low yields by the reaction with nitriles, and reacted very slowly with olefins. The characteristic nature of organocalcium halides in organic reactions remains to be revealed in the future.

Experimental Section

Gas chromatographic analyses were carried out on a Shimadzu GC-4A or GC-4B gas chromatograph. Infrared spectra were recorded on a Japan Spectroscopic Co. Model 402G spectrometer.

Materials.—Methylcalcium iodide was prepared in tetrahydrofuran according to our procedure reported previously.[1] Tetrahydrofuran was purified by distillation in the presence of benzophenone sodium ketyl under a nitrogen atmosphere. Nitrogen was purified by passing through a tube containing copper turnings in a furnace at 170° followed by drying with phosphorus pentoxide. Methyl iodide, acetone, benzophenone, benzaldehyde, benzoyl chloride, acetyl chloride, methyl acetate, diethyl carbonate, methyl crotonate, acetonitrile, benzonitrile, benzyl chloride, cyclohexene, and 1,1-diphenylethylene were purified by usual methods.[32] Authentic samples of 2-methyl-3-penten-2-ol and α,α-diphenylethanol were prepared by the reactions of methylmagnesium iodide with *n*-butyl crotonate and benzophenone, respectively. 1,1-Diphenylpropane was prepared by a conventional procedure.[33,34] Other authentic samples and chemicals were commercial products and were used without further purification.

Procedure.—The reaction vessel was a two-necked flask equipped with two three-way cocks. Each three-way cock was connected with a nitrogen inlet and a rubber serum cap. Methylcalcium iodide was prepared in this flask by the reaction of calcium metal with methyl iodide in tetrahydrofuran at −70°.[1] Various reactants in tetrahydrofuran were added dropwise at −30° to this methylcalcium iodide in the flask over a period of 0.5 hr while stirring at the temperature. Reactons with carbonyl compounds and nitriles were rapid and exothermic, and the stirring was continued for 1 hr at 20° to complete the reaction. Reactions with benzyl chloride, cyclohexene, and 1,1-diphenylethylene were slow and were continued for several hr at 20° after the addition of the reactants. After the reaction, water, methanol, acetic acid, or 6 *N* hydrochloric acid was added to the reaction mixture. The amount of gaseous products evolved during the reaction was determined by a gas burette, and the gas was analyzed by gas chromatography. Qualitative and quantitative analyses of other reaction products were carried out by gas chromatography.

Registry No.—Methylcalcium iodide, 20458-43-9.

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[32] J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York, N. Y., 1970.

[33] C. F. H. Allen and S. Converse, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 226.

[34] M. D. Soffer, M. P. Bellis, H. E. Gellerson, and R. A. Stewart, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N Y., 1963, p 903.

Inversion of Configuration in the Bromination of Vinylic Mercurials[1]

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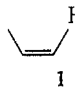
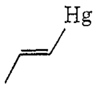
The bromination of *cis*- and *trans*-1-propenyl- and 2-butenylmercury(II) bromide in carbon disulfide occurs with predominant inversion of configuration at the double bond. The rate of bromination of *trans*-2-butenylmercury(II) bromide in carbon disulfide is 75 times as fast as that of *n*-propylmercury(II) bromide. The observed inversion of configuration is consistent with a trans addition of bromine to the carbon–carbon double bond of the vinylic mercurials followed by a trans elimination of mercury(II) bromide. In contrast to the results in carbon disulfide, the bromination of the vinylic mercurials takes place with retention of configuration in pyridine.

A study of the bromination of *cis*- and *trans*-2-butenyl- and 1-propenylmercury(II) bromides (compounds **1**, **2**, **3**, and **4**) in carbon disulfide was initiated in an attempt to generate free propenyl radicals of known stereochemistry and to investigate their stereochemical fate.[2] A free-radical pathway for the bromination of these compounds in carbon disulfide was anticipated at the outset, since Jensen had shown that the bromination of either *cis*- or *trans*-4-methylcyclohexylmercury(II) bromide in degassed carbon disulfide produced the same ratio of *cis*- and *trans*-1-bromo-4-methylcyclohexane and had interpreted the loss of of stereochemistry in terms of a free-radical reaction.[3] The possibility of an alternative pathway involving retention of stereochemistry in the bromination of the vinylic mercurials was also considered, since Jensen[3] had shown that the bromination of the isomeric methylcyclohexyl mercurials in methanol proceeds with 85% retention of stereochemistry. Here, we report the surprising finding that bromination of 1-propenyl and 2-butenyl mercurials leads to propenyl and butenyl bromides of inverted stereochemistry.[4]



1



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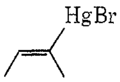

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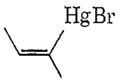

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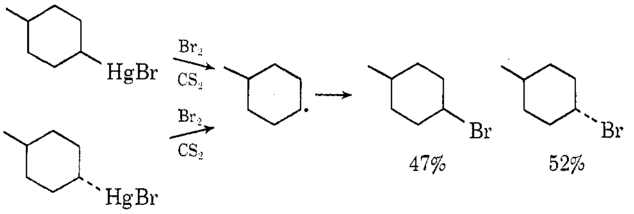

Results

Synthesis and Stereochemistry of Vinylic Mercurials.—*cis*- and *trans*-1-propenyl- and 2-butenylmercury(II)

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[1] Supported in part by the National Science Foundation, Grants GP-28586X and GP-2018.

[2] L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1972, p 239.

[3] F. R. Jensen and L. H. Gale, *J. Amer. Chem. Soc.*, **82**, 148 (1960).

[4] Although the chemistry of *cis*- and *trans*-1-propenylmercury(II) bromides has been studied in detail,[5] the halogenation of these compounds has not been reported.

[5] A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1216 (1959); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1174 (1959).

TABLE I

BROMINATION OF VINYLIC MERCURIALS IN PYRIDINE AND CARBON DISULFIDE

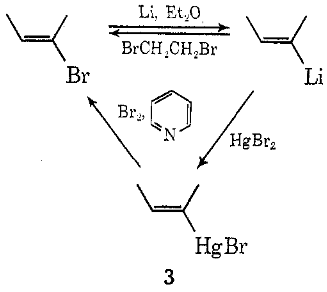
Compd	Conditions	RHgBr, mmol	Br_2, mmol	Vinyl bromides: Cis	Vinyl bromides: trans	Vinyl bromides: Yield, %
Cis, **3**	Pyridine, air, 0.035 *M*	0.25	0.25	99.6	0.4	92
Trans, **4**	Pyridine, air, 0.035 *M*	0.25	0.25	8.9	91.9	95
Cis, **1**	CS_2, air, 0.05 *M*	0.11	0.11	21.8	78.2	
Trans, **2**	CS_2, air, 0.05 *M*	0.10	0.10	73.5	26.5	
Cis, **3**	CS_2, air, 0.03 *M*	0.27	0.27	11.6	88.4	100
Trans, **4**	CS_2, air, 0.06 *M*	0.20	0.20	92.9	7.1	102
Trans, **4**	CS_2, degassed, 0.06 *M*	0.12	0.12	91.8	8.2	
Trans, **4**	MeOH, air, 0.02 *M*	0.02	0.02	77.8	22.2	

bromide were synthesized stereospecifically by reaction of mercury(II) bromide with the corresponding vinylic lithium reagents[6] prepared from stereochemically pure vinylic bromides. The isomeric 1-propenyl- and 2-butenyllithium reagents had been prepared previously and demonstrated to be configurationally stable, once formed.[7-9] The stereochemistry of *cis*- and *trans*-1-propenylmercury(II) bromide, **1** and **2**, was originally assigned by Nesmeyanov[5] on the basis of the method of synthesis from the corresponding lithium reagents. Jensen[10] has recently demonstrated that *exo*- and *endo*-2-norbornylmagnesium bromide react with mercury(II) bromide to give the corresponding alkylmercury(II) bromides with complete retention of configuration. The stereochemistry of di-*cis*- and di-*trans*-propenylmercury(II), **5** and **6**, respectively, has been assigned unambiguously by nmr.[11]

The assignment of stereochemistry of *cis*- and *trans*-2-butenylmercury(II) bromide is based on the method of synthesis and on the nmr spectra of the compounds. Owing to deshielding by the cis mercury atom,[11] the chemical shift of the vinyl proton cis to mercury in **3** is δ 5.56 while the chemical shift of the vinyl proton trans to mercury in **4** is δ 6.25.

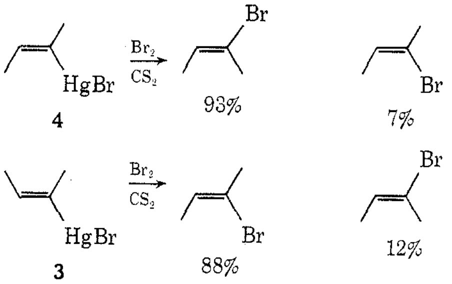
The reaction of alkyl mercurials with bromine in pyridine is stereospecific.[3] We have found that the reaction of the vinylic mercurials **3** and **4** with bromine in pyridine produces the corresponding vinylic bromides with retention of configuration (Table I). The chemical evidence for the assignment of configuration of *cis*-2-butenylmercury(II) bromide, **3**, is shown in Scheme I.

SCHEME I



3

Bromination of Vinylic Mercurials in Carbon Disulfide.—The bromination of the vinylic mercurials **1**, **2**, **3**, and **4** in carbon disulfide was highly stereoselective but gave vinyl bromides having opposite stereochemistry from the mercury compounds from which they were derived (Table I). Similar results were obtained in degassed solutions or in the presence of air, which normally retards free-radical bromination of mercurials.[3] Bromination of **4** in methanol also gave predominantly the vinylic bromide of opposite configuration.



Relative Rates of Bromination of Alkyl and Vinylic Mercurials.—To aid in the determination of the mechanism of the bromination of the vinylic mercurials, it was of interest to determine the relative rates of bromination of 1-hexene, *trans*-2-butenylmercury(II) bromide, **4**, and *n*-propylmercury(II) bromide. Since both vinylic and alkylmercury(II) compounds decolorize carbon disulfide or pyridine solutions of bromine immediately, competition techniques were used to measure relative rates. Dilute carbon disulfide or pyridine solutions of pairs of the substrates were treated with a deficiency of a dilute solution of bromine. The relative yields of the two products were determined by gas chromatography and used to establish the relative rates of bromination shown in Table II.

Discussion

Two mechanisms for the halogenation of organomercurials have been demonstrated.[12] In polar solvents in the presence of air (a free-radical inhibitor), haolgenation of alkylmercury(II) halides proceeds by a stereospecific four-center mechanism leading to retention of configuration. In nonpolar degassed solvents, the halogenation proceeds by a completely nonstereospecific free-radical mechanism. The inversion

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[6] G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

[7] D. Seyferth and L. G. Vaughan, *J. Amer. Chem. Soc.*, **86**, 883 (1964).

[8] A. S. Dreiding and R. J. Pratt, *J. Amer. Chem. Soc.*, **76**, 1902 (1954).

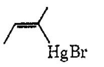
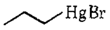
[9] The stereochemistry of 1-propenyllithium reagents has been determined directly by nmr spectroscopy: D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 201 (1963).

[10] F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).

[11] D. Moy, M. Emerson, and J. P. Oliver, *Inorg. Chem.*, **2**, 1261 (1963).

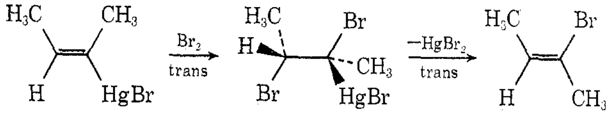
[12] F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, Chapter 4, and references cited therein.

TABLE II
RELATIVE RATES OF BROMINATION IN CARBON DISULFIDE AND PYRIDINE

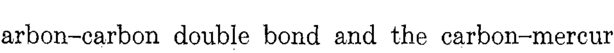
Registry no.	Compd	Relative rate in CS_2	Relative rate in C_5H_5N
25264-93-1		1.0	1.0
	 (4)	2.2	34
18257-68-6		0.029	0.9

of configuration observed in the bromination of the vinylic mercurials is not compatible with either of the two above mechanisms and must be occurring by a different mechanistic pathway.

The predominant inversion of configuration observed in carbon disulfide can best be explained by a trans addition of bromine to the carbon-carbon double bond of the vinylic mercurial followed by a trans elimination of mercury(II) bromide from the resulting adduct. This addition-elimination mechanism implies that the carbon-carbon double bond is more reactive toward bromine than is a carbon-mercury bond. If the addition-elimination mechanism is correct, then, by extension, one would expect a vinylic mercurial to be more reactive than an alkyl mercurial in carbon disulfide. The relative rate studies reported in Table II are in agreement with the proposed addition-elimination mechanism. Thus, *trans*-2-butenylmercury(II) bromide, **4**, is about 75 times more reactive toward bromine in carbon disulfide than is *n*-propylmercury(II) bromide. The vinylic mercurial is about 2.2 times more reactive than 1-hexene.



The retention of configuration observed in the bromination of vinylic mercurials in pyridine must be due to direct electrophilic attack of bromine on the carbon-mercury bond. Pyridine interacts strongly both with organomercurials and with bromine; either interaction could lead to the change in mechanism upon changing solvent from carbon disulfide to pyridine. Bromine reacts with pyridine to produce a bromine-pyridine complex[12] which is a more electrophilic brominating agent than bromine. However, the pyridine-bromine complex should be more reactive toward both the carbon-carbon double bond and the carbon-mercury bond of a vinyl mercurial. Consequently, a change in mechanism would not necessarily be expected upon changing the nature of the electrophile. Pyridine forms complexes with alkylmercury compounds.[12] The electron donation from pyridine to mercury would be expected to activate selectively the carbon-mercury bond of a vinylic mercurial toward reaction with electrophiles. Thus, although in carbon disulfide the carbon-carbon double bond of 1-hexene is 34 times more reactive toward bromine than the carbon-mercury bond of *n*-propylmercury(II) bromide, the two compounds have the same relative reactivity towards bromine in pyridine suggesting an increased relative reactivity of the carbon-mercury bond in pyridine. Similarly, the relative reactivity of *trans*-2-butenylmercury(II) bromide compared with 1-hexene increases from 2.2 to 34 on going from carbon disulfide to pyridine.



The inversion of configuration reported here for the bromination in carbon disulfide of the vinylic mercurials **1**, **2**, **3**, and **4** is surprising, since the extensive research on the halogenation of vinylic mercurials carried out in the research groups of Nesmeyanov and Reutov had previously indicated that halogenation occurred either by a four-center mechanism giving complete retention of stereochemistry or by a totally nonstereospecific free-radical mechanism.[13] The halogenation of vinylic mercurials is normally stereospecific in polar solvents and nonstereospecific in nonpolar solvents. Examples of halogenation occurring with retention of stereochemistry include the bromination of *cis*- and *trans*-stilbenylmercury(II) bromide in dioxane,[14] the iodination of *cis*- and *trans*-β-chlorovinylmercury(II) chloride in methanol, dioxane, or dimethylformamide,[15] and the bromination of *cis*- and *trans*-β-styrylmercury(II) bromide in methanol or dimethyl sulfoxide.[15] In contrast, the same mixture of cis and trans vinylic halides is obtained in the bromination or iodination of *cis*- and *trans*-β-styrylmercury(II) bromide in carbon tetrachloride or in benzene.[15] In a study of the oxymercuration products of allenes, Waters reported that the iodination of *cis*- and *trans*-3-iodomercuri-4-methoxy-2-pentene in carbon tetrachloride and the bromination of *cis*- and *trans*-3-chloromercuri-4-methoxy-2-pentene in pyridine both take place with retention of configuration.[16,17] Thus, the bromination in carbon disulfide of compounds **1**, **2**, **3**, and **4** constitutes the first example so far reported of the inversion of configuration in the halogenation of vinylic mercurials.

The only other examples of inversion of configuration in the halogenation of vinyl metal compounds are found in the chemistry of boron. Matteson[19] has reported that the bromination of *cis*- or *trans*-2-butene-2-boronate gives the vinyl bromide of inverted configuration. The reaction proceeds by the trans addi-

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[13] For a recent review of halogenation of vinylic mercurials emphasizing the work of Russian chemists, see L. G. Makarova in "Organometallic Reactions," Vol. I, E. I. Becker and M. Tsutsui, Ed., Wiley, New York, N. Y., 1970, pp 325-345.

[14] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[15] I. P. Beletskaya, V. I. Karpov, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1707 (1964); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1615 (1964).

[16] W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968).

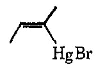
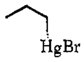
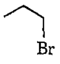
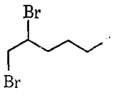
[17] The assignment of stereochemistry of the mercury compounds was made on the assumption that the trans ^{199}Hg-H coupling constant is greater than the cis ^{199}Hg-H coupling constant; this assumption is supported by studies of model compounds.[18] Nonetheless, the assignment may be in error, since the chemical shift of the vinyl hydrogen in the compound assigned the structure *cis*-3-chloromercuri-4-methoxy-2-pentene appears 0.61 ppm downfield from the vinyl hydrogen in the compound assigned the trans structure, although an opposite effect would be expected from the work of Oliver.[11]

[18] W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).

[19] D. S. Matteson and J. D. Leidtke, *J. Amer. Chem. Soc.*, **87**, 1526 (1965).

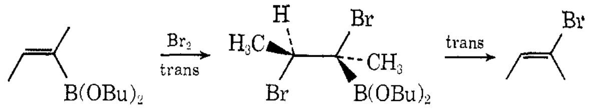
TABLE III

COMPETITION REACTIONS FOR BROMINE IN CARBON DISULFIDE AND PYRIDINE

	Initial concentrations of reactants, 10^2 *M*				Molar ratio of products			
Solvent				Br_2	2-Bromo-2-butene-			Rate ratio
CS_2		0.56	0.56	0.062		1	32	1:34
CS_2	4.1		5.5	2.2	1.42		1.0	2.2:1
C_5H_5N	7.6	8.5		7.1	29.4	1.0		34:1
C_5H_5N		8.3	9.5	10.4		1.0	1.19[a]	1:1.1

[a] Determined by disappearance of 1-hexene.

tion of bromine to the carbon–carbon double bond to give an isolated intermediate dibromide, which then undergoes a base-catalyzed trans elimination. The



carbon–boron bond is relatively inert to bromine[20] and it is not surprising that the carbon–carbon double bond is attacked preferentially in vinyl boron compounds. Brown[21] has recently shown that the dibromide prepared from a vinylborane decomposes in the presence of base by a trans elimination to give a vinyl bromide of inverted configuration; however, thermal decomposition of the dibromide in carbon tetrachloride proceeded by a cis elimination to give a vinyl bromide of the same configuration as the vinylborane.

Experimental Section

trans-**2-Butenylmercury(II) Bromide.**—Mercury(II) bromide (17.0 g, 0.047 mol) was added to an ether solution of *trans*-2-butenyllithium[6] prepared from *trans*-2-bromo-2-butene (6.4 g, 0.047 mol). The reaction mixture was poured into water and the ether layer was separated, washed with water, dried ($MgSO_4$) and concentrated to 100 ml. Cooling to −78° gave white, lustrous crystals of *trans*-2-butenylmercury(II) bromide (3.5 g, 22% yield): mp 110–113°; $\delta_{TMS}^{CH_2Cl_2}$ 6.25 (quartet of multiplets, J = 6.5 Hz, 1 H, H C=C), 2.01 (quintet, J = 1.5, Hz, 3 H, $C{=}CCH_3Hg$), and 1.84 (doublet of quartets, J = 6.5, J' = 1.5 Hz, 3 H, $CH_3C{=}CHg$). Coupling due to ^{199}Hg was also evident: $J_{Hg,\alpha\text{-}CH_3}$ = 188 Hz; $J_{Hg,\beta\text{-}CH_3}$ = 44 Hz.

Anal. Calcd for C_4H_7BrHg: C, 14.32; H, 2.10; Br, 23.81. Found: C, 14.23; H, 2.02; Br, 23.48.

cis-**2-Butenylmercury(II) Bromide.**—Reaction of mercury(II) bromide (9.0 g, 0.024 mol) with an ether solution of *cis*-2-butenyllithium[6] (35 ml, 0.61 *N*, 0.021 mol, 85% cis) at room temperature for 2 days gave a solution containing a gray, flocculent precipitate. The precipitate was collected and dissolved in 200 ml of methylene chloride. The methylene chloride solution was filtered, dried ($MgSO_4$), and cooled to −78° to give white crystals of *cis*-2-butenylmercury(II) bromide (2.4 g), mp 170–172°. Additional *cis*-2-butenylmercury(II) bromide (1.7 g, 4.1 g total, 57% yield) was isolated from the ether solution: nmr $\delta_{TMS}^{CD_2Cl_2}$ 5.56 (quartet of multiplets, J = 6.5 Hz, 1 H, HC=C), 2.00 (m, 3 H, $C{=}CCH_3Hg$), and 1.79 (doublet of quartets, J = 6.5, J' = 1 Hz, $CH_3CH{=}CHg$). Coupling due to ^{199}Hg was evident: $J_{Hg,\alpha\text{-}CH_3}$ = 202, $J_{Hg,\beta\text{-}CH_3}$ = 40 Hz.

Anal. Calcd: C, 14.32; H, 2.10; Br, 23.81. Found: C, 14.23; H, 2.13; Br, 23.52.

trans-**1-Propenylmercury(II) Bromide.**—Reaction of mercury(II) bromide (17.5 g, 0.048 mol) with an ether solution of *trans*-1-propenyllithium[6] (38 ml, 1.25 *N*, 0.047 mol, 87% trans) at room temperature for 1 hr gave a gray precipitate and a yellow solution. The reaction mixture was poured into 100 ml of water, the solid was dissolved in 100 ml of methylene chloride, and the resulting yellow solution was dried ($MgSO_4$), filtered, and concentrated to 40 ml. Cooling the solution to −10° gave white crystals of *trans*-1-propenylmercury(II) bromide (6.7 g, 43% yield), mp 120–123° (lit.[22] mp 120–121.5°).

cis-**1-Propenylmercury(II) Bromide.**—Reaction of mercury(II) bromide (12.5 g, 0.035 mol) with an ether solution of *cis*-1-propenyllithium[6] (25 ml, 1.32 *N*, 0.33 mol, 94% cis) at room temperature gave a dark solution. The ether solution was poured into water, separated, washed with water, dried ($MgSO_4$), filtered, and cooled to −78° to give *cis*-1-propenylmercury(II) bromide (3.0 g, 29% yield), mp 60–64°. Recrystallization from 10 ml of ether gave 2.4 g of *cis*-1-propenylmercury(II) bromide, mp 63–67° (lit.[22] mp 62.5–63.5°).

n-**Propylmercury(II) bromide** was prepared by the method of Slotta and Jacob.[23] Reaction of *n*-propylmagnesium bromide (0.31 mol) with mercury(II) bromide (0.40 mol) in ether gave *n*-propylmercury(II) bromide (58.4 g, 0.19 mol, 59%), mp 136–137° (lit.[23] mp 140°).

Reaction of Vinylic Mercury(II) Bromides with Bromine.—When a 0.1 *N* solution of the vinylic mercury(II) bromide and a 0.1 *N* solution of bromine in either carbon disulfide, methanol, or pyridine were mixed in the presence of air, the bromine color disappeared immediately. The cis:trans ratio of the vinylic bromides formed was determined by glpc on a 12-ft 15% TCEOP column at 30°. In several cases, yields were determined using decane as an internal vpc standard. The vinylic halides were identified by comparison of glpc retention times with authentic samples. In addition, *trans*-2-bromo-2-butene from the bromination of *cis*-2-butenylmercury(II) bromide in carbon disulfide and *cis*-2-bromo-2-butene from the bromination of *trans*-2-butenylmercury(II) bromide were collected from the gas chromatograph and were identified by comparison of their ir spectra with the ir spectra of authentic samples.

In one case, a solution of *trans*-2-butenylmercury(II) bromide and a solution of bromine in carbon disulfide were placed in opposite arms of an inverted U tube. The solutions were degassed by freezing the solutions with liquid nitrogen, evacuating the apparatus with a vacuum pump, closing the system off from the vacuum line, and melting the solutions. This procedure was repeated five times before the solutions were warmed to room temperature and mixed.

The reactions of bromine with the vinylic mercury(II) bromides are summarized in Table I.

Competition Experiments.—The relative rates of bromination of 1-hexene, *n*-propylmercury(II) bromide, and *trans*-2-butenylmercury(II) bromide, **4**, were determined by competition of the substrates for a deficiency of bromine. Dilute carbon disulfide or pyridine solutions of pairs of the substrates were stirred rapidly at room temperature while a dilute carbon disulfide or pyridine solution of bromine was added slowly by syringe. The relative amounts of 1,2-dibromohexane, *n*-bromopropane and 2-bromo-2-butene were determined by gas chromatography using *n*-octane or *n*-nonane as an internal standard (Table III). The yields of all three products were found to be nearly quantitative in separate bromination experiments.

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[20] Tri-*n*-butylborane is not attacked by bromine or iodine in carbon tetrachloride; however, neat bromine attacks both the carbon–boron and the carbon–hydrogen bonds. J. R. Johnson, H. R. Snyder, and M. G. VanCampen, Jr., *J. Amer. Chem. Soc.*, **60**, 115 (1938).

[21] H. C. Brown, D. H. Bowman, S. Misumi, and M. K. Unni, *J. Amer. Chem. Soc.*, **89**, 4531 (1967).

[22] D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **5**, 580 (1966).

[23] K. H. Slotta and K. R. Jacob, *J. Prakt. Chem.*, **120**, 249 (1929).

The relative rates were calculated using the following formula to take into account differences in initial and final concentrations of substrate.

$$\frac{k_A}{k_B} = \frac{\ln A - \ln A_0}{\ln B - \ln B_0}$$

Registry No.—**1**, 6727-46-4; **2**, 6727-44-2; **3**, 40782-37-4; **4**, 40782-38-5; mercury(II) bromide, 7789-47-1; *trans*-2-butenyllithium, 28944-86-7; *cis*-2-butenyllithium, 28944-85-6; *trans*-1-propenyllithium, 6386-72-7; *cis*-1-propenyllithium, 6386-72-7; bromine, 7726-95-6.