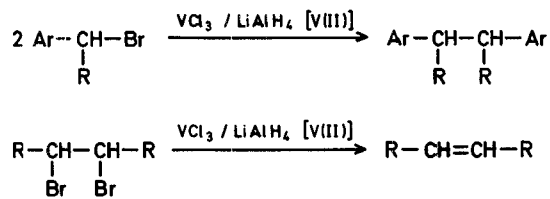


solution the hydrodehalogenation of α -haloketones², deoxygenation of sulfoxides³, reduction of benzils and quinones⁴, hydrogenative cleavage of aryl azides⁵, and reductive dimerization of tropylium salts⁶ with vanadium(II) chloride proceed smoothly and with good yields.

Reductions in nonaqueous media are also of great interest because nonacidic conditions can be employed and potential problems of substrate solubility can be eliminated. We now report the coupling of benzylic and allylic halides and debromination of *vic*-dibromides with a vanadium(II) reagent in tetrahydrofuran. A literature search showed that dicyclopentadienylvanadium has been utilized to couple benzyl chloride⁷ to give a 53% yield of bibenzyl based on gas chromatographic analysis. A kinetic study of dichlorotetrakis[pyridine]vanadium-promoted reductive dimerization⁸ of benzyl halides has also been reported. The difficult availability of the reagents, however, precludes their synthetic applications.

We now wish to describe a convenient and easy to apply generation of a vanadium(II) reagent by the lithium tetrahydroaluminate reduction of vanadium(III) chloride in anhydrous tetrahydrofuran. In order to compare its reducing power with that of the titanium(II) reagent of McMurry⁹, identical molar ratios of VCl_3 to $LiAlH_4$ were used in the reagent mixtures. Dehalogenative coupling of benzylic and allylic halides was accomplished with yields comparable or better than those using the Ti(II) reagent¹⁰. *vic*-Dibromides are similarly converted in good yields into the corresponding alkenes.



Synthetic Methods and Reactions; 34¹. Coupling of Benzylic and Allylic Halides and Debromination of *vic*-Dibromides with Vanadium(III) Chloride/Lithium Tetrahydroaluminate, $VCl_3/LiAlH_4$, Reagent

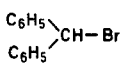
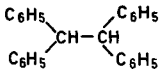
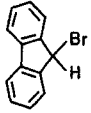
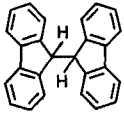
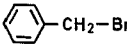
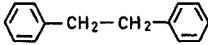

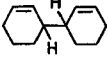
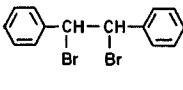
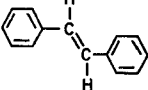


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Recently we described some of our studies relating to the vanadium(II) ion reduction of organic compounds. In acidic

The V(II) systems are experimentally more convenient than the Ti(II) systems since vanadium(III) chloride is stable to air, whereas titanium(III) or (IV) chloride precursors are sensitive to oxygen and moisture. The mixing of VCl_3 and $LiAlH_4$ is only mildly exothermic and therefore less hazardous. Furthermore, the aqueous workup of reaction mixtures of the V(II) reductions is not attended by the formation of voluminous sludges as in the Ti(II) reactions.

Table. Reductive Coupling and Dehalogenation of Halides with V(II) Reagent

Substrate	Product	Yield [%]	m.p. or b.p./torr	Lit. m.p. or b.p./torr
 $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$		95	m.p. 212°	m.p. 214–215° ¹³
		96	m.p. 245°	m.p. 247° ¹³
		82	m.p. 51°	m.p. 52.2° ¹³
		80	90–93°/~5	b.p. 62–63°/0.5 ¹⁴
		97	m.p. 125°	m.p. 124.5–124.8° ¹³
 (E)	 (Z)	68	b.p. 142–145°	b.p. 143° ¹³

Extension of the use of our V(II) reagent to couple benzylic alcohols and aromatic ketones¹¹ has, however, not been as successful owing to the relatively low reduction potential of V(II) species. Benzyl alcohol was recovered unchanged, benzhydrol undergoes coupling to the extent of approximately 40%. Thus the nonaqueous system holds no special advantage over the conventional acidic V(II) reagent¹² for coupling of these compounds.

Reaction of Halides with $\text{VCl}_3/\text{LiAlH}_4$ Reagent:

In a two-necked flask equipped with magnetic stirrer, serum cap, and a refluxing condenser connected to a nitrogen purge was placed a suspension of vanadium(III) chloride (2.36 g, 15 mmol) in dry tetrahydrofuran (20 ml). Lithium tetrahydroaluminate (190 mg, 5 mmol) was added, and after 5 min the halide (5 mmol) was introduced from a syringe as a neat liquid or in the case of solids, as a tetrahydrofuran solution (5 ml). The reaction mixture was then refluxed for the time indicated in the Table, and subsequently quenched with water (80 ml). Benzene extraction (2 × 30 ml) of the aqueous solution yielded, after drying and evaporation, the hydrocarbon product which was distilled or recrystallized. The physical and spectral properties of the products were identical to these reported for pure, authentic materials.

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