

Synthetic Methods and Reactions; XVIII¹. Preparation of Alkenes via Dehalogenation of *vic*-Dihaloalkanes, Coupling of Allyl and Benzyl Halides, Dehalogenative Coupling of Aryl-*gem*-dihaloalkanes using TiCl_3 - or $\text{TiCl}_4/\text{LiAlH}_4$ Reagent

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Some time ago, McMurry reported the reductive coupling of allyl and benzyl alcohols to substituted alkanes² and the reduction of bromohydrins to alkenes³ using his low-valent titanium reagent developed to couple carbonyl compounds. Quite recently, he modified this reagent to couple aliphatic ketones⁴. Since then, several research groups^{5,6}, including ours⁷, have utilized this useful reagent to synthesize several hindered olefins. Corey et al.⁸ have shown that a wide variety of reductive coupling reactions can be effected by slightly modifying the reagent. Mukaiyama et al.⁹ have used $\text{TiCl}_4/\text{LiAlH}_4$ reagent to dehalogenate vinylic and aromatic halides.

We report now our results on dehalogenation of *vic*-dihaloalkanes (**1**) to alkenes (**2**), coupling of allyl and benzyl halides (**3**) to alkanes (**4**), and dehalogenative coupling of aryl-*gem*-dihaloalkanes (e.g. benzylidene dichloride) (**5**, $\text{R}^1 = \text{C}_6\text{H}_5$) to aryl-substituted ethylenes (**6**) using TiCl_3 - or $\text{TiCl}_4/\text{LiAlH}_4$ reagent in tetrahydrofuran.

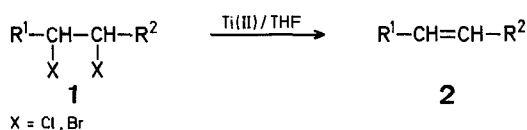
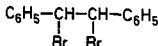
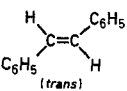
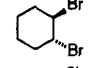

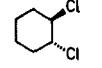

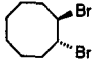

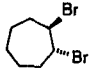

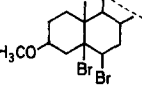
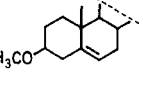
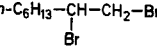
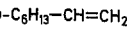
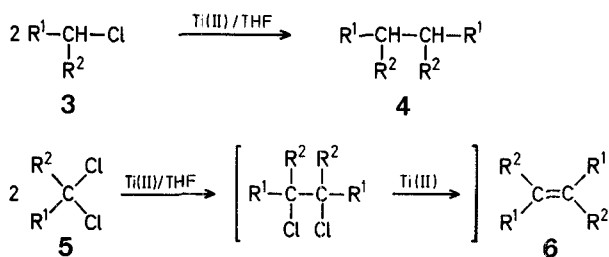


Table 1. Dehalogenation of *vic*-Dihaloalkanes (**1**) to Alkenes (**2**)

1	2^a	Yield ^b [%]
		88
		78
		72
		72
		81
		84
		84

^a All products were identified by comparison of their physical properties with those of authentic samples.

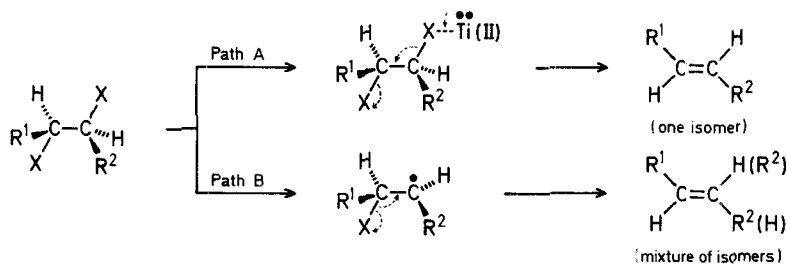
^b Isolated product.



Ti(III) = $\text{TiCl}_3/\text{LiAlH}_4$ or $\text{TiCl}_4/\text{LiAlH}_4$

Zinc/acetic acid, zinc/ethanol, and sodium/ammonia have been so far the most widely employed systems for reductive dehalogenation of *vic*-dihaloalkanes¹⁰. The yields are moderate with the first two reagents, whereas excellent yields are generally obtained with sodium/liquid ammonia, but the method has some operational difficulties. The reaction of *via*-dihaloalkanes (1) with TiCl_3 - or $\text{TiCl}_4/\text{LiAlH}_4$ is clean and generally good yields of alkenes (2) were obtained. 1,2-Dibromostilbene gave *trans*-stilbene as the sole product (Table 1). We have not investigated, however, the stereochemistry of the products in detail.

The mechanism of the reaction may be rationalized by assuming two different pathways (A and B).



There are numerous methods available to couple allylic and benzylic halides¹¹. We consider, however, the reagent obtained from TiCl_3 - or $\text{TiCl}_4/\text{LiAlH}_4$ to be the most efficient coupling reagent so far available. A radical mechanism for the coupling reaction seems most probable.

Table 2. Reductive Coupling of Benzylic and Allylic Halides (3)

3	→	4 ^a	Yield ^b [%]
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{CH}-\text{Cl} \\ \\ \text{C}_6\text{H}_5 \end{array}$	→	$\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \quad \\ \text{CH}-\text{CH} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	85
$\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$	→	$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5$	76
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{CH}-\text{Cl} \\ \\ \text{C}_6\text{H}_5 \end{array}$	→	$\begin{array}{c} \text{H}_3\text{C} \quad \text{C}_6\text{H}_5 \\ \quad \\ \text{CH}-\text{CH} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array}$	83
$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	→	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{CH}_2 \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{CH}_3 \end{array}$	76 ^d

^a All products were identified by comparison of their physical properties with those of authentic samples.

^b Isolated product.

^c The major product is *meso*-2,3-diphenylbutane; m.p. 123–124°¹².

^d b.p. 116°/760 torr (Ref.¹⁴, b.p. 114.3°/760 torr).

gem-Dihaloalkanes have been coupled using Zn-Cu couple¹³. We have now found that aryldichloromethanes (5, $\text{R}^1 = \text{C}_6\text{H}_5$) are coupled in a very similar manner by the titanium(II) reagent to give the corresponding aryl-substituted ethylenes (6) in high yields (Table 3). *trans*-Stilbene was the sole product obtained from benzylidene dichloride.

The reaction presumably proceeds through a *vic*-dihalide intermediate. Aliphatic *gem*-dihalides failed to react under the same reaction conditions. The reported examples are representative and do not limit the application of the reagent to other halides.

Table 3. Reductive Coupling of Aryldichloromethanes (5)

5	→	6 ^a	Yield ^b [%]
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C} \\ \\ \text{C}_6\text{H}_5 \\ \\ \text{Cl} \end{array}$	→	$\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	96
$\text{C}_6\text{H}_5-\text{CHCl}_2$	→	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ (<i>trans</i>)	79

^a Identified by comparison with authentic samples.

^b Isolated product.

Preparation of the Titanium(II) Reagent:

Lithium alanate (LiAlH_4 , 1.9 g, 0.05 mol) is added carefully to a stirred slurry of titanium(III) chloride (15.43 g, 0.1 mol) in tetrahydrofuran (200 ml) under dry nitrogen. Hydrogen evolution is immediate and the resultant black slurry is stirred for 30 min. Alternatively, the same reagent can be prepared from lithium alanate (3.8 g, 0.1 mol) and titanium(IV) chloride (18.0 g, 0.1 mol) as described above.

Dehalogenation of *vic*-Dihaloalkanes (1) to Alkenes (2); General Procedure:

To the titanium(II) reagent prepared as described above, a solution of the *vic*-dihaloalkane 1 (0.1 mol) in dry tetrahydrofuran (50 ml) is added dropwise with stirring over a 30 min period. The mixture is then refluxed for 8 h and worked up by the addition of aqueous ammonium chloride and extraction with ether. The extract is dried, the solvent distilled off, and the product 2 purified by distillation or recrystallization.

Reductive Coupling of Allyl and Benzyl Halides (3) to Substituted Alkanes (4); General Procedure:

To the titanium(II) reagent prepared as described above, a solution of the allyl or benzyl halide 3 (0.1 mol) in tetrahydrofuran (50 ml) is added dropwise with stirring. The mixture is refluxed for 10 h and then worked up as described above.

Reductive Coupling of Aryldichloromethanes (5, $\text{R}^1 = \text{C}_6\text{H}_5$) to Aryl-substituted Ethylenes (6):

The *gem*-dichloro compound 5 (0.05 mol) in tetrahydrofuran (30 ml) is added dropwise to the stirred titanium(II) reagent prepared as described above. The reaction mixture is refluxed for 10 h and the product 6 isolated by work-up as above.

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¹ Part XVII: G. A. Olah, J. Welch, T. L. Ho, *J. Am. Chem. Soc.*, in press.

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