



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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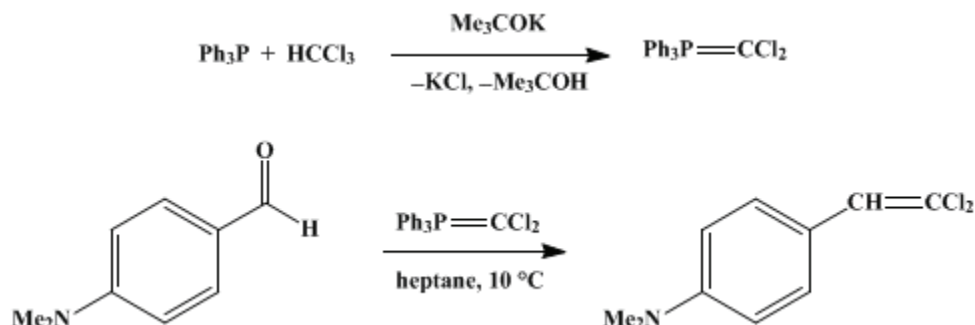
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.361 (1973); Vol. 45, p.33 (1965).*

## DICHLOROMETHYLENETRIPHENYLPHOSPHORANE AND $\beta,\beta$ -DICHLORO-*p*-DIMETHYLAMINOSTYRENE

### [Phosphorane, (dichloromethylene) triphenyl-1]



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### 1. Procedure

A. *Potassium t-butoxide*. To 500 ml. of *t*-butyl alcohol (Note 1) in a 3-l. three-necked flask equipped with an efficient sealed stirrer, a nitrogen inlet (Note 2), a 500-ml. dropping funnel with a pressure-equalizing side tube (Note 3), and a reflux condenser there is added 20 g. (0.5 g. atom) of clean potassium metal. After the potassium has reacted, the condenser is replaced by a 12-in. distillation column and the excess *t*-butyl alcohol is removed by distillation until crystals begin to form in the solution. There is added 2 l. of dry heptane and the distillation is continued until the head temperature reaches 98° (Note 4) and (Note 5). The residual mixture is adjusted to a 1.5-l. volume by addition of dry heptane and the resulting slurry of potassium *t*-butoxide in heptane is cooled to 0–5° in an ice bath (Note 6).

B. *Dichloromethylenetriphenylphosphorane*. In one portion 131 g. (0.5 mole) of triphenylphosphine (Note 7) is added to the cooled suspension of potassium *t*-butoxide in heptane, and to the well-stirred mixture a solution of 59.5 g. (0.5 mole) of chloroform in 500 ml. of dry heptane is added dropwise over a period of 1 hour, maintaining the temperature below 5° and an atmosphere of purified nitrogen. The resulting stirred suspension is concentrated to a 750-ml. volume at reduced pressure and at 15–20° (Note 8).

C.  $\beta,\beta$ -*Dichloro-p*-dimethylaminostyrene. To the heptane suspension of the phosphorane there is added over a period of 30 minutes 74.5 g. (0.5 mole) of *p*-dimethylaminobenzaldehyde in six equal portions; the reaction temperature is maintained below 10°. The mixture is stirred for 2 hours in an ice bath, for an additional 5 hours at room temperature, and is then allowed to stand overnight. The precipitated phosphine oxide is filtered and the solvent is removed from the filtrate at 45–50° using a rotary evaporator. The resulting brown solid is recrystallized from methanol to yield 74–85 g. (68–79%) of crude olefin, m.p. 56–60°. The major impurity is unreacted triphenylphosphine.

The crude product is dissolved in absolute ethanol (10 ml. per gram of material), and a saturated solution of mercuric chloride (1 g. per 5 g. of crude olefin) in absolute ethanol is added (Note 9). The precipitate is filtered (Note 10) and washed with absolute ethanol. The filtrate is concentrated to half of its original volume (Note 11) and cooled in an ice bath. The yield of olefin is 42–60 g. (39–56%), m.p. 71–72°.

### 2. Notes

1. The *t*-butyl alcohol should be distilled from metallic sodium before use, care being taken to exclude

moisture.

2. The nitrogen was purified by passing it through two wash bottles containing Fieser's solution<sup>2</sup> and single wash bottles containing concentrated sulfuric acid and solid anhydrous calcium chloride, respectively.
3. If available, it is more convenient to use a flask which also accommodates a thermometer extending into the reaction mixture.
4. It may be necessary to add more heptane during the distillation, as the slurry of potassium *t*-butoxide in heptane becomes very difficult to stir if the total volume is less than 1 liter.
5. About 2 hours is required for removal of all the excess *t*-butyl alcohol.
6. The potassium *t*-butoxide prepared in this manner is a 1:1 complex with *t*-butyl alcohol; neutralization equivalent calculated for (CH<sub>3</sub>)<sub>3</sub>COH·(CH<sub>3</sub>)<sub>3</sub>COK, 186. Found: 184, 182. The complex can be isolated by simply removing the solvent at 20–25 mm. pressure on a steam bath. It can be stored for several months under a nitrogen atmosphere.
7. Triphenylphosphine was used as supplied by Eastman Organic Chemicals.
8. It is desirable to remove the *t*-butyl alcohol formed during the generation of dichlorocarbene because the *t*-butyl alcohol reacts with the phosphorane, thus lowering the yield of olefin. The evaporation is best accomplished with a vacuum pump (*e.g.*, a Langdon pump) since the removal of *t*-butyl alcohol and heptane by water aspiration is very slow at this temperature. It is imperative that this step be accomplished as rapidly as possible and that the temperature be maintained below 20°. Although the suspension of phosphorane in heptane can be stored overnight under a nitrogen atmosphere, it is better to use it immediately.
9. Mercuric chloride forms with triphenylphosphine a double salt which is insoluble in ethanol.
10. It is necessary to use a fine or ultra-fine sintered-glass funnel or Whatman No. 1 filter paper because the precipitate is finely divided.
11. The checkers obtained better results by reducing the volume to one-third the original volume.

### 3. Discussion

Dichloromethylenetriphenylphosphorane has been prepared by the direct reaction of triphenylphosphine with carbon tetrachloride.<sup>3</sup> 1,1-Dichloroethylenes have been prepared by dehydrochlorination of 1,1,1-trichloro compounds<sup>4,5,6</sup> or by specialized methods applicable only to specific compounds.<sup>7,8</sup>

### 4. Merits of the Preparation

The procedure described illustrates a general method for the preparation of 1,1-dichloroethylenes. Dichloromethylenetriphenylphosphorane has been treated with a variety of aldehydes and ketones including *p*-nitrobenzaldehyde, 2,6-dichlorobenzaldehyde, cinnamaldehyde, lauraldehyde, acetaldehyde, cyclohexanone, and benzophenone to give the corresponding 1,1-dichloroethylene in good yield.<sup>9</sup>

Chlorofluoromethylenetriphenylphosphorane has been utilized in an extension of this method to prepare chlorofluoroethylenes.<sup>10</sup>

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### References and Notes

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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

Phosphorane, (dichloromethylene) triphenyl-1

ethanol (64-17-5)

acetaldehyde (75-07-0)

methanol (67-56-1)

chloroform (67-66-3)

Cyclohexanone (108-94-1)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

Benzophenone (119-61-9)

sodium (13966-32-0)

mercuric chloride (7487-94-7)

potassium (7440-09-7)

cinnamaldehyde

p-Nitrobenzaldehyde (555-16-8)

heptane (142-82-5)

2,6-Dichlorobenzaldehyde (83-38-5)

t-butyl alcohol (75-65-0)

p-Dimethylaminobenzaldehyde (100-10-7)

triphenylphosphine (603-35-0)

Dichloromethylenetriphenylphosphorane (6779-08-4)

β,β-DICHLORO-p-DIMETHYLAMINOSTYRENE (6798-58-9)

phosphine oxide

Chlorofluoromethylenetriphenylphosphorane

potassium t-butoxide (865-47-4)

lauraldehyde (112-54-9)

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