

CHEMISTRY OF THE WITTIG REACTION, IV<sup>1</sup>  
SIMPLE CONVERSION OF ALDEHYDES TO 1,1-DICHLOROALKANE AND 1,1-DICHLORO-  
-1-ALKENE DERIVATIVES, USEFUL INTERMEDIATES FOR THE SYNTHESIS OF  
ACETYLENIC COMPOUNDS

Peter VINCZER<sup>a,\*</sup>, Szilvia STRUHAR<sup>a</sup>, Lajos NOVAK<sup>b</sup> and Csaba SZANTAY<sup>a,b,\*</sup>

<sup>a</sup>Central Research Institute for Chemistry of the Hungarian Academy of  
Sciences  
1525 Budapest, P.O.Box 17, HUNGARY

<sup>b</sup>Institute for Organic Chemistry, Technical University  
1521 Budapest, P.O.Box 91, HUNGARY

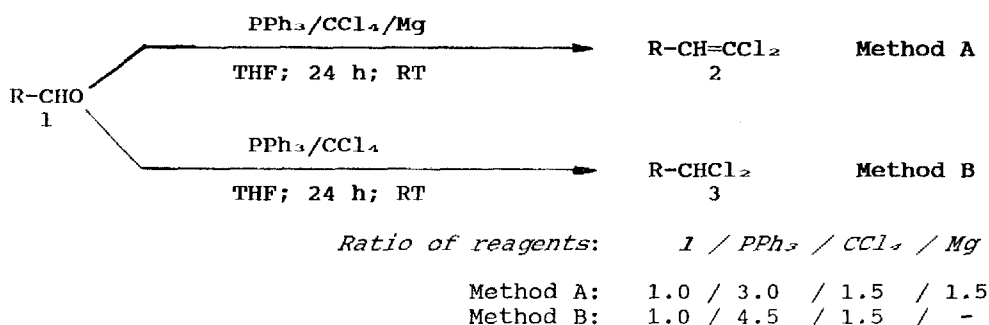
**Key Words:** 1,1-Dichloroalkanes; 1,1-Dichloro-1-alkenes; Wittig Reaction;  
Acetylene from Aldehyde;

**ABSTRACT:** *The formation of 1,1-dichloroalkanes and 1,1-dichloro-1-alkenes from aldehyde is described using triphenylphosphine - carbon tetrachloride reagent system. Different products can be formed by changing the reaction conditions.*

The formation of terminal, disubstituted and 1-halo-1-alkynes is often an important step in the synthesis of natural products. The transformation of aldehydes to acetylenes usually involves a two-step procedure<sup>2</sup>. The triphenylphosphine - carbon tetrabromide system<sup>2,3</sup> is the reagent of choice for this conversion. An improvement of this method is the addition of zinc to the reaction mixture decreasing or eliminating the formation of side products<sup>2a,b</sup>. These methods have some disadvantages. Carbon tetrabromide is an expensive and very hygroscopic reagent. Other problem is the yielding of volatile 1,1-dibromo-1-alkenes from the reaction mixture.

Changing the CBr<sub>4</sub> for the less expensive and non-hygroscopic carbon tetrachloride<sup>4</sup> results in the formation of a mixture of 1,1-dichloroalkane (3) and 1,1-dichloro-1-alkene (2). The separation of these compounds is rather difficult.

Now we wish to report a new method for the preparation of either 1,1-dichloro-1-alkene or 1,1-dichloroalkane from the same aldehyde simply by choosing the proper conditions of reaction (Scheme 1).

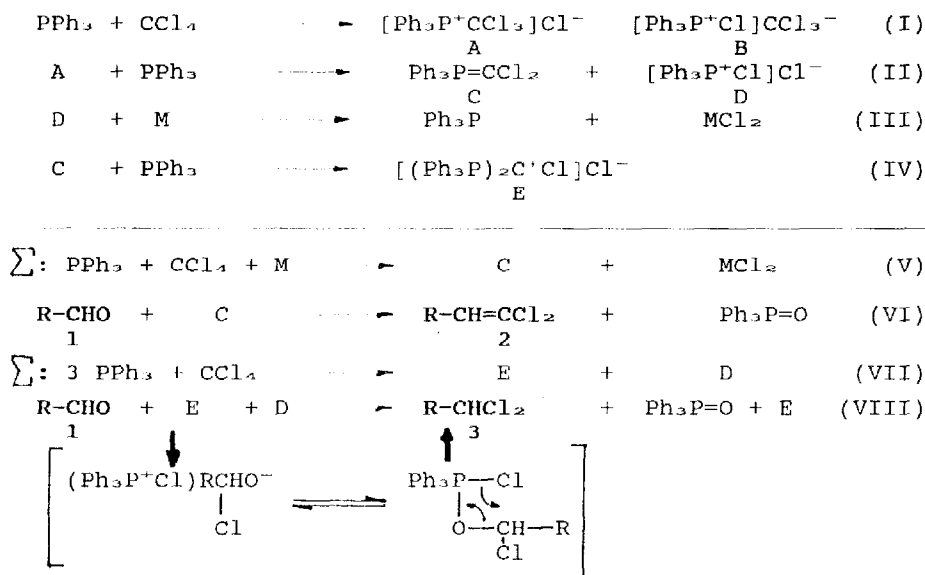


SCHEME 1.

The proposed mechanism of this reaction is shown in Scheme 2.

Carbon tetrachloride reacts with triphenylphosphine to form a mixture of ylide C and chlorotriphenylphosphonium chloride (D). C forms 1,1-dichloro-1-alkene (2) from aldehyde (1) and D forms the 1,1-dichloroalkane (3).

To form 2 from aldehyde (1) D must be eliminated from the mixture. It can be done by addition of zinc powder (Scheme 2; Eq. III., M=Zn). The effectivity of zinc depends on its activity and the concentration.



SCHEME 2.

To improve this process the zinc was replaced by activated magnesium.

The chips is the best form of magnesium. The powder is too active and produces side reactions through Grignard-type intermediate.

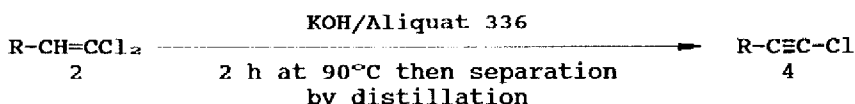
The sufficient activation of the granular form of Mg is difficult. Generally, the purification of the surface of the metal by washing thoroughly with dry ether is enough<sup>5</sup>.

The products ( Table 1.) are isolated by chromatographic methods (flash or SDC<sup>6</sup>) from the reaction mixture, after filtration of the precipitated triphenylphosphine oxide and magnesium chlorides. If the product is highly volatile and difficult to separate from the solvent, the crude reaction mixture can also be used for further transformation (e.g.: elimination of chloride by base) after filtration of the precipitated side products.

To preface 3 from aldehydes, C can be eliminated by adding a third equivalent of Ph<sub>3</sub>P to form E which precipitate from the mixture (Scheme 2, Eq. IV).

The advantages of these methods are the mild and neutral conditions and the simple preparation procedures. The final products can be isolated by distillation, or chromatography or used up in elimination processes without any purification.

Finally, we have also developed an effective procedure for the preparation of 1-chloro-1-alkynes (4) from 2 using PTC conditions without solvent.



SCHEME 3.

**General Procedure for the Formation of 1,1-Dichloro-1-alkenes (2) from Aldehydes:**

*Triphenylphosphine (3.0 equiv.) was dissolved in dry THF (5.0 ml/g PPh<sub>3</sub>) and carbon tetrachloride (1.5 equiv.) was added to the solution at 25°C. The resulting mixture was stirred at 25°C for 2 h and activated magnesium (1.5 equiv.) was added to the mixture. After stirring for 30 min, the aldehyde (1; 1.0 equiv.) was added to the well-stirred suspension, stirred for overnight and filtrated through a silica gel bed (wetting by THF; Kieselgel 60, 0.063-0.200 mm, 70-230 mesh, MERCK) containing 50% of dry magnesium sulfate. The resulting filtrate can be used without purification or purified by flash chromatography or SDC<sup>6</sup> method, after evaporation of solvent in vacuo.*

**General Procedure for the Formation of 1,1-Dichloroalkanes (3) from Aldehydes:**

*To a solution of triphenylphosphine (4.5 equiv.) in dry THF (3.0 ml/g PPh<sub>3</sub>) carbon tetrachloride (1.5 equiv.) was added and stirred at 25°C for 3 hours. After filtration of the precipitate (E) formed, the aldehyde (1; 1.0 equiv.) was added to the filtrate and stirred at 25°C for 24 hours. After evaporation of the solvent the product (3) was isolated by*

chromatography (flash or SDC<sup>®</sup>) or in case of volatile compounds the filtrated reaction mixture was used for further transformations.

Above 10 g of starting compound (1) the formation of **E** needs 5-7 h. When the temperature is higher than 25°C the yields of 1,1-dichloroalkanes (3) were moderate and no any precipitate was formed.

#### General Method for the Preparation of Distillable 1-Chloro-1-alkynes:

The mixture of 1,1-dichloro-1-alkene (2; 1.0 equiv.), powdered KOH (1.0 equiv.) and Aliquat 336 (ALDRICH; 0.2 ml/g 2) was stirred at 90°C for 2 h. The product (4)<sup>°</sup> was distilled off directly from the reaction mixture.

TABLE 1.	1		Yield of		
	R= X-(CH <sub>2</sub> ) <sub>n</sub> - X	n	2	3	4
	CH <sub>3</sub>	3	70	50	50
	CH <sub>3</sub>	5	85	70	80
	CH <sub>3</sub>	6	75	70	80
	CH <sub>3</sub>	7	75	70	90
	CH <sub>3</sub>	10	80	90	90
	CH <sub>3</sub> OOC	7	60	75	50 <sup>†</sup>

<sup>†</sup> During the elimination the ester group was hydrolyzed and the acid formed couldn't distilled from the mixture. However, after neutralisation we can extract this acid by toluene.

#### REFERENCES AND NOTES

- Part III.: VINCZER, P.; NOVAK, L. and SZANTAY, Cs.: *Org. Prep. Proced. Int.*, 1991, (23) 443-447.
- a) COREY, E.J. and FUCHS, L.R.: *Tetrahedron Lett.*, 1972, 3769-3772.  
b) VILLIERAS, J.; PERRIOT, F. and NORMANT, J.F.: *Synthesis*, 1975, 458-461  
c) BESTMANN, H.J. and FREY, H.: *Liebigs Annalen Chem.*, 1980, 2061-2071.  
d) BESTMANN, H.J. and LI, K.: *Chem. Ber.*, 1982, (115) 828-831.
- RAMIREZ, F.; DESAI, N.B. and MCKELVIE, N.: *J. Am. Chem. Soc.*, 1962, (84) 1745-1747.
- a) APPEL, R.: *Angew. Chem.*, 1975, (87) 863-874.  
b) APPEL, R.; KNOLL, F.; MICHEL, W.; MORBACH, W.; WIHLER, H.D. and VELTMANN, H.: *Chem. Ber.*, 1976, (109) 58-70.
- Activation of Mg, see:
- a) LAI, Y.-H.: *Synthesis*, 1981, 585-604.  
b) BAKER, K.V.; BROWN, J.M.; HUGHES, N.; SKARNULIS, A.J. and SEXTON, A.: *J. Org. Chem.*, 1991, (56) 698-703 and references cited therein.
- SDC= Semi-Dry Column Chromatography. (See the details in Ref. 1.)
- Characteristic NMR data of 1,1-dichloro-1-alkenes (2):  
<sup>1</sup>H-NMR (100 MHz; CDCl<sub>3</sub>): 2.1(-CH<sub>2</sub>C=); 5.9(-CH=) ppm.  
<sup>13</sup>C-NMR (25.2 MHz; CDCl<sub>3</sub>): 28.1-28.3(-CH<sub>2</sub>C=); 130.1-130.3(-CH=); 119.7-119.8(=CCl<sub>2</sub>) ppm.
- Characteristic NMR data of 1,1-dichloroalkanes (3):  
<sup>1</sup>H-NMR (100 MHz; CDCl<sub>3</sub>): 2.1-2.3(-CH<sub>2</sub>-CHCl<sub>2</sub>); 5.7-5.8(-CHCl<sub>2</sub>) ppm.  
<sup>13</sup>C-NMR (25.2 MHz; CDCl<sub>3</sub>): 43.6-43.8(-CH<sub>2</sub>-CHCl<sub>2</sub>); 73.6-73.8(-CHCl<sub>2</sub>) ppm
- Characteristic NMR data of 1-chloro-1-alkynes (4):  
<sup>1</sup>H-NMR (100 MHz; CDCl<sub>3</sub>): 2.1-2.5(-CH<sub>2</sub>-C≡) ppm.  
<sup>13</sup>C-NMR (25.2 MHz; CDCl<sub>3</sub>): 18.3-18.6(-CH<sub>2</sub>-C≡); 69.5-69.9(-CH<sub>2</sub>-C≡); 56.5-56.9(≡C-Cl) ppm.

(Received in UK 26 November 1991)