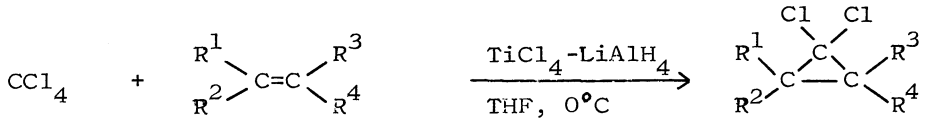
CHEMISTRY LETTERS, pp. 711-712, 1975. Published by the Chemical Society of Japan

A CONVENIENT METHOD FOR THE PREPARATION OF gem-DICHLOROCYCLOPROPANE DERIVATIVES BY THE USE OF $TiCl_4$ AND $LiAlH_4$

Teruaki MUKAIYAMA, Manzo SHIONO, Kenzo WATANABE, and Makoto ONAKA
Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113

gem-Dichlorocyclopropane derivatives are obtained in good yields by the application of low valent titanium chloride, prepared from $TiCl_4$ and $LiAlH_4$, to carbon tetrachloride in the presence of olefins.

In the course of our continuing study on the exploration of new synthetic reactions using low valent titanium chloride, it was recently found that various β -hydroxysulfides were converted into the corresponding olefins in good yields by way of the reductive β-elimination.[1] In this paper we deal with the preparation of gem-dichlorocyclopropane derivatives from carbon tetrachloride and olefins by way of the reductive α-elimination using low valent titanium chloride. The low valent titanium chloride was prepared by the treatment of $TiCl_4$ with an equimolar amount of $LiAlH_4$ in THF. The application of the reagent thus prepared to carbon tetrachloride in the presence of olefins at 0°C under an argon atmosphere resulted in the formation of gem-dichlorocyclopropane derivatives in good yields.



Concerning the synthesis of gem-dichlorocyclopropane derivatives, the following representative methods are well known[2], namely, A) the reaction of chloroform with bases as alkyllithiums, alkali metal alkoxides, and alkali metal hydroxides along with quaternary ammonium salts[3]; B) the thermal decomposition of trichloroacetate ions, C) the reaction of trichlorocarbonyl compounds with bases as potassium t-butoxide, D) the thermal decomposition of phenyltrihalomethylmercury, and E) the reaction of polyhalomethane with alkyllithium. In the above mentioned methods, it is pointed out that methods A), C), and E) generally require strongly basic conditions, method D) is inconvenient in the point of view that the starting material is not readily available, and method B) does not always afford satisfactory yields.

The characteristic feature of the present method is apparently different from the above mentioned methods in the following points; 1) the reaction is carried out under slightly acidic condition, and 2) the starting materials as carbon tetrachloride, $TiCl_4$, and $LiAlH_4$ are readily available.

Table. Preparation of gem-Dichlorocyclopropane Derivatives.

Olefin	Yield,%	Purity,% (G.L.P.C.)	Bp, °C (mmHg)
Cyclohexene	79	98	73-76 (12)
Cyclooctene	82	98	109-112 (20)
α-Methylstyrene	60	97	81-82 (3)
2,3-Dimethyl-2-butene	65	99	65 (20)
Dihydropyran	82	95	76-79 (8)

The following procedure is representative. To a stirred suspension of $TiCl_4$ (4.334 g, 22.8 mmol) in 30 ml THF was added a solution of $LiAlH_4$ (0.866 g, 22.8 mmol) in 20 ml THF at 0°C. During the addition of $LiAlH_4$, hydrogen was vigorously evolved and the reaction mixture turned to black, which was presumed to indicate the formation of low valent titanium chloride. After stirring the mixture for 30 min at room temperature, cyclohexene (5.121 g, 62.4 mmol) and then a solution of carbon tetrachloride (3.192 g, 20.8 mmol) in 10 ml THF was successively added to the resulting mixture at 0°C. After being stirred for an additional 1 hr at 0°C, the reaction mixture was poured into an aqueous sodium bicarbonate solution, and extracted with hexane. The combined hexane solution was washed with water, dried over anhydrous sodium sulfate, and distilled. There was obtained 2.690 g (79% yield) of 7,7-dichloro [4,1,0] heptane, bp 73-76°C (12 mmHg), whose purity by glpc was approximately 98%. In a similar manner, various gem-dichlorocyclopropane derivatives were prepared in good yields as shown in the above Table.

It is noted that the present method would be useful for the preparation of gem-dichlorocyclopropane derivatives in respect that the reaction is performed under mild conditions and that the starting materials are readily available.

Further works on the scope and the utility of the present reaction are now in progress.

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(Received May 22, 1975)