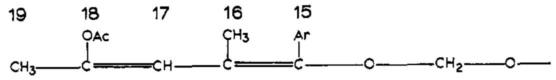
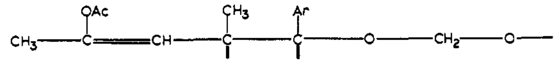
varone,[2] VII and VIII (b_{VII} and b_{VIII}). However, these same protons occur, respectively, in the aliphatic methyl region and as an AB quartet[6] in the 100-MHz spectra of streptovaricins A and C, and of V and VI as well, indicating introduction of a C-15,C-16 double bond in the periodate oxidation. Similar evidence is provided by the shift of the C-17 olefinic proton from the unconjugated to the conjugated region after oxidation.



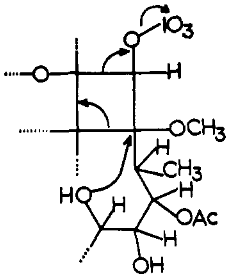
	19	18	17	16	15	
b_{II} τ	7.89sb	7.86s	3.48q	7.98s		4.2-4.9mb
J,Hz			1.5			
b_{VII}			3.34	7.98s		4.1-4.9mb
b_{VIII}	7.90		3.12sb	7.96s		4.2-5.0mb



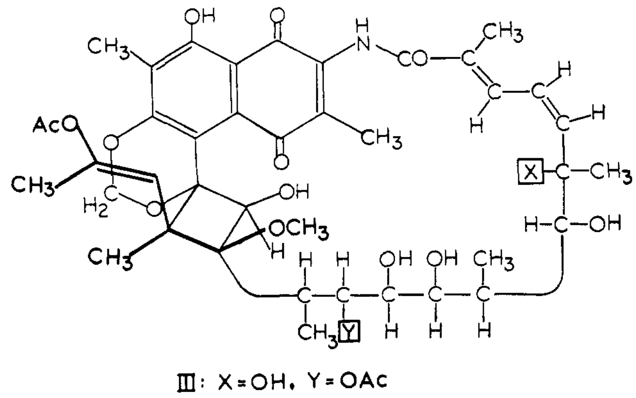
	19	18	17	16	15	
b_{III} τ	7.75s		4.41sb	8.83s		4.26d, 4.80d
J,Hz						4.3
b_{IV}	7.81s		4.37	8.87s		4.22d, 4.86d
b_{V}	7.90s		4.46sb	8.88s		4.22d, 4.88d 4.3
b_{VI}	7.74s		4.44sb	8.84s		4.20d, 4.85d 4.3

Thus, the linkage of C-13 and C-14 to streptovarone must be at C-15 and C-16, *i.e.*, in a cyclobutanol ring. Biosynthetic considerations (acetate–propionate pathway) suggest a C-14,C-15 linkage.

Oxidation of the substituted cyclobutanol unit then accounts for the uptake of the second mole of periodate in III and of the single mole in IV and V. Although periodate oxidation of an alcohol is unusual, it can be rationalized by the mechanism shown.



The structure of streptovaricin A is then assigned as III and that of streptovaricin C as IV. This represents the second identification of an *ansa* macrolide in nature, the first being rifamycin B, whose structure is related.[8]



III: X = OH, Y = OAc

IV: X = H, Y = OH

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[9] Holder of Union Carbide and Standard Oil of California Fellowships, and of Koppers and U. S. Rubber Summer Fellowships.

[10] Du Pont Teaching Fellow, National Science Foundation Summer Fellow.

Kenneth L. Rinehart, Jr., Hari H. Mathur
Kazuya Sasaki, Preston K. Martin,[9] Charles E. Coverdale[10]
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois 61801

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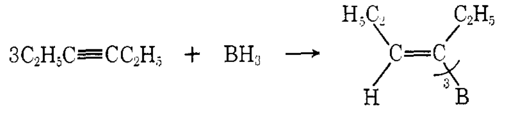
A Stereoselective Synthesis of Conjugated Dienes from Alkynes *via* the Hydroboration–Iodination Reaction[1]

Sir:

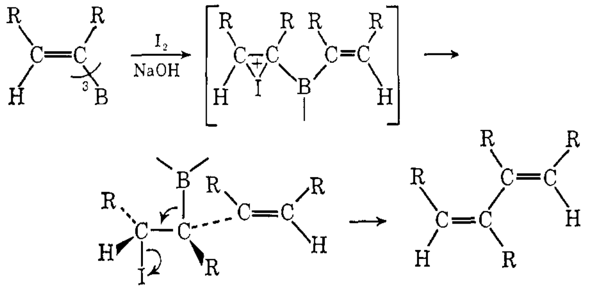
Recently we reported that the addition of iodine to vinyldialkylboranes in tetrahydrofuran solvent results in the migration of one alkyl group from boron to the adjacent carbon atom to afford isomerically pure *cis* olefins.[2] In the course of a study to establish the migratory aptitudes of various groups, and to determine whether the migrating group retains its configuration in the rearrangement step, we have now investigated the iodination of di- and trivinylboranes.

The hydroboration of disubstituted alkynes with borane in a 3:1 ratio in tetrahydrofuran solvent gives the corresponding trivinylboranes. Thus, 3-hexyne is converted by this procedure into tris(*cis*-3-hex-3-enyl)borane in excellent yield[3] (eq 1). Addition



(1)

of iodine and sodium hydroxide to the tetrahydrofuran solution of this vinylborane gives a 68% yield of *cis*,-*trans*-4,5-diethyl-3,5-octadiene. The formation of the *cis,trans*-diene may be rationalized in terms of an initial addition of iodine to the double bond followed by the subsequent migration of a vinyl group from boron to the adjacent carbon atom to give the β-iodoorganoborane (eq 2). It has been suggested that



(2)

the migration of an alkyl group, which results from the iodination of a dialkylvinylborane, proceeds with inversion at the migration terminus, and that the

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[1] This research was supported by National Science Grant No. GP-6633.

[2] G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 3652, (1967).

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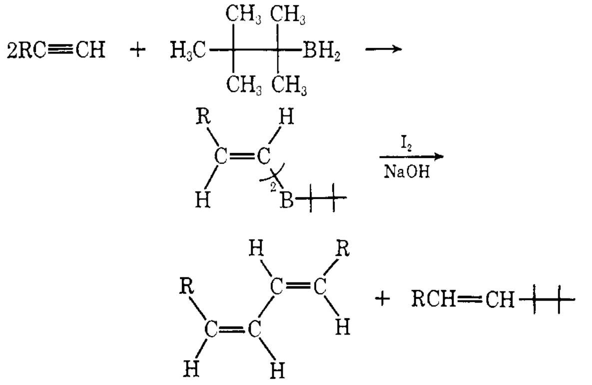
Table I. Synthesis of Conjugated Dienes from Alkynes

Vinylborane or vinylalane from	Diene[c]	Isomeric purity, %[d]	Isolated yield, %
2-Butyne + RBH_2[a]	*cis,trans*-3,4-Dimethyl-2,4-hexadiene	99	49
2-Butyne + R_2AlH[b]	*cis,cis*-3,4-Dimethyl-2,4-hexadiene	100	79
3-Hexyne + BH_3	*cis,trans*-4,5-Diethyl-3,5-octadiene	100	68[e]
3-Hexyne + RBH_2[a]	*cis,trans*-4,5-Diethyl-3,5-octadiene	100	69
3-Hexyne + R_2AlH[b]	*cis,cis*-4,5-Diethyl-3,5-octadiene	99	78
1-Hexyne + RBH_2[a]	*cis,trans*-5,7-Dodecadiene	98	65
Cyclohexylacetylene + RBH_2[a]	*cis,trans*-1,4-Dicyclohexyl-1,3-butadiene	96	64

[a] RBH_2 = thexylborane. [b] R_2AlH = diisobutylaluminum hydride. [c] The stereochemical assignments for the dienes are based on ir, uv' and nmr data. [d] Determined by glpc before distillation. [e] Based on the production of 1 mol of diene for 1 mol of trivinylborane.

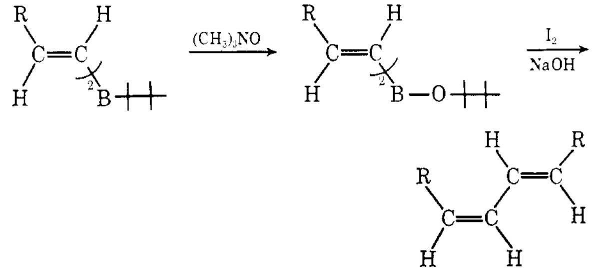
deboronoiodination occurs in a *trans* manner.[2] Provided that the migration and elimination reactions of the trivinylboranes exhibit the same stereoselectivity, the vinyl group must retain its configuration in the rearrangement step.

The hydroboration of 1-alkynes, such as 1-hexyne, with borane does not proceed to the trivinylborane stage, but results predominantly in the formation of 1,1-diboroalkanes.[3,4] However, 1-hexyne reacts with thexylborane (2,3-dimethyl-2-butylborane) to give the corresponding divinylthexylborane.[5] Unfortunately, addition of iodine and sodium hydroxide to this divinylborane results in the migration of both the vinyl and the thexyl moieties to give *cis,trans*-5,7-dodecadiene and thexyl olefin in a 52:48 ratio[6] (eq 3). Likewise, the divinylborane derived from the hydroboration of 3-hexyne also yields, after addition of iodine and sodium hydroxide, a mixture of the *cis,trans*-diene (73%) and the corresponding thexyl olefin (27%).



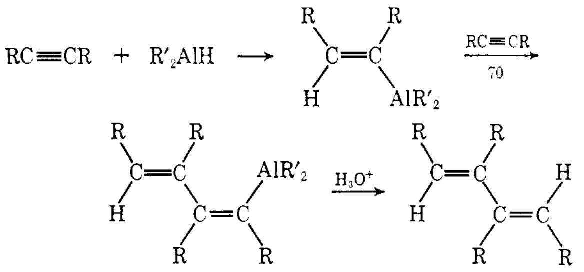
(3)

In exploring possible ways to increase the alkyne utilization in the diene formation, we have now found that treatment with trimethylamine oxide[7] of divinylthexylboranes derived from either terminal or disubstituted alkynes results in the selective oxidation of the thexyl moiety to afford the corresponding divinylborinate derivatives (eq 4). In the presence of iodine and sodium hydroxide, these intermediates rearrange to give *cis,trans*-1,3-butadiene derivatives. Thus, hydroboration of 1-hexyne with thexylborane followed by successive treatments of the divinylthexylborane with trimethylamine oxide and iodine gives a 65% isolated yield of *cis,trans*-5,7-dodecadiene. In this reaction all of the alkyne is utilized for diene formation. Similarly, by applying the same sequence of reactions to 3-hexyne, a 69% yield of *cis,trans*-4,5-diethyl-3,5-octadiene is obtained. The experimental results are summarized in Table I.



(4)

It is also of interest to note here that a convenient synthesis of *cis,cis*-dienes has previously been achieved *via* the reaction of disubstituted alkynes with diisobutylaluminum hydride in a 2:1 ratio followed by hydrolysis of the intermediate dienylalanes.[8] Several results using this procedure which have been obtained in the present work are given in Table I.



(5)

The simplicity of the present procedure for converting alkynes into *cis,trans*-1,3-dienes is illustrated by the following example.

A solution of 1-hexyne (8.2 g, 0.10 mol) in tetrahydrofuran (20 ml) was placed in a 200-ml flask equipped with a thermometer, a pressure-equalizing funnel, and a magnetic stirrer. Hydroboration was achieved at 0° by the dropwise addition of 37.3 ml of a solution of thexylborane (1.34 *M*) in tetrahydrofuran. The solution was then stirred for an additional hour at 0–5°. To the vinylborane solution obtained was added 3.8 g (50 mmol) of solid trimethylamine oxide at a rate such that the temperature remained between 0 and 5°. After being stirred for an additional hour at this temperature the resulting solution was treated, while maintaining the temperature between 0 and 5°, with 50 ml of 3 *N* sodium hydroxide followed by the dropwise addition of a solution of iodine (12.7 g,

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(4) G. Zweifel and H. Arzoumanian, *J. Amer. Chem. Soc.*, **89**, 291 (1967).

(5) G. Zweifel and H. C. Brown, *ibid.*, **85**, 2066 (1963).

(6) It is noteworthy that, in contrast to the iodination reaction, the thexyl group exhibits a low aptitude for migration from boron to carbon in the carbonylation of thexyldialkylboranes: H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967).

(7) R. Köster and Y. Morita, *Angew. Chem. Int. Ed. Engl.*, **5**, 580 (1966).

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50 mmol) in tetrahydrofuran (30 ml). Any excess iodine was then decomposed by adding a small amount of aqueous sodium thiosulfate. The diene product was extracted into pentane. Distillation gave 5.42 g of *cis,trans*-5,7-dodecadiene (65%), bp 68–69° (0.8 mm); $n^{22}\text{D}$ 1.4652; uv_{max} (hexane) 234 mμ (ε 25,100).

George Zweifel, Norman L. Polston, Charles C. Whitney
Department of Chemistry, University of California
Davis, California 95616
Received August 19, 1968

Monomer and Excimer Emission of Acetone

Sir:

The fluorescence of acetone has been the subject of many investigations.[1–8] Recently, Borkman and Kearns[1] reported that (a) the fluorescence spectrum and quantum yield of acetone with 313-mμ excitation is independent of solvent and (b) there is an abnormally large displacement between the absorption and emission wavelength maxima.

Fluorescence measurements with 285-mμ excitation obtained in this laboratory indicate that the emission of acetone is concentration dependent and that the fluorescence spectrum reported by Borkman and Kearns[1] for 0.2 *M* acetone in *n*-hexane with 313-mμ excitation is that of the acetone excimer. Our results are directed to points a and b above and indicate that the emission wavelength maximum of acetone at 405 ± 3 mμ with 313-mμ excitation is the result of excimer emission and that the fluorescence wavelength maximum of acetone in dilute solutions of *n*-hexane excited at 285 mμ (ε 13.9) occurs at 345 ± 3 mμ. The larger extinction coefficient of acetone at 285 mμ relative to 313 mμ permits dilute solutions (2.7×10^{-4}–2.2×10^{-2} *M*) to be studied, whereas Borkman and Kearns[1] used 313-mμ excitation and concentrations which were $\geq 10^2$ times larger than those in the present study. The results presented in Figure 1 for acetone in *n*-hexane show two concentration-dependent emitting species. The lack of evidence for dimer formation in the ground state eliminates the possibility of absorbing dimers.

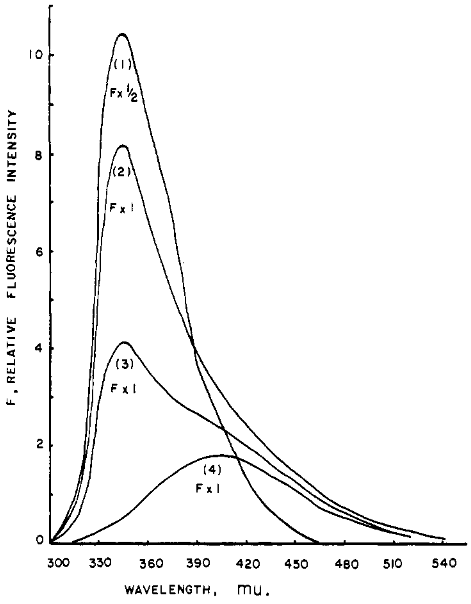

Figure 1. Concentration dependence of monomer and excimer fluorescence of acetone in *n*-hexane solutions at 25° (λ_{exc} 285 mμ): (1) 2.7×10^{-4} *M*, (2) 2.7×10^{-3} *M*, (3) 1.1×10^{-2} *M*, (4) 2.2×10^{-2} *M*.

In Figure 2 we have plotted on a wave-number scale the absorption of acetone together with the emission of monomer and excimer. It is quite evident that the large displacement reported by Borkman and Kearns[1] is due to the comparison of monomer absorption with excimer emission.

In contrast to the lack of solvent effect on the emission reported by these workers, the n,π* singlet of acetone is expected and does exhibit absorption and fluorescence shifts with solvent polarity. The results presented in Table I show that the absorption bands exhibit the characteristic blue shift with increasing polarity and hydrogen-bonding ability of the solvents. The fluorescence wavelength maximum of the excimer is independent of the solvent; however, the monomer emission exhibits a red shift upon increasing the dielectric constant of the solvent. Hydrogen-bonding solvents, such as methanol, give rise to wavelength shifts in the n,π* absorption process but have little or no effect on the excited state from which emission occurs, since the hydrogen bond is broken in the n,π* transition.[9] The excited-state dipole moment has been estimated to be 0.86 and 1.84 D, both values being smaller than the ground-state value of 2.84 D.[10,11] Since reorganization with respect to the solvent cage occurs in the excited state prior to emission, the fluorescence shifts to higher wavelengths in solvents of increasing dielectric constants.[9,12]

Table I. Solvent Effects on Absorption and Fluorescence Wavelength Maxima of Acetone at 25°

Solvent	Absorption λ_{max}, mμ	Fluorescence (λ_{exc} 285 mμ) Monomer λ_{max}, mμ	Excimer λ_{max}, mμ
n-Hexane	279	345	405
Ethyl ether	276	355	405
Methanol	271	363	405
Acetonitrile	274	366	405

The ratio of fluorescence intensities for monomer to excimer of acetone in *n*-hexane is estimated to be 10. The relative fluorescence yields were determined according to the method of Parker and Rees.[13] The values obtained in hexane for the monomer and excimer are 0.01 and 0.001, respectively, relative to the value of 0.09 for tryptophan.[14] The accuracy of these values is

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(1) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

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(12) A. Weisstuch and A. C. Testa, *ibid.*, **72**, 1982 (1968).

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(14) V. G. Shore and A. B. Pardee, *Archiv. Biochem. Biophys.*, **60**, 100 (1956).