stable [(diethoxyphosphinyl)difluoromethyl]zinc bromide (IV) which is acylated with acyl chlorides to yield (2-oxo-1,1-difluoroalkyl)phosphonates. However, acylation of IV with ethyl chloroformate gave little or no II. However, catalysis with cuprous bromide gave a smooth reaction of IV and ethyl chloroformate to provide a good yield of II. Similar catalysis permitted the acylation of IV with diethylcarbamoyl chloride to give the corresponding amide derivative.

Conversion of II to I was accomplished via selective silylation of II at the phosphonic ester site to give V.6 Further silylation of V with the more reactive iodotrimethylsilane gave the trialkylated ester VI.7 Dissolution of VI in water immediately gave I in quantitative yield. I is extremely hygroscopic but may be isolated as a white crystalline monoamine salt (VII) or as a stable monohydrate of the disodium salt (VIII) of I.

Aqueous titration of I gave two breaks with a stoichiometry of 1.993 (± 0.013) to 1 indicative of three acidic protons. Ionization constants of I were determined from titration of multiple independent titrations. The ionization constants were calculated by fitting the titration data to a titration function via a nonlinear least-squares program.8 Table I summarizes the ionization constants of I relative to phosphonoacetic acid and the analogous (difluoromethylene)bisphosphonic acid.9

A typical preparation of II is described with operational details. To a 3-L flask equipped with a reflux condenser and cooled in an ice bath was added 267.0 g (1.0 mol) of III and 500 mL of dry monoglyme. Then 65.4 g (1.0 mol) of acid-washed zinc powder was added in one portion. The temperature was allowed to slowly rise until a vigorous exothermic reaction was initiated. After 4 days at room temperature, the solution was filtered in a Schlenk funnel (medium frit) and diluted with 250 mL of dry CH2CN. Then 2.0 g (0.014 mol) of CuBr was added followed by 115 mL (1.2 mol) of ethyl chloroformate. The reaction mixture was stirred overnight and the volume was reduced by rotary evaporation and then diluted with 500 mL of water. The insoluble Inorganic salts were separated by mixture was stirred overnight and the volume was reduced to phosphonoacetic acid and the analogous (difluoromethylene)bisphosphonic acid.

Summary: 2,3-Bis(trimethylstannyl)-1,3-butadiene and 1,4-Bis(trimethylstannyl)-2-butyne

Sir: We report here procedures for the preparation of a wide variety of 2,3-disubstituted 1,3-butadienes using two new synthetic equivalents of the 2,3-dianion of 1,3-butadiene, mono and bis derivatizations with electrophiles such as haloisilanes, disulfides, selenium, alkyl halides, aldehydes, and ketones have been carried out.

Organotin Chemistry. Preparation of 2,3-Disubstituted 1,3-Butadienes Using 2,3-Bis(trimethylstannyl)-1,3-butadiene and 1,4-Bis(trimethylstannyl)-2-butyne


(4) Compound I can be reliably isomerized to 2 by treatment with a catalytic amount of (CH3)3SnLi or CH3Li in THF/HMPA (2 equiv) at 25 °C for 30 min. The minimum conditions needed for the isomerization vary with the batch of (CH3)3SnLi. One-pot conversion of 1,4-dichloro-2-butyne to 2 can be accomplished in 70% yield. To reproducibly obtain 1 free of 2, the original reaction mixture must be quenched with H2O at -78 °C (84% yield). Trisilylethylidihydrochlorosilane was prepared by the procedure of Tamborski, C.; Ford, F. E.; Soloski, E. J. J. Org. Chem. 1963, 28, 237. We found it necessary to employ lithium wire containing 1% sodium.
We have explored the utility of 3 as a precursor to 2-X-3-(trimethylstannyl)-1,3-butadienes and found that silylation, alkylaion (1° iodides and bromides), selenylation, selenenylation, and hydroxyalkylation could be carried out in generally good yields (Table I). The amounts of allenic products formed were small or undetectable in most cases. However, when 3 was converted to the Grignard reagent by reaction with MgBr₂ in ether/benzene, formation of allene was observed on reaction with aldehydes and ketones (Table I, entry 9). Lithium reagent 3 was also converted to a cuprate and this used for conjugate addition reactions (Table I, entry 10). No allene was seen in this reaction.

If the groups introduced during the above reactions are stable toward strong bases, a second Li/Sn exchange—derivationization can be performed. Several butadienes prepared in this way together with reagents and yields are shown in Scheme II.

The Li/Sn exchange of 2 and the monoderivatized butadienes 6 appears to be more rapid than the reaction of methyllithium with many electrophiles, so that double derivatizations can be carried out in situ by simply adding 2–3 equiv of MeLi to a solution of 2 and 2 equiv of the electrophile in THF at −78 °C. Scheme II also gives several examples of this technique.

Propargylstannanes and silanes generally undergo electrophilic substitution with the formation of allenes. Two sequential reactions of the bis(stannyl)acetylene 4 should thus lead to butadienes. Two successful examples of this process are the reaction with iodine to give the easily polymerizable 2,3-diodobutadiene (8) and with Eschenmoser's salt to give the bis(dimethylamino)methyl diene (9).

Several others we have tried (Lewis acid catalyzed...
Redox-Switched Crown Ethers. Cyclic–Acyclic Interconversion Coupled with Redox between Dithiol and Disulfide

Summary: Synthesis, ion affinity, and redox properties of a pair of "redox-switched" crown analogues with a dithiol group at α,ω-positions (Crred) and a disulfide bond in the ring (Crox) are described.

Sir: Macrocyclic polyethers contain intramolecular cavities delineated by molecular segments and are capable of specific chelation with alkali and alkaline earth metal cations. It is now established that the specificity stems largely from the size of the intramolecular cavities, one may expect that if the topological ring shape can be reversibly changed, it would lead to the control of ion-binding ability and ion selectivity. The photo- and pH-responsive crown ethers are typical examples. It occurred to us that the most direct change in the cavity shape would be attained by reversible bond formation and bond scission leading to cyclic–acyclic interconversion and the redox reaction of a thiol–disulfide couple would be the most suitable candidate for this. We here report a pair of new "redox-switched" crown ether analogues bearing a disulfide bond in the ring and a dithiol group at its α,ω-positions. The oxidized form (Crox: 2,3-benzo-1,4,7,10,17,20-hexaoxa-13,14-dithiacyclococos-2-ene) is a coronand analogue and expected to bind metal ions in the cavity. The reduced form (Crred: 10,11-benzo-3,6,9,12,15,18-hexaoxaecos-10-ene-1,20-dithiol) is a podand analogue and expected to show poor ion affinity.

Crred was synthesized by route 1 and finally isolated by a TLC method. On the other hand, purification of Crred was very difficult because of ready oxidation either to Crred or to oligomeric materials. We thus used route 2 in which the final step (H2NNH2 treatment) proceeded under reductive atmosphere. As the product was protected from air oxidation, Crred could be easily isolated.

The ion-binding ability of Crred was estimated by anaerobic solvent extraction of alkali metal salts of 8-anilinonaphthaleine-1-sulfonate (ANS) from water to chloroform and was compared with that of monobenzo-

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