

Preliminary communication

Chemistry of alkali metal-unsaturated hydrocarbon adducts IX★. Radical-anionic coupling of Group IV organometalloidal compounds

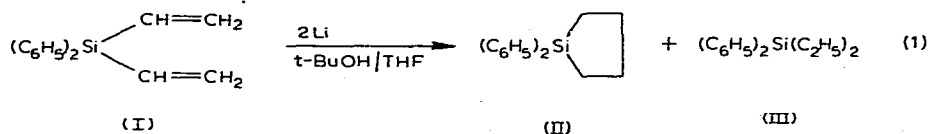
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Attempts to extend the bimolecular couplings observed with triphenyl(vinyl)silane¹ and with cyclopropyl(triphenyl)silane² to other compounds of silicon or Group IV metalloids have often led to polymerization or cleavage processes. For example, treatment of either diphenyl(divinyl)silane or triphenyl(vinyl)germane with lithium metal in tetrahydrofuran at -75° leads to polymeric products. Since a recent ESR study has shown that such vinylic organometalloids form very short-lived radical-anionic intermediates³, we realized that a controlled coupling could only be achieved by chemical quenching of anionic intermediates at an early stage. In this Communication we wish to report a synthetically useful extension of such bimolecular coupling and to offer some evidence on the relative reactivity of radical anions of the type, $R_3E-\dot{C}H-\dot{C}HR'$, where $E = Si, Ge$ or Sn .

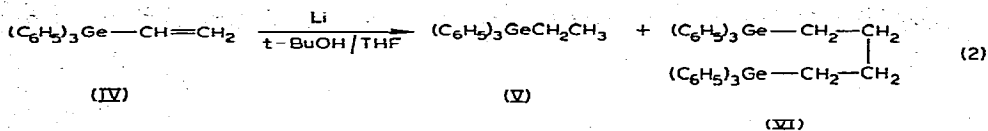
The slow addition of a mixture of the vinylic organometalloid and *t*-butyl alcohol⁴ to a slurry of one gram-atom equivalent of lithium pieces in anhydrous THF at -75° and the usual hydrolytic work-up led only to monomeric or dimeric reduction products. When this procedure was applied to diphenyl(divinyl)silane (I) (with use of 2 equivalents of lithium and the alcohol), a 50% yield of 1,1-diphenylsilacyclopentane (II)⁵ was obtained; the balance of the product was diethyl(diphenyl)silane (III):



The ready availability of various divinylsilanes makes this intramolecular coupling reaction an appealing route to silicon heterocycles.

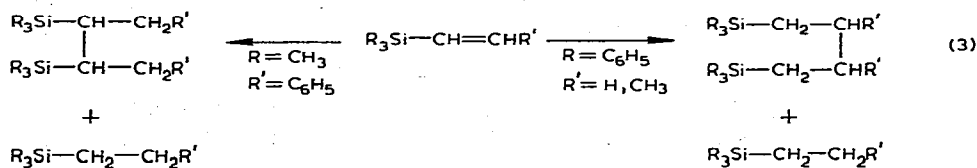
★ For Part VIII see ref. 3.

In a similar manner, the treatment of triphenyl(vinyl)germane (IV) gave no polymer but some germanium-vinyl bond cleavage did occur, leading to triphenylgermane. The major products were ethyl(triphenyl)germane (V) and 1,4-bis(triphenylgermyl)butane (VI) in 60% and 35% yields, respectively. The nature of VI was confirmed by the preparation of an authentic sample from 1,4-dibromobutane and triphenylgermyllithium⁶.

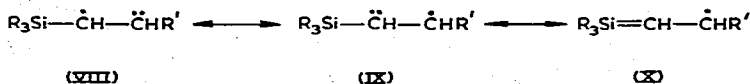


Extension of the procedure to triphenyl(vinyl)tin (VII) led exclusively to tin-vinyl bond cleavage. In fact, when VII in 1,2-dimethoxyethane was exposed to a potassium mirror at -75° and the worked up, a 91% yield of hexaphenyldistannane was realized^{6,7*}.

The site of bimolecular coupling in vinylsilanes of the type, $\text{R}_3\text{Si}-\text{CH}=\text{CHR}'$, was also shown to vary with structure. Whereas triphenyl(vinyl)silane¹ and triphenyl(1-propenyl)silane underwent coupling at the carbon β to silicon, trimethyl(*trans*- β -styryl)silane underwent coupling through the carbon α to silicon:



The foregoing behavior of vinylic metalloids, taken together with the ESR detection of radical-anionic intermediates in some of these reactions³, can be interpreted in terms of relative radical-anionic stabilization. In the first place, the sites of bimolecular coupling in eq. 3 suggest that the phenyl group increases the resonance contribution of VIII over that of IX ($\text{R}=\text{CH}_3$, $\text{R}'=\text{C}_6\text{H}_5$), while resonance structure IX seems to be more important, when $\text{R}=\text{C}_6\text{H}_5$ and $\text{R}'=\text{H}$ or CH_3 :



Secondly, the radical-anions $(\text{C}_6\text{H}_5)_3\text{E}-\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}_2$, seem to decrease in stability as $\text{E}=\text{Si}$, Ge or Sn , successively. Thus, the germanium compound polymerizes under conditions where the silicon analog smoothly dimerizes, and the tin member must undergo immediate devinylation to yield the observed hexaphenyldistannane. The superior stabilization of $(\text{C}_6\text{H}_5)_3\text{Si}-\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}_2$ over $(\text{C}_6\text{H}_5)_3\text{Ge}-\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}_2$ can be ascribed to greater $d_{\pi-p\pi}$ bonding in the former⁸, as indicated in structure X.

* Although the cleavage of $\text{R}_3\text{Sn}-\text{CH}=\text{CH}_2$ by lithium metal with the formation of Sn or R_3SnLi has been reported (ref. 7), the formation of $\text{R}_3\text{Sn}-\text{SnR}_3$ in such reactions has not. An appealing, but not compelling, mode of forming the distannane would be the encounter between radical anions of VII and their coupling through the tin centers with loss of vinyl anions.

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