

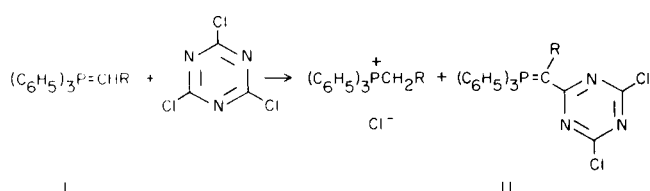
## The Reaction of Cyanuric Chloride with Methylenephosphoranes

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Although cyanuric chloride has been found (1) to undergo condensation with a large variety of nucleophiles, no reaction of this type has been reported (2) with methylenephosphoranes. The investigation of this reaction was prompted by interest in preparing disubstituted methylenephosphoranes (II) in which one of the substituents contained the *s*-triazinyl functionality.

The preparation of II was achieved by reacting cyanuric chloride with monosubstituted methylenephosphoranes in which the substituent was electron-withdrawing. Upon treatment of two moles of phosphorane (I) with one mole of cyanuric chloride, one isolates, in addition to the phosphonium chlorides, good yields of the disubstituted methylenephosphoranes (II).



- a, R = CO<sub>2</sub>CH<sub>3</sub>  
 b, R = CN  
 c, R = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*  
 d, R = C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>-2,4

The reaction with cyanuric chloride is quite selective and even the presence of a large excess of I (as much as six moles of I per mole of cyanuric chloride) does not result in replacement of more than one chlorine atom. However, both chlorine atoms of II are easily displaced by amines as witnessed by the synthesis in high yield of  $\alpha$ -(4,6-dipiperidino-2-*s*-triazinyl)- $\alpha$ -carbomethoxymethylenetriphenylphosphorane by the condensation of IIa with piperidine.

## EXPERIMENTAL

$\alpha$ -(4,6-Dichloro-2-*s*-triazinyl)- $\alpha$ -carbomethoxymethylenetriphenylphosphorane (IIa).

A mixture of 20.1 g. (0.060 mole) of carbomethoxymethylenetriphenylphosphorane (3) (Ia) and 5.5 g. (0.030 mole) of

cyanuric chloride in 200 ml. of dry benzene was heated on the steam bath for one hour. The reaction mixture was cooled and 11.0 g. (99%) of the phosphonium chloride was filtered off. To the filtrate was added one liter of petroleum ether and the crystals which formed were filtered to give 13.2 g. (91%) of phosphorane (IIa), m.p. 206-210°. An analytical sample was obtained by recrystallization from benzene-petroleum ether, m.p. 212-213°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>P: C, 59.77; H, 3.76; Cl, 14.70; N, 8.71; P, 6.42. Found: C, 59.96; H, 3.68; Cl, 14.82; N, 8.79; P, 6.33.

$\alpha$ -(4,6-Dichloro-2-*s*-triazinyl)- $\alpha$ -cyanomethylenetriphenylphosphorane (IIb).

A mixture of 6.03 g. (0.020 mole) of cyanomethylenetriphenylphosphorane (4) (Ib) and 1.84 g. (0.010 mole) of cyanuric chloride in 100 ml. of dry benzene was heated on the steam bath for two hours. The reaction mixture was cooled and filtered. The cake which weighed 7.48 g. consisted of both the phosphonium chloride and phosphorane IIb. It was washed thoroughly with cold water to remove the salt and the solid which remained was dried to yield 4.09 g. (91%) of IIb, m.p. 275-280°. An analytical sample recrystallized from chloroform-petroleum ether had m.p. 282-283°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>4</sub>P: C, 61.49; H, 3.36; Cl, 15.78; N, 12.47; P, 6.90. Found: C, 61.41; H, 3.46; Cl, 15.95; N, 12.35; P, 6.94.

$\alpha$ -(4,6-Dichloro-2-*s*-triazinyl)- $\alpha$ -(*p*-nitrophenyl)methylenetriphenylphosphorane (IIc).

To a stirred slurry of 17.35 g. (0.040 mole) of *p*-nitrobenzyltriphenylphosphonium chloride (5) in 500 ml. of dry benzene under an atmosphere of nitrogen was added 26.3 ml. (0.040 mole) of a hexane solution of butyl lithium (15.0% by weight). The mixture was allowed to stir at room temperature for three hours at which time was added 3.69 g. (0.020 mole) of cyanuric chloride dissolved in 45 ml. of dry benzene. The dark red color changed to yellow-orange and stirring was continued for 16 hours. The mixture was filtered and the filtrate diluted with two liters of petroleum ether. The yellow solid that precipitated was filtered and washed with cold methanol to give 3.71 g. (34%) of phosphorane (IIc), m.p. 243° dec. An analytical sample was obtained by recrystallization from chloroform-petroleum ether and had m.p. 247° dec.

*Anal.* Calcd. for C<sub>28</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>P: C, 61.67; H, 3.51; Cl, 13.00; N, 10.27; P, 5.68. Found: C, 61.78; H, 3.39; Cl, 13.63; N, 10.13; P, 5.59.

$\alpha$ -(4,6-Dichloro-2-*s*-triazinyl)- $\alpha$ -(2,4-dinitrophenyl)methylenetriphenylphosphorane (IIId).

A mixture of 6.63 g. (0.0150 mole) of 2,4-dinitrobenzylidene-triphenylphosphorane (6) (Id) and 1.39 g. (0.0075 mole) of cyanuric chloride in 200 ml. of dry benzene was heated on the

steam bath for two hours. The phosphonium chloride was formed as a gum on the bottom of the flask. The hot benzene was decanted and the gum washed twice with 50-ml. portions of hot benzene. To the combined benzene solution was added one liter of petroleum ether. The orange phosphorane (II<sub>d</sub>) which precipitated was filtered and washed with cold methanol. The product weighed 3.84 g. (87%) and had m.p. 260-264° dec. An analytical sample recrystallized from chloroform-petroleum ether melted at 264-265° dec.

*Anal.* Calcd. for C<sub>28</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>5</sub>O<sub>4</sub>P: C, 56.97; H, 3.07; Cl, 12.01; N, 11.86; P, 5.24. Found: C, 56.56; H, 3.28; Cl, 11.95; N, 11.54; P, 5.32.

$\alpha$ -(4,6-Dipiperidino-2-s-triazinyl)- $\alpha$ -carbomethoxymethylenetriphenylphosphorane.

A solution of 4.82 g. (0.010 mole) of II<sub>a</sub> and 4.26 g. (0.050 mole) of piperidine in 100 ml. of benzene was refluxed for two hours. The piperidine hydrochloride, m.p. 246-247°, was removed by filtration and weighed 2.32 g. (95%). The filtrate was evaporated to dryness *in vacuo*. The residue was triturated with petroleum

ether and filtered to yield 5.54 g. (96%) of product, m.p. 230-235°. An analytical sample was recrystallized from methanol-water and had m.p. 245-248°.

*Anal.* Calcd. for C<sub>34</sub>H<sub>38</sub>N<sub>5</sub>O<sub>2</sub>P: C, 70.45; H, 6.61; N, 12.08; P, 5.34. Found: C, 70.54; H, 6.35; N, 12.19; P, 5.09.

#### REFERENCES

- (1) E. M. Smolin and L. Rapoport, "s-Triazines and Derivatives," Interscience Publishers, Inc., New York, N. Y., 1959, p. 53.
- (2) A. Maercker, *Org. Reactions*, 14, 291 (1965).
- (3) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta*, 40, 1242 (1957).
- (4) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).
- (5) R. Ketcham, D. Jambotkar and L. Martinelli, *J. Org. Chem.*, 27, 4666 (1962).
- (6) J. J. Pappas and E. Gancher, *ibid.*, 31, 1287 (1966).

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