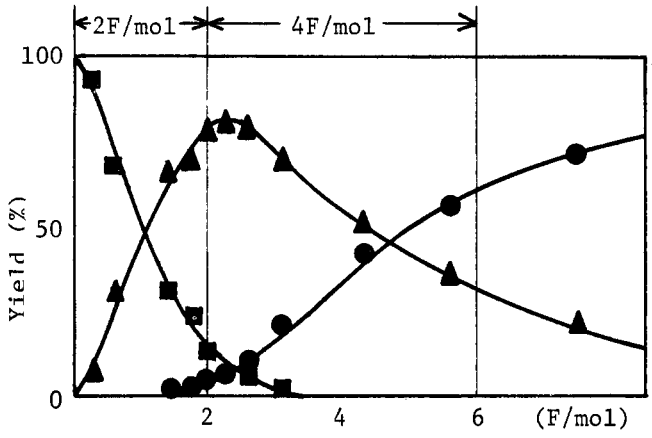
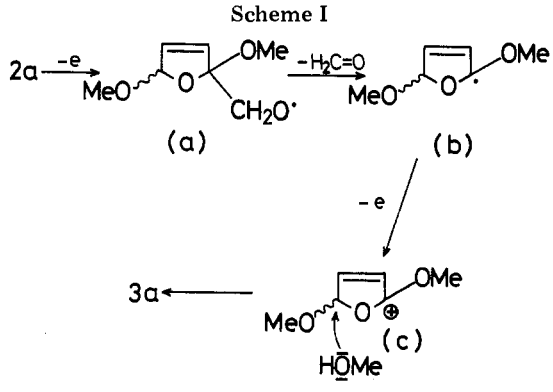


Figure 2. Current density 0.20 A/cm^2. Symbols follow: **1a** (■), **2a** (▲), and **3a** (●).

Scheme I



anol would produce the ring opening product **3a** via the cation intermediate c. In the course of the electrolysis two-electrons oxidation of formaldehyde is also expected to afford methyl formate. After all, the conversion of **2a** to **3a** should require four electrons on the anode. As shown in Figure 1, the conversion of ca. 80% of **2a** was achieved when 4 Faradays/mol of electricity was passed.

Experimental Section

All the boiling points are uncorrected. NMR spectra were recorded on a Hitachi R-24 spectrometer. Ir spectra were measured on neat liquids using a JASCO model IRA-1 spectrometer.

Materials. Commercially available furfuryl alcohol (**1a**) and furfural (**4**) were distilled under reduced pressure before use. 2-Acetoxymethylfuran (**2a**)[13] and 2-furoic acid (**6**)[14] were prepared according to the procedure described in the literature.

General Procedure of the Electrolysis. 2-Substituted furans **1a, 1b, 2a, 4, 5,** and **6** were dissolved in MeOH (20 ml) containing Et_4NClO_4, Et_4NClO_4–Et_3N, and/or NH_4Br–Et_3N as a supporting electrolyte. The solutions were electrolyzed under a constant current in a compartment cell equipped with two platinum foil electrodes (2 × 3 cm^2). The solution was condensed under reduced pressure, taken up in EtOAc, washed with aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). After evaporation of the solvent the residue was distilled by using a short-path distillation apparatus, to give the products **2a, 2b, 3a, 3b,** and **5.** The detailed reaction conditions and results of electrolyses of 2-substituted furans and the related compounds are listed in Table I. Analytically pure samples were obtained by column chromatography on silica gel with benzene–EtOAc (20/1).

2,5-Dimethoxy-2-hydroxymethyl-2,5-dihydrofuran (2a): bp 82–85 °C (7.5 mm) [lit.[15] bp 106–110 °C (18 mm)]; ir (neat) 3440 (OH), 2820 (CH_3O), 1633 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.68 (m, 1 H, OH), 3.15–3.72 (8 H, 2 CH_3O, CH_2O), 5.45–6.16 (3 H, CHO, CH=CH).

2-Acetoxymethyl-2,5-dimethoxy-2,5-dihydrofuran (2b): bp 105–109 °C (11 mm) [lit.[15] bp 117–119 °C (12 mm)]; ir (neat) 2820 (CH_3O), 1745 (C=O), 1632 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.07 (s, 3 H, CH_3CO), 3.15, 3.24 (2 s, 3 H, CH_3O), 3.43, 3.51 (2 s, 3 H, CH_3O), 3.88–4.48 (m, 2 H, CH_2O), 5.45–6.23 (3 H, CHO, CH=CH).

Methyl (*Z*)-4,4-Dimethoxy-2-butenoate (3a): bp 74–78 °C (12 mm); ir (neat) 2820 (CH_3O), 1728 (C=O), 1657 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.33 (s, 6 H, *gem*-CH_3O), 3.68 (s, 3 H, CH_3O), 5.68 (d, J = 7.2 Hz, 1 H, CH=), 5.87 (s, 1 H, CHO), 5.92 (d, J = 7.2 Hz, CH=).

Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.53; H, 7.64.

Methyl (*E*)-4,4-Dimethoxy-2-butenoate (3b):[3,4] bp 75–78 °C (12 mm); ir (neat) 2820 (CH_3O), 1726 (C=O), 1668 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.33 (s, 6 H, *gem*-CH_3O), 3.77 (s, 3 H, CH_3O), 4.96 (diffused d, J = 4.2 Hz, 1 H, CHO), 6.17 (diffused d, J = 16.2 Hz, 1 H, CH=), 6.76 (dd, J = 4.2, 16.2 Hz, 1 H, CH=).

2,5-Dimethoxy-2-dimethoxymethyl-2,5-dihydrofuran (5): bp 65–70 °C (7 mm) [lit.[15] bp 107–110 °C (13 mm)]; ir (neat) 2824 (CH_3O), 1632 (C=C), 1019, 1027, 978 cm^{-1}; NMR ($CDCl_3$) δ 3.18–3.52 (m, 12 H, CH_3O), 3.75–4.21 (1 H, CHO), 5.50–6.30 (m, 3 H, HC=CH, CHO).

Registry No.—**1a,** 98-00-0; **1b,** 623-17-6; **2a,** 19969-71-2; **2b,** 41991-02-0; **3a,** 57314-31-5; **3b,** 32815-00-2; **4,** 98-01-1; **5,** 59906-91-1; **6,** 88-14-2.

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A Novel Intermolecular Transfer Reaction of Alkenyltrialkylborates with Aqueous Bases and Its Application to the Protonolysis of Alkenylboron Derivatives

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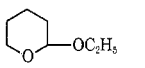
Conversion of organoboranes into organic products is most commonly achieved by either oxidation or protonolysis.[1] Whereas the alkaline hydrogen peroxide oxidation is a highly general reaction,[1] protonolysis with carboxylic acids suffers from a few difficulties, such as the incompatibility with various acid-sensitive functional groups and the frequent need for high temperatures (>100 °C).[2,3] In view of the growing significance of alkenylboron derivatives as synthetic intermediates, development of general and mild procedures for their protonolysis that are complementary to the existing acidic procedure is especially desirable.

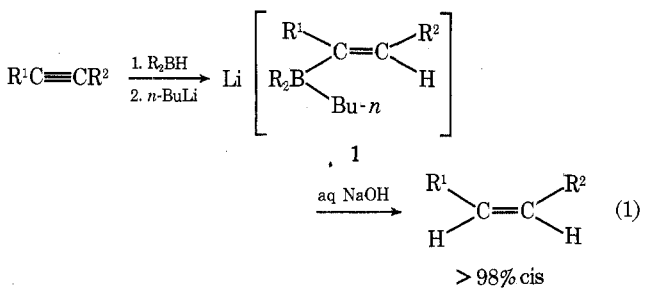
We have found that alkenyltrialkylborates (**1**), readily obtainable by the treatment of alkenyldialkylboranes with an alkyllithium reagent, undergo a selective protonolysis reaction

Table I. Reaction of Lithium Alkenyltrialkylborates (1) with Aqueous Sodium Hydroxide[a]

Entry	Alkenyltrialkylborate (1) R¹	R²	R	Registry no.	Product[b]	Registry no.	Yield,[c] %
1	*n*-C_4H_9	*n*-C_4H_9	c-C_6H_{11}	59643-33-3	*cis*-5-Decene	7433-78-5	92
2	*n*-C_4H_9	*n*-C_4H_9	Sia[e]	59643-34-4	*cis*-5-Decene		90
3	*n*-C_4H_9	*t*-C_4H_9	c-C_6H_{11}	59643-36-6	*cis*-2,2-Dimethyl-3-octene	59574-63-9	90
4	CH_3	*t*-$C_4H_9OC_2H_5$	c-C_6H_{11}	59643-39-9	*cis*-5-*tert*-Butoxy-2-pentene	59574-64-0	87
5	H	c-C_6H_{11}	c-C_6H_{11}	59643-38-8	Cyclohexylethene[f]	695-12-5	93
6	H	*t*-$C_4H_9OC_2H_5$	c-C_6H_{11}	59643-35-5	4-*tert*-Butoxy-1-butene[f]	22498-04-0	86
7	H		c-C_6H_{11}	59643-37-7	4-(2′-Tetrahydropyranyloxy)-1-butene[g]	59574-65-1	95

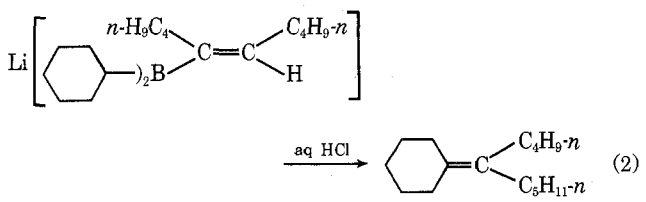
[a] Unless otherwise mentioned, the reaction was carried out over 48 h at ~25 °C. [b] All products except cyclohexylethene yielded satisfactory NMR, ir, and mass spectra. Cyclohexylethene was identified by GLC. [c] By GLC. [d] By isolation. [e] Sia = 3-methyl-2-butyl. [f] The reaction time was 12 h (25 °C). [g] Refluxed overnight.

of the alkenyl groups with aqueous sodium hydroxide to produce the corresponding alkenes in excellent yields. The stereochemistry of the internal alkene product in each case has been found to be ≥98% cis by a combination of GLC, ^1H and ^{13}C NMR, and ir (absence of the trans band at ~970 cm^{-1}).



R^1 = alkyl or H; R^2 = alkyl

The basic protonolysis reported here is highly unique in that it appears to represent the first example of the conversion of alkenylborates into the corresponding alkenyl derivatives via coupling with electrophiles, i.e., proton, which proceeds with retention of all of the structural features of the alkenyl group of **1**. It should also be noted that treatment of the corresponding alkenyldialkylboranes with aqueous sodium hydroxide does not proceed at any appreciable rate under comparable reaction conditions. Moreover, treatment of the borate **1** with aqueous acids takes an entirely different reaction path from that shown in eq 1, undergoing an intramolecular carbon–carbon bond formation between the alkenyl and one of the alkyl groups (R).[4,5] For example, treatment of lithium 5-decenyldicyclohexyl (*n*-butyl)borate with hydrochloric acid produces nearly exclusively 5-cyclohexylidenedecane (eq 2). Only a trace amount of 5-decene is formed under these conditions.[4]



The mechanism of the basic protonolysis of **1** is, at present, not clear. An intuitively plausible mechanism which involves the dissociation of **1** into the corresponding alkenyllithium and trialkylborane does not appear to be operating. For treatment of **1** with another mole of *n*-butyllithium in a mixture of hexane and ether does not show any sign of exchange or displacement. Thus, the ^1H chemical shift and integration of the alkenyl proton of **1** as well as the ^1H chemical shift of the α protons of *n*-butyllithium (δ −1.1 ppm) remain unchanged on mixing **1** with *n*-butyllithium, the only noticeable change being a slow disappearance of *n*-butyllithium presumably owing to its reaction with ethyl ether.

In conclusion, alkenylboron derivatives can now be protonolyzed readily in a highly stereospecific manner to produce the corresponding alkenes under either acidic or basic conditions.

Experimental Section

5-Decyne, cyclohexylethyne, 3-butyn-1-ol, cyclohexene, isobutylene, dihydropyran, and *n*-butyllithium in hexane are all commercial reagents and used without further purification. Borane in THF was prepared as described in detail by Brown.[6] Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Varian T-60A and Varian CFT-20 spectrometers, respectively. GLC analyses were performed on a Perkin-Elmer 3920 gas chromatograph using 6 ft × 0.125 in. o.d. 10% SE-30 and 10% Carbowax 20M columns.

General Procedure for the Protonolysis of Alkenyltrialkylborates. The following conversion of 5-decyne into *cis*-5-decene is representative. 5-Decyne (10 mmol) was hydroborated with 10 mmol of dicyclohexylborane[6,7] in THF (50 ml) at 0 °C. To this solutio were added, in sequence, 10 mmol of *n*-butyllithium in hexane (0 °C, 1 h) and 5 ml of 6 N sodium hydroxide. The reaction mixture was stirred vigorously at room temperature for 48 h.[8] GLC examination of the mixture, after oxidation with 30% hydrogen peroxide, indicated the presence of 9.2 mmol (92%) of 5-decene. After the alcoholic products and other impurities were removed by column chromatography on a short alumina (neutral) column using petroleum ether as a solvent, evaporation of the solvent provided 8.3 mmol (83%) of 5-decene (99% pure by GLC and 99% cis by ^{13}C NMR): ^1H NMR (CCl_4) δ 0.90 (t, J = 5 Hz, 6 H), 1.07–1.56 (m, 8 H), 1.71–2.25 (m with peaks at 1.97 and 2.06 ppm, 4 H), and 5.20 ppm (t, J = 5 Hz, 2 H); ^{13}C NMR [CCl_4, $(CO_3)_2CO$] δ 22.40, 31.13, 35.75, 40.91, and 138.60 ppm; ir (neat) 2900 (s), 2820 (s), 1650 (w), 1455 (s), 1445 (s), 1370 (m), 720 cm^{-1} (w).

The other olefin products were obtained in similar manners. Minor changes in reaction conditions are indicated in Table I.

4-*tert*-Butoxy-1-butyne and 5-*tert*-Butoxy-2-pentyne. 4-*tert*-Butoxy-1-butyne was prepared according to a literature procedure[9] by treating 3-butyn-1-ol in dichloromethane with an excess of isobutylene in the presence of an acid catalyst at room temperature. To 4-*tert*-butoxy-1-butyne in THF were added in sequence an equimolar amount of *n*-butyllithium and a threefold excess of methyl iodide at 0 °C. The reaction mixture was stirred overnight at room temperature. After addition of water, the mixture was extracted with diethyl ether and dried over $MgSO_4$. 5-*tert*-Butoxy-2-pentyne obtained quantitatively after removal of the volative substances was sufficiently pure by GLC and ^1H NMR and was used without further purification: ^1H NMR (CCl_4) δ 1.15 (s, 9 H), 1.72 (t, J = 2 Hz, 3 H), 2.18 (tq, J = 7 and 2 Hz, 2 H), and 3.34 ppm (t, J = 7 Hz, 2 H).

4-Tetrahydropyranyloxy-1-butyne. To 400 mmol of dihydropyran, freshly distilled from sodium hydroxide pellets, were added four drops of concentrated hydrochloric acid and 100 mmol of 3-butyn-1-ol. The reaction mixture was initially cooled in an ice bath and was then allowed to stand for 3 h at room temperature. After

addition of 40 ml of diethyl ether, the mixture was washed with 30 ml of 10% NaOH, dried over $MgSO_4$, and distilled to provide the title compound quantitatively: bp 51 °C (2 mm); $n^{23}D$ 1.4559; ^1H NMR (CCl_4) δ 1.2–1.76 (m, 6 H), 1.87 (t, J = 2 Hz, 1 H), 2.40 (td, J = 7 and 2 Hz, 2 H), 4.06 (m, 4 H), and 4.60 ppm (s, 1 H); ir (neat) 3235 (s), 2910 (s), 2840 (s), 2110 cm^{-1} (w).

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Registry No.—5-Decyne, 627-19-0; 4-*tert*-butoxy-1-butyne, 59574-66-2; 5-*tert*-butoxy-2-pentyne, 59574-67-3; 4-tetrahydropyranyloxy-1-butyne, 40365-61-5; dihydropyran, 110-87-2; 3-butyn-1-ol, 927-74-2; 2,2-dimethyl-3-octyne, 19482-57-6; cyclohexylethyne, 931-48-6.

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Preparation of Cyanoformates. Crown Ether Phase Transfer Catalysis

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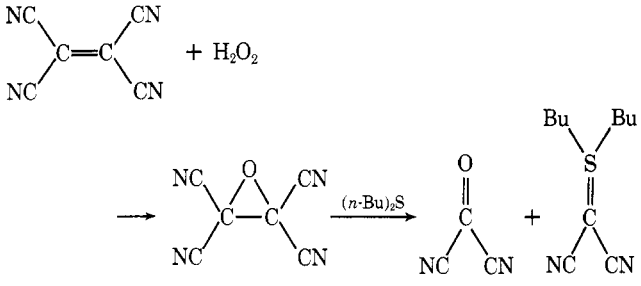
While the chemistry of chloroformates is extensive, that of cyanoformates is not. Thermal decomposition of primary alkyl chloroformates leads to alkyl chlorides and carbon dioxide at reasonable temperatures (150–200 °C).[1-3] By comparison, benzyl cyanoformate decomposes smoothly at 700 °C in the gas phase to yield benzyl nitrile and carbon dioxide.[4] The cyano group of cyanoformates can function as a dienophile in Diels–Alder reactions. For example, reaction of tetraphenylcyclopentadienone with phenyl cyanoformate yields 3,4,5,6-tetraphenylpyridine-2-carboxylic acid after hydrolysis.[5] Photolysis of ethyl cyanoformate in the presence of alkenes yields oxetanes. For example, photolysis of ethyl cyanoformate in 1,1-diphenylethylene yields 2-cyano-2-ethoxy-3,3-diphenyloxetane.[6] Photolysis of ethyl cyanoformate in cyclohexane yields products which may be rationalized as arising from primary cyano and ethoxycarbonyl radicals: cyclohexyl cyanide and ethyl cyclohexanecarboxylate respectively.[7,8] Finally, *tert*-butyl cyanoformate reacts with amino acids to yield *N*-*tert*-butyloxycarbonyl derivatives which are useful in peptide synthesis[9,10].

Table I. Preparation of Cyanoformates by Phase Transfer Catalysis

R	Yield, %	Bp, °C (mm)	Lit. bp, °C (mm)	Ref
Methyl	76	95–96 (760)	99 (760)	4
Ethyl	72	115–116 (760)	117 (760)	4
n-Butyl	90	55–56 (25)		
Isobutyl	94	52–53 (20)		
2,2,2-Trichloroethyl	88	100 (25)		
Isopropyl	62	36–37 (25)	35 (20)	11
2-Octyl	88	113–114 (25)		
Cyclohexyl	90	96–97 (20)	43 (1)	11
Benzyl	65	66–67 (0.6)	80 (2.5)	4
Phenyl	82	52–53 (mp)	51.6–53 (mp)	4, 11

The apparent lack of interest in this class of compounds may be due to difficulty in their synthesis. Benzyl, methyl, and ethyl cyanoformates have been prepared (~30% yield) by reaction of the corresponding alkyl chloroformates with powdered sodium cyanide.[4] Far better yields (70–90%) have been reported for the reaction of carbonyl cyanide with a wide variety of alcohols.[11] Unfortunately, carbonyl cyanide is not a commercially available reagent. It can be prepared (~60% yield) in two steps starting from tetracyanoethylene.[12,13] However, the price of tetracyanoethylene makes this a costly procedure.



An alternative preparation of *tert*-butyl cyanoformate involves several steps.[9] Recently, trimethylsilyl cyanide has been shown to react with methyl and ethyl chloroformates to yield the corresponding cyanoformates.[14] However, a drawback to this latter procedure is the necessity to prepare trimethylsilyl cyanide.[15-17]

We should like to report that cyanoformates can be prepared in good to excellent yields by the 18-crown-6[18] catalyzed reaction of potassium cyanide with the corresponding chloroformates in dichloromethane solvent. This is an example of solid–liquid phase transfer catalysis.[17,19-21] The reaction is also related to the preparation of benzoyl cyanides by reaction of benzoyl chlorides with cyanide ion under PTC conditions.[22] The preparation of cyanoformates is a cleaner reaction, since no formation of dimers which was a major side reaction in the preparation of benzoyl cyanides under PTC conditions was observed to occur. The reaction is quite general and is successful for primary, secondary, benzyl, and phenyl cyanoformates (see Table I). Isolated yields of distilled cyanoformates are reported. The reaction, however, fails for the case of *tert*-butyl cyanoformate. This may be due to the well-known instability of *tert*-butyl chloroformate.[23] Also attempts to prepare carbonyl cyanide directly by the PTC reaction of potassium cyanide with phosgene failed under a wide variety of experimental conditions.