

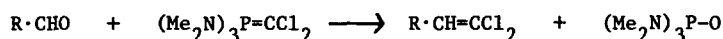
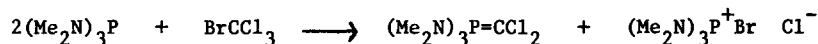
DICHLOROMETHYLENETRISDIMETHYLAMINOPHOSPHORANE.
PREPARATION OF 1,1-DICHLOROÖLEFINS FROM ALDEHYDES.

William G. Salmond

The Upjohn Company, Kalamazoo, Michigan 49001

(Received in USA 26 January 1977; received in UK for publication 23 February 1977)

A recent publication¹ concerning an improved synthesis of dichloromethylenetriphenylphosphorane from triphenylphosphine and bromotrichloromethane prompts us to disclose our efforts towards the preparation of 1,1-dichloroölefins. These are obtained in good yield from aldehydes and dichloromethylenetrisdimethylaminophosphorane prepared by the interaction of bromotrichloromethane and hexamethylphosphoroustriamide (HMP) according to the scheme:



In work directed towards one of our syntheses of 25-hydroxycholesterol² we required a convenient and less expensive alternative to the combination of triphenylphosphine and carbon tetrabromide³, and in addition, we wanted to avoid the cumbersome separation of our steroidal products from triphenylphosphineoxide in the conversion of aldehyde (4) to the corresponding dichloroölefin.


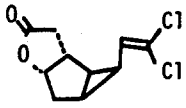
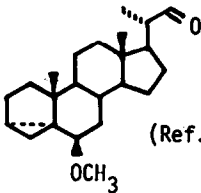
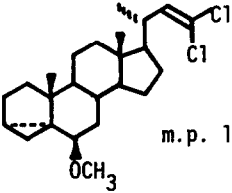
The reaction of aldehydes with HMP and carbontetrachloride at -78° is reported⁴ to give 1,1-dichloroölefins in yields of 50-55%. The present method uses temperatures of -20° to -10° and a solution of HMP in methylene chloride is simply added to a mixture of the aldehyde and bromotrichloromethane in methylene chloride. The by-products, hexamethyl phosphoric triamide and bromotrisdimethylaminophosphonium chloride, are easily removed, workup is straightforward and the yields encountered were in the range of 85-94%. The reaction appears to be general; aliphatic (1), aromatic (2), cyclopropyl (3), and steroidal (4) aldehydes have been converted under entirely similar conditions to the dichlorovinyl products (see Table)⁵. The chiral centers of the latter two aldehydes retained their stereochemical integrity under the conditions of the reaction. Ketones reacted sluggishly or not at all under these conditions to give poor yields of product.

General Procedure

The aldehyde (1 mmole) and the bromotrichloromethane (1 mmole) are dissolved in 30 ml methylene chloride and cooled to -20° . While maintaining the temperature between -20° and -10° , a solution of HMP (1/10 molar in methylene chloride) is added dropwise, until 2 mmoles of HMP

have been added or until TLC (or some other means of analysis of the reaction) indicates total consumption of the aldehyde. Typically an excess of 5-10% of HMP is employed. The reaction mixture is then poured into water and hexane added to make the organic layer uppermost. The organic layers are now washed with water, dilute HCl, again with water, and then dried and evaporated to leave a residue of the 1,1-dihalo-vinyl compound. This residue is now filtered through a very small amount of silica gel, eluting with hexane, to remove traces of phosphorus containing polymeric material. The product may now be distilled, crystallized or otherwise isolated pure.

TABLE

Aldehyde	Product	Yield
1. $nC_5H_{11} \cdot CHO$	$nC_5H_{11} \cdot CH=CCl_2$, oil	94%
2. $C_6H_5 \cdot CHO$	$C_6H_5 \cdot CH=CCl_2$, oil	86%
3.  (Ref. 6)	 oil	85%
4.  (Ref. 7)	 m.p. 135-137°	85%

References

1. B.A.Clement and R.L.Soulen, *J. Org. Chem.* **41**,556(1976).
2. W.G.Salmond, M.C.Sobala and K.D.Maisto accompanying paper.
3. F.Ramirez, N.B.Desai and N.McKelvie, *J.A.C.S.* **84**,1745(1962).
4. J.C.Combret, J.Villieras and G.LaVielle, *Tetrahedron Letters*, 1035(1971).
5. All products had analytical and spectral characteristics in accord with the proposed structures.
6. R.C.Kelly, V.VanRheenen, I.Schletter and M.D.Pillai, *J.A.C.S.* **95**,2746(1973).
7. F.W.Heyl and A.P.Centolella, U.S.P. 2,623,052, Dec. 23, 1952. *C.A.* **47**,10016c(1953).