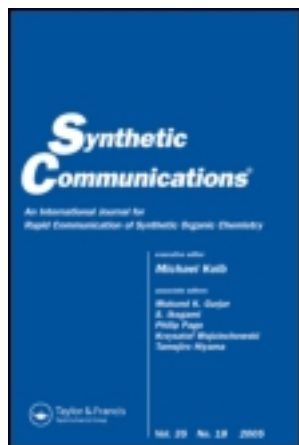


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Chlorine Substitution Reactions using Trichloroisocyanuric Acid with Triphenylphosphine

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CHLORINE SUBSTITUTION REACTIONS USING
TRICHLOROISOCYANURIC ACID WITH TRIPHENYLPHOSPHINE

Gene A. Hiegel,* Jenny Ramírez, and Robert K. Barr

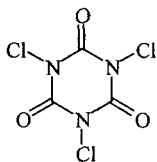
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ABSTRACT: Trichloroisocyanuric acid with triphenylphosphine in anhydrous acetonitrile will convert alcohols into alkyl halides, carboxylic acids into acid chlorides, 1,3-diketones into vinyl chlorides, and amides into nitriles.

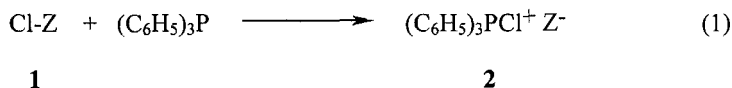
Alkyl chlorides, acid chlorides, and vinyl chlorides can be prepared from alcohols, carboxylic acids, and 1,3-diketones, respectively, by using phosphorus pentachloride, phosphorus trichloride, sulfuryl chloride, or dichlorotriphenylphosphorane [(C₆H₅)₃PCl₂]. The same reagents also convert amides into nitriles.¹

We wish to report that a mixture of trichloroisocyanuric acid (**1**) [1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; TCICA] and triphenylphosphine in anhydrous acetonitrile will effectively carry out the same reactions described above. TCICA is a relatively stable and inexpensive reagent which has been used previously for the chlorination and oxidation of various types of compounds.²

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**1**

Since TCICA is a chlorinating agent, it seemed reasonable to assume that it could form a reactive complex (**2**) with triphenylphosphine (eq 1) in a manner similar to that of chlorine. It would also seem reasonable that complex **2** would have properties similar to those of dichlorotriphenylphosphorane, phosphorus pentachloride, and related reagents.



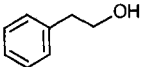
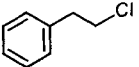
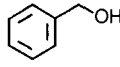
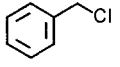
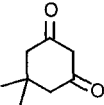
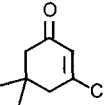
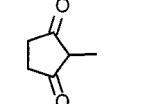
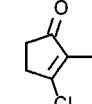
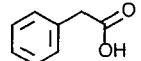
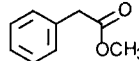
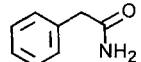
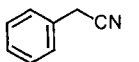
When solid TCICA was added slowly to a solution of triphenylphosphine in anhydrous acetonitrile, a highly exothermic reaction took place to give a yellow mixture. The mixture was used immediately to carry out the transformations described in the first paragraph above. The products were isolated by means of flash chromatography.³ Reaction conditions and product yields are summarized in the Table.

One of the advantages of the procedure described here is that both triphenylphosphine and TCICA are stable until combined in anhydrous acetonitrile so that at the time of preparation the reactive complex **2** will be fresh.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 1650 series FT-IR. ¹H NMR

Table. Reactions Using Trichloroisocyanuric Acid with Triphenylphosphine

<u>Reactant</u>	<u>Product</u>	<u>Reaction Conditions</u>	<u>Purified Yield</u>	<u>GC Purity</u>
		reflux, 2 hr	74%	96.2%
		80° C, 2 hr	82%	97.2%
		60° C, 3 hr	82%	98.7%
		60° C, 3 hr	63%	98.0%
		60° C, 1 hr ^a	95%	94.6%
		reflux, 3 hr	39%	99.7%

^a After 1 hr at 60° C, 5 eq of anhydrous methanol was added and heating was continued for 30 min.

spectra were recorded on a Bruker AC 200 using CDCl₃ as the solvent and TMS as the standard. TLC was done with Merck pre-coated silica gel 60 F 254 sheets using ethyl acetate for development in most cases. GC was performed using a Hewlett-Packard 5890 Series II chromatograph with a 6 ft x 1/8 in 10% SP-2100 or 10% Carbowax 20M column. Flash chromatography was carried out with Merck 60 Å silica gel (230-400 mesh). TCICA was obtained from Chem Lab

Products (99% pure) and triphenylphosphine and anhydrous acetonitrile were obtained from Aldrich, and all were used as received.

All products except for the vinyl chlorides were compared with authentic samples by means of IR, ^1H NMR, and GC. The spectra for the vinyl chlorides were in agreement with published data: 2-methylcyclopentan-1,3-dione; IR (film) 1712, 1647 cm^{-1} ; [lit.⁶ (film) 1712, 1640 cm^{-1}]; ^1H NMR 1.79 (t, $J = 2$ Hz, 3 H), 2.52-2.59 (m, 2 H), 2.78-2.88 (m, 2 H); [lit.⁶ 1.78 (t, $J = 2$ Hz, 3 H), 2.40-2.67 (m, 2 H), 2.67-2.98 (m, 2 H)]. The reaction procedure described below is typical.

3-Chloro-5,5-dimethyl-2-cyclohexen-1-one. To a solution of 2.530 g (9.65 mmol) of triphenylphosphine in 20 mL anhydrous acetonitrile was added slowly while stirring 0.830 g (3.57 mmol; 10.71 equivalents) of TCICA.⁴ The reaction was exothermic and gave a cloudy yellow mixture. After 15 min, 1.197 g (8.541 mmol) of 5,5-dimethylcyclohexan-1,3-dione was added to this mixture, and the flask was placed in a 60° C oil bath. After 3 hr, the mixture was filtered to remove the white solid,⁵ and most of the solvent was removed from the filtrate by means of a rotary evaporator. Flash chromatography of the residue gave 1.115 g (82%) of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one; GC purity 98.7%; IR (film) 1681, 1613 cm^{-1} ; [lit.⁶ (film) 1678, 1610 cm^{-1}]; ^1H NMR 1.10 (s, 6 H), 2.26 (s, 2 H), 2.57 (d, $J = 1.5$ Hz, 2 H), 6.22 (t, $J = 1.5$ Hz, 1 H); [lit.⁶ (CDCl_3) 1.10 (s, 6 H), 2.26 (s, 2 H), 2.55 (d, $J = 2$ Hz, 2 H), 6.22 (t, $J = 2$ Hz, 1 H)].

ACKNOWLEDGEMENT

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3. The acid chloride was converted into the methyl ester before isolation.
4. TCICA is reported to be about 88% reactive as determined by a thiosulfate titration of the iodine liberated on reaction with iodide so a slight excess was used. See Eaton, E. *Mfg. Chemist and Aerosol News* **1964**, *35* (12), 45.
5. The IR of the solid matched that of cyanuric acid ($C_3H_3O_3N_3$).
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