Table I. Products from the Carbonylation–Oxidation of Representative Dicyclohexylmonoalkylboranes Containing Functional Groups

Unsaturated compound	Product[a]	Physical properties	Yield,[b] %
1-Octene	Cyclohexyl *n*-octyl ketone		(79)[c]
1-Dodecene	Cyclohexyl *n*-dodecyl ketone		(84)[c]
Methyl 10-undecenoate	Methyl 12-cyclohexyl-12-oxo-dodecanoate	Mp 37.5–38.0°	53
10-Undecenyl benzoate	12-Cyclohexyl-12-oxododecyl benzoate	Mp 43.5–44.0°	61
Allyl benzoate	4-Cyclohexyl-4-oxobutyl benzoate	Mp 60–61°	43
Ethyl vinylacetate	Ethyl 5-cyclohexyl-5-oxo-pentanoate	Bp 96° (0.35 mm), n^{20}D 1.4643	44
Allyl cyanide	4-Cyclohexyl-4-oxobutyl cyanide	Bp 102° (0.5 mm), n^{20}D 1.4731	45

[a] Analytical data within accepted limits were obtained for all new compounds. [b] Isolated, except where otherwise indicated. [c] Analysis by glpc.

decenylbenzoate (50 mmoles) was added. The solution was heated to 45° for 1 hr to complete the hydroboration. Then water, 1.4 ml, was added, and the carbonylation initiated, maintaining the temperature at 45°. A total of 44 mmoles of carbon monoxide was taken up in 20 hr.[5] The mixture was then oxidized by the addition of 17 ml of 3 *M* sodium acetate,[6] followed by the dropwise addition of 17 ml of 30% hydrogen peroxide, maintaining the temperature at 50–60°. After an additional 0.5 hr at this temperature, the reaction mixture was cooled and extracted with pentane. Crystallization from the pentane solution afforded 12 g (61%) of 12-cyclohexyl-12-oxododecyl benzoate.

It has been established that the Baeyer–Villiger oxidation of a wide variety of cyclohexyl alkyl ketones proceeds with the preferred migration of the cyclohexyl grouping to form the corresponding cyclohexylcarboxylates.[7] This suggested the possibility of using this new ketone synthesis as a means of introducing the carboxylate linkage into olefins. This is illustrated by the following conversion of 1-octene into nonanoic acid.

A solution of 2.24 g (10 mmoles) of cyclohexyl *n*-octyl ketone (from 1-octene, Table I) in 50 ml of methylene chloride was introduced into a 100-ml flask. *m*-Chloroperbenzoic acid, 4.42 g, was added, and the mixture was heated to reflux. Trifluoroacetic acid (60 mmoles) was added, and the mixture was heated under reflux for 24 hr. The methylene chloride was stripped off, and the mixture hydrolyzed with 2 *M* potassium hydroxide and extracted with ether to remove cyclohexanol and other neutral materials. Ether extraction of the acidified solution revealed a 79% yield of nonanoic acid (glpc).

Similarly, 1-dodecene has been converted into tridecanoic acid, methyl 10-undecenoate into dodecanedioic acid (5), and 10-undecenyl alcohol into 12-hydroxydodecanoic acid.[8] (6)

$$CH_2{=}CH(CH_2)_8CO_2CH_3 \longrightarrow HO_2C(CH_2)_{10}CO_2H \quad (5)$$

$$CH_2{=}CH(CH_2)_8CH_2OH \longrightarrow HO_2C(CH_2)_{10}CH_2OH \quad (6)$$

It is apparent that this simple synthesis of ketones containing functional substituents is capable of wide variations which should be of considerable value synthetically. We continue to explore the scope of this synthesis.

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(5) Actually, the reaction can be completed in less time. However, the carbonylation proceeds automatically, and it was convenient to allow it to run overnight.

(6) In the usual procedure[4] sodium hydroxide is used. However, the presence of groups which are sensitive to alkali made a shift to sodium acetate desirable.

(7) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958); M. F. Hawthorne and W. D. Emmons, *ibid.*, **80**, 6398 (1958).

(8) Clathration with urea provides a convenient means to separate such straight-chain derivatives from *m*-chlorobenzoic acid and other by-products in the reaction mixture: H. Schlenck and R. Holman, *J. Am. Chem. Soc.*, **72**, 5001 (1950).

(9) This study was assisted by financial support provided by Grant No. 5 ROI-GM-10937 from the National Institutes of Health.

(10) National Science Foundation Fellow, 1964–1966.

A Novel Method for the Synthesis of Both *cis*- and *trans*-Vinyl Bromides from 1-Alkynes *via* Hydroboration

Sir:

It was recently reported that the halogenation of the vinylalane from the reaction of 1-hexyne with diisobutylaluminum hydride produces the isomerically pure *trans*-1-hexenyl halide.[1] We wish to report that addition of bromine to *trans*-1-hexenyldisiamylborane,[2] derived from the reaction of 1-hexyne with bis(3-methyl-2-butyl)borane, gives either *cis*- or *trans*-1-bromo-1-hexene, depending upon the procedure used to eliminate the elements of disiamylboron bromide from the dibromide intermediate.

Hydrolysis yields the *cis* derivative, thermal decomposition (in refluxing carbon tetrachloride) yields the *trans*. Since the reaction of bromine presumably proceeds through the usual bromonium ion mechanism to give *trans* addition to the double bond, solvolysis must involve a *trans* elimination[3] and thermal decomposition a *cis*[4] (1).

This procedure was applied to a number of 1-alkynes, with essentially identical results. However, when it was extended to phenylacetylene, we were surprised to note that in this case solvolysis of the intermediate yielded *trans*-bromostyrene, with thermal decomposition yielding the *cis*—the precise opposite of the

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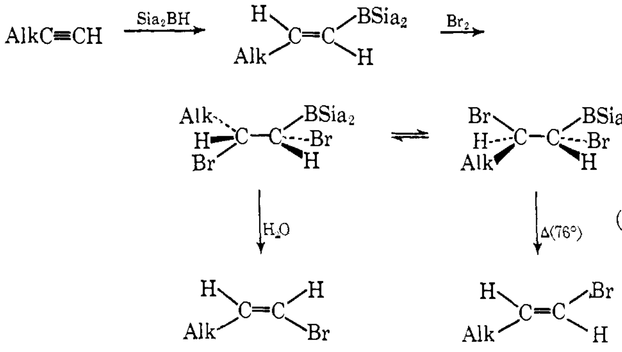
(1) G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1967).

(2) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

(3) D. S. Matteson and J. D. Liedtke, *ibid.*, **87**, 1526 (1965), have suggested that bromine adds *trans* to vinylboronic acids and that deboronobromination involves a stereospecific *trans* elimination.

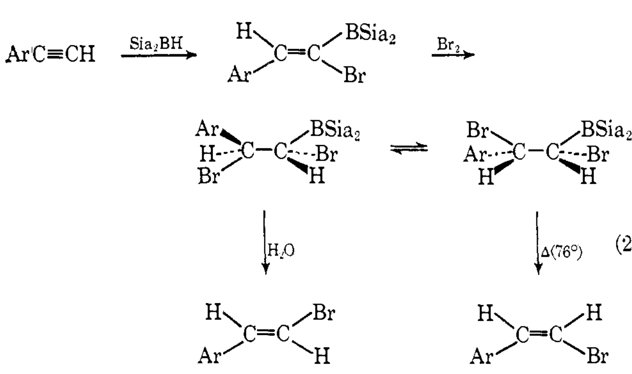
(4) In the case of the alanes[1] it was assumed that the reaction involves a direct attack of the halogen on the carbon–aluminum bond, with retention. This is reasonable. However, the possibility cannot now be excluded that the reaction involves both a fast addition of the halogen to the double bond and a fast thermal *cis* elimination, in analogy to the present observation.



(1)

geometrical isomers formed with the 1-alkynes. This observation was checked repeatedly.

We have not attempted to investigate the precise cause of this inversion in the structure of the geometrical isomers produced. However, it is possible that addition of bromine to phenyl-substituted vinylborane results in a *cis* addition, rather than the usual *trans* (2).



(2)

Such a change has been observed previously in additions of chlorine, where the electron-deficient intermediate involves a benzylic center.[5]

The experimental results are summarized in Table I.

Table I. Vinyl Bromides from Acetylenes *via* Hydroboration

		Solvolysis		Thermal decompn	
Acetylene	Product	Yield, %[a]	*cis*: *trans*[a]	Yield, %[a]	*cis*: *trans*[a]
1-Pentyne	1-Bromo-1-pentene	65	97:3	40	0:100
1-Hexyne	1-Bromo-1-hexene	67	95:5	75	12:88
1-Heptyne	1-Bromo-1-heptene	76	97:3	60	12:88
1-Octyne	1-Bromo-1-octene	68	98:2	50	6:94
Phenylacetylene	β-Bromostyrene	88	4:96	78	82:18

[a] Yield and isomer distribution by glpc analysis.

The experimental procedure follows. A 100-ml, three-necked flask fitted with a reflux condenser, a thermometer, a rubber septum, and a pressure-equalized addition funnel was flushed with nitrogen. Fifty mmoles of disiamylborane, in tetrahydrofuran, was prepared as previously described,[2] and the solvent was then removed under vacuum. Carbon tetrachloride, 30 ml, was added to dissolve the reactant, and 50 mmoles of the acetylene was added at a rate such that the temperature did not rise above 5°. Then a solution of 52.5 mmoles of bromine in 30 ml of carbon tetrachloride was added, maintaining the temperature at 0-5°. The product underwent hydrolysis practically instantaneously upon the addition of 2 *M* sodium hydroxide. The carbon tetrachloride solution was separated, dried, and analyzed by glpc, using a tricresyl phosphate column, with comparisons using authentic samples. In the thermal decomposition procedure, the carbon tetrachloride solution of the dibromide was refluxed for 6 hr under nitrogen.

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[5] S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, 78, 4939 (1956); R. E. Buckles and D. F. Knaak, *J. Org. Chem.*, 25, 20 (1960).

[6] Research assistant, 1961-1963, on a project supported by the Ethyl Corporation at Purdue University.

[7] Postdoctorate research associates, 1963-1964, on Grant GM 10937 from the National Institutes of Health.

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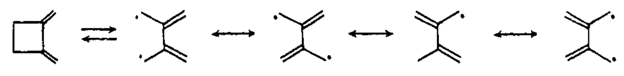
Tetramethyleneethane. The Degenerate Thermal Rearrangement of 1,2-Dimethylenecyclobutane

Sir:

Our interest in the pyrolyses of unsaturated hydrocarbons which may proceed *via* orbitally degenerate diradical intermediates led to the suspicion that the intermediate postulated in the allene dimerization,[1] namely, the tetramethyleneethane diradical[2] (**2**), could be responsible for a thermal self-interconversion of 1,2-dimethylenecyclobutane (**1**).



1 **2**

To test this hypothesis, 1,2-bis(dideuteriomethylene)-cyclobutane (**3a**) was prepared from predominantly *trans*-1,2-dicyanocyclobutane by a standard synthetic sequence[3] with the deuterium atoms being incorporated at the stage of reduction of the corresponding bis-(N,N-dimethylamide). Pure **3a** (99+% by capillary vpc) was obtained in moderate yield upon vacuum pyrolysis of the bis(dimethylamine oxide) and passage of the pyrolysate through a calcium chloride trap; nmr of **3a**: singlet at δ 2.58 (the two two-proton resonance singlets at δ 4.61 and 5.05 present in the perprotio derivative **1** were absent in **3a**), mass of **3a**: 84.0873 (calcd for $C_6D_4H_4$, 84.0877).

Pyrolysis of **3a** in the gas phase (15 μl in a 100-ml carefully neutralized tube sealed at −78° under nitrogen at 120 mm) for 2 hr at 275° gave tetradeuterio-1,2-dimethylenecyclobutane in 35% recovery (relative to benzene internal standard); no other materials of near-comparable volatility were observed. The remainder of the product consisted of less volatile compounds, as indicated by their much-delayed emergence from gas

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[1] For a brief review see J. D. Roberts and C. M. Sharts, *Org. Reactions*, 12, 1 (1962).

[2] (a) Hückel molecular orbital theory[2b] predicts orbital energies for this diradical of 2.0β, 1.0β, 0.0β, 0.0β, −1.0β, and −2.0β and a total π energy of $6\alpha + 6\beta$. Its delocalization energy relative to two double bond and two radical fragments is 2β; relative to two allylic radicals the DE is 0.35β. (b) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1, Pergamon Press, New York, N. Y., 1965, p 7.

[3] A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, 82, 3619 (1960).