**Registry No.**—Vinyl acetate, 108-05-5; purine, 273-26-7; 7-vinylpurine, 56468-28-1; 9-vinylpurine, 56468-29-2; theophylline, 58-55-9; 7-vinyltheophylline, 22247-84-3; 7-ethylpurine, 39253-23-1; 9-ethylpurine, 5427-23-6; 7-ethyltheophylline, 23043-88-1.

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# Addition of Trichloromethane Phosphonyldichloride and Its Derivatives to Vinylic Monomers and Other Olefins

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The addition of trichloromethyl compounds to olefins under iron or copper chloride catalysis is a general process, without almost any restriction on the olefin, and provides for high yields of 1:1 adducts without telomerization.[1]

Trichloromethane phosphonyldichloride reacts in a similar fashion, via a redox chain. The phosphonylchloride function is retained in the adducts, as expected.

$$2CuCl_2 + C{=}C \longrightarrow 2CuCl + Cl{-}C{-}C{-}Cl \quad \text{initiation} \qquad (a)$$

$$\left.\begin{array}{l} CuCl + CCl_3POCl_2 \rightleftharpoons CuCl + \cdot CCl_2POCl_2 \\ C{=}C + \cdot CCl_2POCl_2 \longrightarrow C{-}C{-}Cl_2POCl_2 \\ CuCl_2 + \cdot C{-}C{-}CCl_2POCl_2 \longrightarrow \\ \qquad CuCl + Cl{-}C{-}C{-}CCl_2POCl_2 \end{array}\right] \text{propagation} \quad \begin{array}{r} (b) \\ (c) \\ \\ (d) \end{array}$$

Reactions of trichloromethane phosphonyldichloride with 1-butene at 110 and 125° with *tert*-butyl perbenzoate as the initiator gave only a 10% yield of adduct, together with unconverted material and heavier products.[2] In comparison, catalysis by iron chloride afforded 90% adduct. Copper chloride (for the vinylic monomers) likewise gave high yields (Table I).

Dimethyl and diethyl trichloromethanephosphonate also gave clean reactions, which, however, stopped at low conversion (compare, e.g., the reactions of butadiene in Table I). This seems to be the result of a gradual alkylation of chloride ions, since dialkyl phosphonates alkylate chloride ion,[3] and especially the dialkyl trichloromethanephosphonates are known[4] to be good alkylating agents. Without chloride ligands on copper(II) or iron(III) ion, radicals formed in c are not trapped anymore by the metal salt as in d[5] (dialkyl ester instead of dichloride), and the redox chain breaks down. In accord with this view, the dichloride and the diphenyl ester, which do not alkylate chloride ions, were fully converted into the corresponding adducts. Also, the reaction of butadiene with dimethyl trichloromethanephosphonate stopped after only 25% conversion of the latter, whereas the diethyl ester, which can be expected to be a less powerful alkylating agent, reached 50% under the same conditions. Finally, in a copper chloride catalyzed addition of diethyl trichloromethanephosphonate to acrylonitrile at 100°, an explosive polymerization of the monomer took place. This is only possible in the absence of chloride ions[5] and never occurred in additions of the phosphonyldichloride instead of the diester.

**Twofold Addition.** Under more drastic conditions, excess ethylene reacted with trichloromethane phosphonyldichloride to give mainly the "twofold" addition product (**2**) as distinguished from the 2:1 telomer $Cl(CH_2CH_2)_2CCl_2POCl_2$. Such "twofold" addition products have been mistaken for the isomeric 2:1 telomers in reactions of excess methyl acrylate with carbon tetrachloride, chloroform, or ethyl trichloroacetate under drastic conditions.[6] The isomers are readily distinguished by NMR, the "twofold" adducts having spectra which are very similar to the corresponding 1:1 adducts.

The NMR spectrum of the carbon tetrachloride "twofold" addition product of ethylene $CCl_2(CH_2CH_2Cl)_2$, mp 34–35[7] [$\delta$ 2.7 (4 H, t) and 3.8 (4 H, t)], is also very close to that of **2**, whereas the spectrum of the isomeric 2:1 telomer $Cl(CH_2CH_2)_2CCl_3$ is quite different: $\delta$ 1.9 (4 H, m), 2.7 (2 H, m), and 3.6 (2 H, m).

## Experimental Section

NMR was on a Varian A-60 instrument.

The solvents were dried over calcium chloride; anhydrous iron(III) chloride and triethylammonium chloride were Merck analytical. Copper(II) chloride hydrate was made anhydrous by heating at 120° until constant weight. Dimethyl and diethyl trichloromethanephosphonate[8] and trichloromethane phosphonyldichloride[9] were prepared by published procedure. The latter compound (mp 156°) was frequently used as a concentrated (~50%), distilled solution in 1,2,4-trichlorobenzene or in *o*-dichlorobenzene, boiling range 93–98 and 80–95° (25 mm), respectively. Such solutions were easier to handle than the solid phosphonyldichloride, and the solvent served as an internal standard for monitoring the conversion by GLC. Also, unconverted phosphonyldichloride was entrained by the high-boiling solvent without clogging the condenser. The concentration of these stock solutions was determined either by GLC (2 ft × 0.25 in. column, 10% UC-W98 on Chromosorb P, 100–200°, 15° $min^{-1}$) or by titration of chloride ion after hydrolysis (see below).

**Analytical.** A convenient, quantitative determination of trichloromethane phosphonyldichloride and its adducts was based on their hydrolysis according to $RCCl_2POCl_2 + H_2O \rightarrow RCCl_2PO(OH)Cl + HCl$, in aqueous DMF.[10] A sample was dissolved in three to four times its weight in DMF containing 30% water, under considerable evolution of heat. After standing at room temperature for 1 hr, the solution was made up to 500 ml with water, and chloride ion was titrated in an aliquot by standard procedure.

Correct chlorine analyses were obtained, either by hydrolysis or by combustion. The NMR spectra of the reported adducts are consistent with the assigned structure. The signal for protons on carbon separated from $^{31}P$ by not more than an –O– or a $-CCl_2$ linkage is split by phosphorus, as was reported for numerous organic phosphorus compounds.[11]

**Reactions.** The reactions were carried out in sealed glass ampoules in the absence of air, and in the case of ethylene and propylene, in a glass-lined autoclave. (see Table I). Upon completion of the reaction, the conversion of trichloromethane phosphonyldichloride or the corresponding diester and the yield of adduct was

**Table I**
**Addition of Trichloromethane Phosphonyldichloride and Esters (0.05 Mol) to Olefins**[f]

| Compd no. | | Solvent, ml | | Temp, °C | Time, hr | Conversion, % | Yield[a] % | Adduct structure | Bp, °C (mm) |
|---|---|---|---|---|---|---|---|---|---|
| | | $CH_2Cl_2$ | MeCN | | | | | | |
| | | | | | Trichloromethane Phosphonyldichloride | | | | |
| 1 | Ethylene (0.2) | | 5 | 125 | 24 | 90 | 80 | $CH_2ClCH_2CCl_2POCl_2$ | 105–107 (4) |
| 1 | Ethylene (0.2)[b] | 5 | | 110 | 24 | 75 | 75 | $CH_2ClCH_2CCl_2POCl_2$ | |
| 2 | Ethylene (0.2)[c] | 15 | 2 | 150 | 48 | 95 | 68 | $(CH_2ClCH_2)_2CClPOCl_2$ + 20% (1) | mp 60–62 |
| 3 | Vinyl chloride (0.1) | | 5 | 125 | 24 | 90 | 90 | $CHCl_2CH_2CCl_2POCl_2$ | 66–67 (0.1) |
| 4 | Vinylidene chloride (0.1) | | 5 | 125 | 17 | 90 | 85 | $CCl_3CH_2CCl_2POCl_2$ | 69 (0.04) |
| 5 | 1-Butene (0.1)[b] | 10 | | 110 | 5.5 | 50 | 90 | $C_2H_5CHClCH_2CCl_2POCl_2$ | 64–66 (0.05) |
| 6 | Butadiene (0.1) | 20 | | 110 | 7.5 | 100 | 78 | $CH_2ClCH{=}CHCH_2CCl_2POCl_2$ | 92–93 (0.05) |
| 7 | Methyl acrylate (0.1) | | 5 | 125 | 20 | 100 | 90 | $CH_3O(O)CCHClCH_2CCl_2POCl_2$ | 83 (0.04) |
| 8 | Acrylonitrile (0.1) | | | 110 | 15 | 85 | 77 | $N{\equiv}CCHClCH_2CCl_2POCl_2$ | 90–91 (0.04) |
| | | | | | Diethyl Trichloromethanephosphonate | | | | |
| 9 | Vinyl chloride (0.1)[d] | | 10 | 125 | 24 | 25 | 87 | $CHCl_2CH_2CCl_2PO(OC_2H_5)$ | 108–110 (0.15) |
| 10 | 1-Butene (0.1)[b] | | 10 | 110 | 9 | 65 | 62 | $C_2H_5CHClCH_2CCl_2PO(OC_2H_5)_2$ | 95–96 (0.1) |
| 11 | Butadiene (0.1) | | 10 | 110 | 9 | 50 | 80 | $CH_2ClCH{=}CHCH_2CCl_2PO(OC_2H_5)_2$ | 120–125 (0.15) |
| | | | | | Dimethyl Trichloromethanephosphonate | | | | |
| 12 | Butadiene (0.1) | | 10 | 110 | 9 | 25 | 83 | $CH_2ClCH{=}CHCH_2CCl_2PO(OCH_3)_2$ | 119–122 (0.15) |
| | | | | | Diphenyl Trichloromethanephosphonate | | | | |
| 13 | Ethylene (0.6)[e] | 30 | 15 | 150 | 44 | 95 | 68 | $CH_2ClCH_2CCl_2PO(OC_6H_5)_2$ | mp 73.4–74 |
| 14 | Propylene (0.5)[e] | 30 | 15 | 150 | 44 | 95 | 63 | $CH_3CHClCH_2CCl_2PO(OC_6H_5)_2$ | mp 39.5–40.5 |

[a] Based on converted phosphonyldichloride or ester and on GLC. [b] Catalyst: 1 mmol Fe(III) chloride, 2 mmol triethylammonium chloride. Initiator: 1 mmol benzoin. [c] Catalyst: 2 mmol Cu(II) chloride, 3 mmol triethylammonium chloride. [d] Initiator: 5 mmol isobutyraldehyde. [e] 0.15 mol diphenyl phosphonate, 6 mmol Cu(II) chloride, 9 mmol triethylammonium chloride. [f] Catalyst: 1 mmol Cu(II) chloride, 1.5 mmol triethylammonium chloride.

assessed by GLC (2 ft 10% UC-W98, 100–250, 15° $min^{-1}$). The catalyst was extracted with ice-cold 1 *N* HCl and water. After drying on calcium chloride, the adducts were isolated by fractionation in vacuo. Yields based on actual isolation were considerably lower than those based on GLC, owing to partial hydrolysis on treatment with water.

**Diphenyl Trichloromethanephosphonate.** To a solution of 71 g (0.3 mol) of trichloromethane phosphonyldichloride and 56.5 g (0.6 mol) of freshly distilled phenol in 400 ml of dry methylene chloride, 61 g (0.6 mol) of triethylamine in 100 ml of methylene chloride was added at such a rate that the temperature did not rise above 5°. Stirring and cooling were continued for 1 hr. The reaction vessel was protected from moisture by a calcium chloride tube. The amine hydrochloride precipitated, and was dissolved in 0.1 *N* HCl. After two additional extractions with water, the organic layer was dried over calcium chloride and methylene chloride was removed by distillation, first at atmospheric pressure and then in vacuo. According to GLC, diphenyl dichloromethanephosphonate and triphenyl phosphate are also formed in small amounts. The residue solidified, and was recrystallized from 2-propanol, mp 64–65° (72 g). Anal. Calcd for $C_{13}H_{10}Cl_3O_3P$: Cl, 30.30. Found: Cl, 29.72.

**Addition of Ethylene to Diphenyl Trichloromethanephosphonate (13).** A solution of 52.7 g (0.15 mol) of diphenyl trichloromethanephosphonate, 804 mg (6 mmol) of Cu(II) chloride, and 1236 mg (9 mmol) of triethylammonium chloride in 15 ml of acetonitrile and 30 ml of methylene chloride was heated with 17 g (0.6 mol) of ethylene at 150° during 44 hr, after displacement of air, in a glass-lined autoclave of 300 ml. During this time, the pressure decreased from 1800 to 1400 psi. After cooling and release of excess ethylene, the dark brown solution was washed twice with 0.5 *N* HCl and once with water, and dried over calcium chloride. The solvent was evaporated in vacuo, and the residue was refluxed with active charcoal in 200 ml of 2-propanol. Filtering and cooling afforded 20 g of **13**, mp 72.5–73.5°. A second crop of 13 g (mp 70–72.5°) was obtained after concentrating and cooling again. After an additional crystallization from hexane, the melting point was 73.5–74°.

**Addition of Propylene to Diphenyl Trichloromethanephosphonate (14).** The above experiment was repeated with 20 g (0.5 mol) of propylene instead of ethylene. Diphenyl trichloromethanephosphonate was no longer present (GLC). Evaporation in vacuo at 50° left 47 g of residue, which was dissolved in 80 ml of 2-propanol and kept at 0° overnight. Adduct **14** crystallized (25 g), mp 39–40°, after recrystallization from hexane mp 39.5–40.5°.

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**Registry No.**—**1**, 39981-18-5; **2**, 56172-72-6; **3**, 39950-62-4; **4**, 39981-19-6; **5**, 37696-45-0; **6**, 39950-70-4; **7**, 39950-72-6; **8**, 39950-68-0; **9**, 56172-73-7; **10**, 56172-74-8; **11**, 56172-75-9; **12**, 56172-76-0; **13**, 56172-77-1; **14**, 56172-78-2; ethylene, 74-85-1; vinyl chloride, 75-01-4; vinylidene chloride, 75-35-4; 1-butene, 106-98-9; butadiene, 106-99-0; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; propylene, 115-07-1; trichloromethane phosphonyldichloride, 21510-59-8; diethyl trichloromethanephosphonate, 866-23-9; dimethyl trichloromethanephosphonate, 29238-81-1; diphenyl trichloromethanephosphonate, 23614-63-3.

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