4b: IR 3050, 1720, 1240, 1010, 890 cm^{-1}; mass spectrum, *m/e* 194 (M^+), 152 (base), 134 (M^+ – HOAc); ^1H NMR (CCl_4) δ 1.08–2.40 (m, 15 H, s at δ 1.89), 4.92 (2 d, *J* = 11, 17 Hz, 2 H), 5.96 (dd, *J* = 11, 17 Hz, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.84; H, 9.18.

4c: IR 3050, 1705, 1160, 985, 895 cm^{-1}; mass spectrum, *m/e* 180 (M^+, trace), 134 ($M^+ - HO_2CH$), 91 (base); ^1H NMR (CCl_4) δ 1.40–2.40 (m, 12 H), 4.93 (2 d, *J* = 11, 17 Hz, 2 H), 5.95 (dd, *J* = 11, 17 Hz, 1 H), 7.80 (s, 1 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.00; H, 8.84.

8: IR 1720, 1145 cm^{-1}; mass spectrum, *m/e* 152 (M^+), 97 (base); ^1H NMR (CCl_4) δ 0.82 (d, *J* = 6 Hz, 3 H), 1.04–2.44 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 224.0 (s), 59.3 (s), 40.2 (d), 38.1 (t), 37.5 (t), 33.7 (t), 30.9 (t), 22.9 (t), 19.4 (t), 15.5 (q). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.72.

9b: mp 32–33 °C; IR 1705, 1160, 890 cm^{-1}; mass spectrum, *m/e* 226 (M^+, not detected), 180 ($M^+ - HO_2CH$), 134 (base); ^1H NMR ($CDCl_3$) δ 1.01 (d, *J* = 6 Hz, 3 H), 1.50–2.80 (m, 13 H), 7.82 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.0 (s, 2 C), 86.5 (s, 2 C), 44.4 (d), 35.4 (t, 2 C), 28.5 (t, 2 C), 20.6 (t), 19.9 (t), 7.9 (q). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.86; H, 8.06.

9c: IR 3400, 1700, 1170, 980 cm^{-1}; mass spectrum, *m/e* 198 (M^+, not detected), 152 ($M^+ - HO_2CH$), 124 (base); ^1H NMR (CCl_4) δ 0.98 (d, *J* = 6 Hz, 3 H), 1.36–2.60 (m, 14 H), 7.87 (s, 1 H).

Kinetic Measurements. The rates of the buffered acetolysis of **1d** were measured by the titrimetric method as previously described.[3c]

Lithium Aluminum Hydride Reduction of 1b,c and 4b,c. A 60-mg (0.31 mmol) sample of **1b** in 2 mL of ether was added dropwise to a suspension of 11.8 mg (0.31 mmol) of lithium aluminum hydride in 2 mL of ether, and the mixture was stirred at room temperature for 1 h. Water was added followed by 1 N hydrochloric acid, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined extracts were washed with sodium bicarbonate solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave 44 mg (93%) of **1a**.[5] In a similar manner, 26 mg of **1c** gave 20 mg (95%) of **1a**, 20 mg of **4b** gave 14 mg (93%) of **4a**, and 55 mg of **4c** gave 46 mg (98%) of **4a**.

4a: IR 3400, 3050, 1625, 1110, 990, 890 cm^{-1}; mass spectrum, *m/e* 152 (M^+); ^1H NMR (CCl_4) δ 1.00–2.40 (m, 13 H), 5.02 (2 d, *J* = 11, 17 Hz, 2 H), 5.85 (dd, *J* = 11, 17 Hz, 1 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.59; H, 10.66.

Hydroboration–Oxidation of 4a. To a stirred suspension of 46 mg (0.63 mmol) of **4a** and 18 mg (0.47 mmol) of sodium borohydride in 5 mL of THF was added 0.08 mL (0.63 mmol) of boron trifluoride etherate dropwise via syringe, and the mixture was stirred at room temperature for 3 h. Water (0.05 mL), 0.1 mL of 3 N sodium hydroxide solution, and 0.1 mL of 30% hydrogen peroxide were added dropwise, and then the solution was allowed to stand overnight. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was washed with saturated sodium chloride solution and dried (Na_2SO_4). Evaporation of the solvent gave 95 mg (89%) of the diol **5** as white solid which was recrystallized from ether–petroleum ether: mp 99–100 °C; IR 3250, 1030, 1000 cm^{-1}; mass spectrum, *m/e* 170 (M^+, trace), 128 (base); ^1H NMR ($CDCl_3$) δ 1.30–2.00 (m, 14 H), 2.60–3.40 (br, 2 H), 3.79 (t, 2 H). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.79; H, 10.64.

Alternate Preparation of 4a. A 2.46-g (10 mmol) sample of 70% *m*-chloroperbenzoic acid (MCPBA) was added portionwise to a solution of 980 mg (6.5 mmol) of the cyclobutanone **6** in 30 mL of chloroform, and the solution was stirred at room temperature for 20 h. The solution was washed with sodium sulfite solution, sodium bicarbonate solution, and water and then dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with 20% ether–petroleum ether gave 494 mg (48%) of the γ-lactone **7**: IR 1760, 1230, 1190, 1160, 1130, 950 cm^{-1}; mass spectrum, *m/e* 166 (M^+), 110 (base); ^1H NMR (CCl_4) δ 1.40–2.30 (m, 12 H), 2.43 (s, 2 H).

A 431-mg sample of **7** was reduced with lithium aluminum hydride in a manner similar to that described for **1b** to afford 336 mg (87%) of the diol **5** which was identical in melting point, IR, and GLC with the sample obtained by the hydroboration–oxidation of **4a**.

Lithium Aluminum Hydride Reduction of 9b and 9c. The reduction of **9b** and **9c** was carried out as described for that of **1b** except that chloroform was used for extraction. The diol **9a** was obtained from **9b** and **9c** in 67% and 47% yields, respectively. A pure sample of **9a** was obtained by recrystallization from ether: mp 148–150 °C; IR 3300, 980 cm^{-1}; mass spectrum, *m/e* 170 (M^+, trace), 152 (base, $M^+ - H_2O$); ^1H NMR ($CDCl_3$) δ 1.03 (d, *J* = 6 Hz, 3 H), 1.20–2.20 (m, 15 H). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.15; H, 10.73.

Registry No. **1a**, 79483-08-2; **1b**, 79483-09-3; **1c**, 79483-10-6; **1d**, 79483-11-7; **3**, 79483-12-8; **4a**, 79483-13-9; **4b**, 79483-14-0; **4c**, 79483-15-1; **5**, 79483-16-2; **6**, 71734-13-9; **7**, 79483-17-3; **8**, 79547-85-6; **9a**, 79483-18-4; **9b**, 79483-19-5; **9c**, 79483-20-8.

Simple and Direct Synthesis of *trans*-1,2-Bis(tri-*n*-butylstannyl)ethylene

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Vinylstannanes are versatile precursors to a variety of funtionally substituted organic molecules. While indirect methods of synthesis from a number of sources (alkynes,[2] alkynoates,[3] vinylmetals,[4] β-substituted acrylates[6]) exist, delivery of an intact vinylstannyl residue to a substrate may be readily accomplished with *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene (**3**) via transmetalation with *n*-butyllithium[7] or electrophilic destannylation.[8] Although **3** is available in excellent yield by hydrostannation of tri-*n*-butylethynylstannane (**1**) with tri-*n*-butyltin hydride,[9] the large-scale preparation of **1** is often attended with difficulty. This problem prompted the Corey group to devise a more complicated procedure utilizing derivatives of chloroacetylene.[10]

Herein we describe an efficient synthesis of **1** from a solution of tri-*n*-butyltin chloride and lithium acetylide in tetrahydrofuran which affords the prduct directly in 75% yield (Scheme I). The remaining 25% of the reaction mixture consists largely of bis(tri-*n*-butylstannyl)acetylene (**2**) which may be conveniently separated from **1** by simple distillation. During the course of this study, a procedure was developed for converting the side product **2** to **1** in 65% yield by treatment with lithium acetylide in tetrahydrofuran. Thus, large quantities of **1** are readily available in yields in excess of 90%.

Experimental Section

Tri-*n*-butylethynylstannane (1). A solution of 150 mL (233 mmol) of *n*-butyllithium in hexane in 500 mL of dry tetrahydrofuran was stirred under an acetylene atmosphere at 0 °C

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(2) For a review, see: Negishi, E.-I. "Organometallics in Organic Synthesis"; Wiley: New York, 1980; pp 410–412.
(3) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263.
(4) Seyferth, D.; Stone, F. G. A. *J. Chem. Soc.* **1957**, *79*, 515. Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 194.
(5) Piers, E.: Morton, H. E. *J. Org. Chem.* **1979**, *44*, 3437. Piers, E.; Morton, H. E. *J. Chem Soc., Chem. Commun.* **1978**, 1033.
(6) Seitz, D. E.; Lee, S.-H. *Tetrahedron Lett.*, in press.
(7) Corey, E. J.; Wollenberg, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 5581.
(8) Seitz, D. E.; Cartaya, C. P., manuscript in preparation.
(9) Nesmeyanov, A. N.; Borisov, A. E. *Dokl. Akad. Nauk SSSR.* **1967**, *174*, 96. For an improvement of this procedure, see ref. 7, footnote 6.
(10) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 3788.

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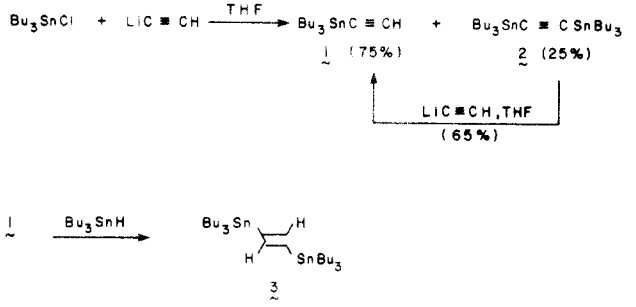
Scheme I



for 1 h at which time 60.0 g (180 mmol) of tri-*n*-butyltin chloride were added dropwise over a period of 30 min. The reaction mixture was warmed to room temperature and stored under a closed acetylene atmosphere for 12 h. Water (10 mL) was added, and the reaction mixture was concentrated in vacuo. Heptane (250 mL) was added, and the reaction mixture was washed with one 100-mL portion of water, dried over $MgSO_4$, and concentrated in vacuo to furnish an oil. Distillation afforded 43 g (75%) of tri-*n*-butylethynylstannane (1): bp 200 °C (2 mm) [lit.[11] bp 76 °C (0.2 mm)]. The NMR and IR spectra of 1 were identical with those of material previously reported.[12]

Conversion of Bis(tri-*n*-butylstannyl)acetylene (2) to Tri-*n*-butylethynylstannane (1). A solution of 80.0 mL (124 mmol) of *n*-butyllithium in hexane in 250 mL of dry tetrahydrofuran was stirred under an acetylene atmosphere at 0 °C for 1 h at which time 30.0 g of the accumulated residues, consisting largely of 2, was added dropwise over a period of 30 min. The reaction mixture was warmed to room temperature and stored under a closed acetylene atmosphere for 15 h. The isolation and purification procedure described above gave 22 g (65%) of 1. The remaining residue may be recycled for the preparation of more 1.[1c]

Registry No. 1, 994-89-8; 2, 994-71-8; 3, 14275-61-7; Bu_3SnCl, 1461-22-9.

(11) Zavgorodnii, V. S.; Sharanina, L. G.; Petrov, A. A. *J. Gen. Chem. USSR.* (*Engl. Transl.*) **1967**, *37*, 1469.
(12) Wollenberg, R. H. Ph. D. Thesis, Harvard University, 1976.

Nonprotic Procedure for Transesterification of Methyl Esters[1]

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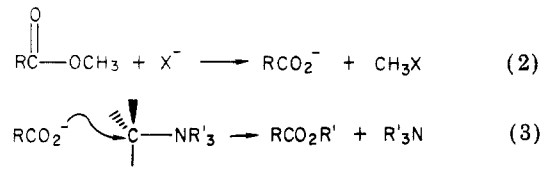
In the course of an unrelated investigation in our laboratory if became necessary to carry out a series of transesterifications under rigorously neutral conditions. A survey of the literature produced only an isolated example which remotely met these needs.[2] We report here our development of one procedure which does meet these qualifications and whose general synthetic applicbility appears to be moderate to good.

Treatment of the methyl ester of various carboxylate acids with tetra-*n*-alkylammonium halide at elevated

Scheme I



temperature leads to the production of the corresponding *n*-alkyl ester (eq 1). Thus, reaction of methyl cinnamate

$$\underset{\mathbf{1}}{RCO_2CH_3} + n\text{-}R'_4N^+X^- \rightarrow \underset{\mathbf{2}}{RCO_2R'} + CH_3X \quad (1)$$

with tetra-*n*-butylammonium bromide at 140 °C for 72 h under anhydrous conditions results in its quantitative conversion to *n*-butyl cinnamate (3). The same reaction repeated with the corresponding tetra-*n*-alkylammonium chloride or iodide under optimized conditions produces, respectively, 78% and 69% yields of 3.

The applicability of this procedure to a representative series of methyl ethers is summarized in Table I. Several aspects about this data deserve brief comment. For example, the rate of reaction, in HMPA solution, exhibits the following dependence on halogen: $Cl^- > Br^- > I^-$. No reaction is observed with $n\text{-}Bu_4N^+BF_4^-$.

Second, higher concentrations of tetra-*n*-butylammonium halide promote higher product yields, a fact which may be related to the further observation that, in general, most solvents have a deleterious effect on the course of this reaction.[3] Thus, in general, optimum results are obtained in the absence of any solvent. Although the use of hexamethylphoshoramide (HMPA) seems to cause little or no diminution in product yield, the workup, isolation, and purification of products obtained from reactions performed in HMPA are generally more difficult.

Third, entries 31 and 32 summarize the influence which the structure of the alkyl group in the tetra-*n*-alkylammonium halide has on the transesterification. Lower yields appear to obtain with tetra-*n*-propyl- than with tetra-*n*-butylammonium halide. In general, the influences of time, solvent, and reactant ratios parallel those presented in Table I.

Mechanistically, we believe the transformation defined by eq 1 is occurring by the pathway outlined in Scheme I. Thus, eq 2 defines the well-known *O*-alkyl cleavage of a methyl ester by nucleophilic displacement while eq 3 presents the alkylation of a carboxylate anion by an onium ion. This scheme is consistent with (i) the previously observed influence which the nature of the group R in the OR functionality has on the *O*-alkyl cleavages of esters,[4,5] (ii) an increasing recognition of the moderately nucleophilic nature of carboxylate ions under *aprotic* conditions,[6] and (iii) the influence exerted by the nature of the alkyl group

(1) This work was supported by the National Science Foundation, Grant 80-17045.
(2) Brasen, W. R.; Hauser, C. R. *Org. Synth.* **1954**, *34*, 58.

(3) Experiments performed in dimethylformamide (DMF) and *N*-methylpyrrolidone produced no significant yield of transesterification product. Transesterification can be effected by using ether tri- or tetraglyme solvent; however, the yields are 20–30% less than those observed for the equivalent reactions performed neat or in HMPA.
(4) Consistent with earlier observations[5] that *O*-alkyl cleavage of esters by nucleophilic displacement is effective only when the alkyl group is methyl, we have observed that treatment of *ethyl* octanoate with 4 equiv of $(n\text{-}C_4H_9)_4N^+Cl^-$ at 140 °C for 36 h produced a 9% yield of *n*-butyl octanoate. Similar treatment of *n*-propyl octanoate failed to yield any (<1%) *n*-butyl octanoate.
(5) Taschner, E.; Liberek, B. *Rocz. Chem.* **1956**, *30*, 323. Elsinger, F.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1960**, *43*, 113. Meyer, W. L.; Levinson, A. S. *J. Org. Chem.* **1963**, *28*, 2184. Krakower, G. W.; Brown, J. W.; Fried, J. *Ibid.* **1962**, *27*, 4710. Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1970**, 4459. McMurry, J. E.; Wong, G. B. *Syn. Commun.* **1972**, *2*, 389 and references therein.
(6) San Filippo, J., Jr.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514 and references therein.

0022-3263/81/1946-5222$01.25/0