Assignment of the δ values was based on chemical-shift theory,[4] the cmr data on the models isopimaradiene (**4a**) and $\Delta^{8(9)}$-isopimaradiene (**4b**)[1] and chemical-shift changes expected on introduction of hydroxy and keto groups into cyclic hydrocarbon skeletons.[5]



4a, $\Delta^{7(8)}$
b, $\Delta^{8(9)}$



5a, ■[1-^{13}C]acetate
b, ●[2-^{13}C]acetate

Addition of sodium [1-^{13}C]acetate to the mushroom culture medium, isolation of virescenoside A (**1c**), hydrolysis to isovirescenol A (**3a**), and inspection of the cmr spectrum of the latter revealed strong signal enhancement of the carbons depicted in **5a**. Similar treatment of the culture with sodium [2-^{13}C]acetate, isolation of virescenosides A (**1c**) and B (**1d**), conversion into isovirescenols A (**3a**) and B (**3b**), and perusal of the cmr spectra of the ^{13}C-enriched alcohols showed intense signal enlargement of the carbons portrayed in **5b**.[6] These results fit the present theory of terpene biosynthesis.[7]

(4) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965); E. F. Mooney and P. H. Winson, *Annu. Rev. Nucl. Magn. Resonance Spectrosc.*, **2**, 153 (1969).

(5) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970); F. J. Weigert and J. D. Roberts, *ibid.*, **92**, 1347 (1970).

(6) Quantitative data on the ^{13}C incorporation will be reported in connection with a parallel ^{14}C incorporation study (J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, and P. Ceccherelli, unpublished observations).

(7) H. J. Nicholas in "Biogenesis of Natural Compounds," P. Bernfeld, Ed., Pergamon Press, New York, N. Y., 1967.

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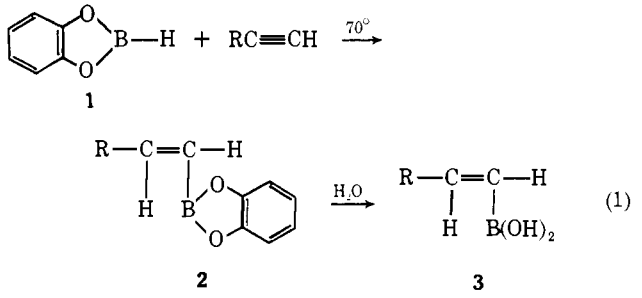
Catecholborane (1,3,2-Benzodioxaborole) as a New, General Monohydroboration Reagent for Alkynes. A Convenient Synthesis of Alkeneboronic Esters and Acids from Alkynes *via* Hydroboration

Sir:

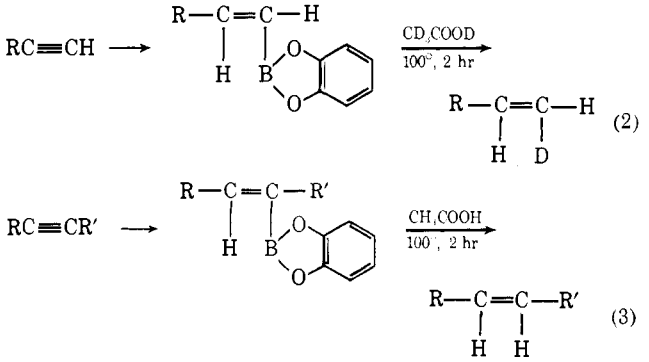
1,3,2-Benzodioxaborole (**1**), now conveniently available[1] through the reaction of catechol with borane in tetrahydrofuran (THF), reacts rapidly at 70° with alkynes to give stereospecific and regioselective monohydroboration products, the 2-alkenyl-1,3,2-benzodioxaboroles (**2**), in nearly quantitative yields. The esters **2** are readily hydrolyzed to the corresponding alkeneboronic acids (**3**) (eq 1). The ready protonolysis



(1)

1 **2** **3**

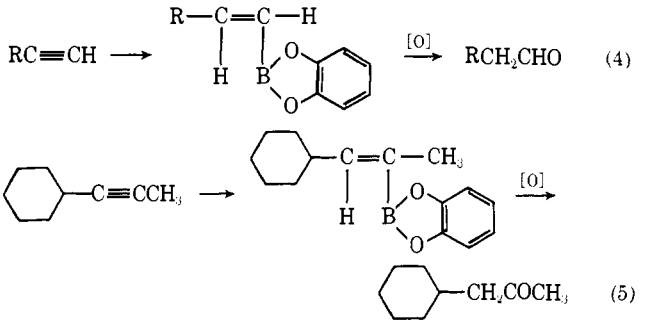
or deuterolysis of 2-alkenyl-1,3,2-benzodioxaboroles provides a new procedure for the conversion of the alkynes into the corresponding cis olefins *via* hydroboration (eq 2 and 3). Finally, oxidation of these



(2)

(3)

derivatives **2** provides the corresponding aldehydes or ketones (eq 4 and 5).

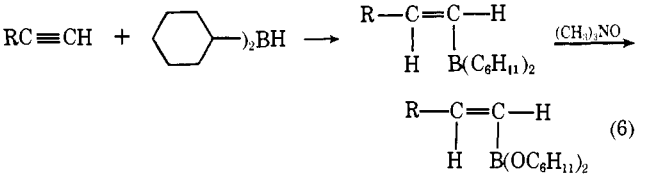


(4)

(5)

This novel development, therefore, provides a facile, clean, and highly convenient synthesis of the alkeneboronic esters and acids, cis olefins, and aldehydes and ketones from the corresponding alkynes *via* hydroboration.[2]

Recent investigations have led to the discovery of several new reactions which reveal the increasing importance of alkenylboranes[3] and alkeneboronic esters and acids[4] in organic synthesis. The alkenylboranes are available *via* the treatment of alkynes with borane[2] and its alkyl derivatives.[3] A convenient, general procedure for the synthesis of alkeneboronic acids and esters, however, is presently not available. Organometallic reagents, for example, have been treated with organic borates to give simple, functionally unsubstituted alkeneboronic acids and esters.[4,5] A two-step procedure involving the hydroboration of alkynes with dicyclohexylborane followed by the selective oxidation of the resulting alkenyldialkylborane has been developed by Zweifel, *et al.*[6] (eq 6). The hydroboration of alkynes



(6)

with a dialkoxyborane, such as 4,4,6-trimethyl-1,3,2-dioxaborinane,[7] or with an alkylazaborane, such as 1-alkyl-1,2-azaborolidine,[8] has also been studied recently. These reagents, however, are poor hydroboration reagents[9] and the reactions are slow even at elevated temperatures.

(1) H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, **93**, 1816 (1971).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(3) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Amer. Chem. Soc.*, **93**, 3395 (1971), and references cited therein.

(4) D. S. Matteson, *Accounts Chem. Res.*, **3**, 186 (1970); D. S. Matteson, *Progr. Boron Chem.*, **3**, 117 (1970).

(5) G. D. Schaumberg and S. Donovan, *J. Organometal. Chem.*, **20**, 261 (1969); W. G. Woods, I. S. Bengelsdorf, and P. L. Hunter, *J. Org. Chem.*, **31**, 2766 (1966); B. M. Mikhailov, Yu. N. Bubnov, and S. N. Korobeinikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2466 (1969); D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron*, **25**, 1557 (1969).

(6) G. Zweifel, personal communication, 1970.

(7) W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966), and references cited therein; see also, R. H. Fish, *ibid.*, **90**, 4435 (1968).

(8) V. A. Dorokhov, O. G. Boldyreva, and B. M. Mikhailov, *Zh. Obshch. Khim.*, **40**, 1528 (1970).

(9) The hydroboration of 1-heptyne with 4,4,6-trimethyl-1,3,2-dioxaborinane, for example, proceeded at 110° for 2 days followed by 1 day at 210° to give, after distillation, 69% yield of the desired product.[7] The hydroboration of alkynes with 1-alkyl-1,2-azaborolidines proceeded at 130–150° to give the desired alkenylborolidines in unspecified yields.[8]