The intermediacy of carbonium ions in the reaction of alkyl halides with molybdenum(V) chloride is supported by the fact that treatment of 1-iodo-2-phenylethane-2,2-d_2[10] (1) with molybdenum(V) chloride produces a 1:1 mixture of 1-chloro-2-phenylethane-2,2-d_2 and 1-chloro-2-phenylethane-1,1-d_2. When this experiment was carried to ~50% completion, the recovered starting halide was found to consist of a 1:1 mixture of 1 and 1-iodo-2-phenylethane-1,1-d_2.[15,16]

Synthetically, the reaction of alkyl halides with molybdenum(V) chloride expands the utility of halogen interconversion to alkyl fluorides in particular, and to tertiary halides in general. Moreover, the conversion of alkyl halides to alkyl chlorides using molybdenum(V) chloride can be accomplished selectively and under conditions that are comparatively milder than those required for the analogous conversion involving displacement by chloride ion. As such, the replacement of fluoride, bromide, and iodide by chloride using molybdenum(V) chloride offers a useful compliment to halide interconversion procedures that proceed by SN2 displacement.

Experimental Section[18]

Molybdenum(V) chloride was prepared by the literature procedure.[19] 2-Fluorooctane,[13] 1-iodo-2-phenylethane,[10] and 1,1-difluorocyclohexane[20] were prepared using known procedures.

Procedures for Halogen Interchange. Similar procedures were used to effect the halogen interchange listed in Table I.

Conversion of 2-Fluorooctane to 2-Chlorooctane. Molybdenum(V) chloride (1.20 g, 4.39 mmol) was placed in a flame-dried, 25-ml flask containing a Teflon-coated stirrer bar. Methylene chloride (3 ml) was added by syringe followed by the slow addition of a solution of 2-fluorooctane (1.16 g, 8.78 mmol) in methylene dichloride (2 ml) over a 5-min period. This mixture was stirred for 2 hr, then cautiously hydrolyzed with water (1 ml). The organic layer was separated, dried ($MgSO_4$), and passed through a short column of alumina. GLC analysis of the eluent indicated a 71% yield of 2-chlorooctane. A collected sample had the retention time and ir spectrum equivalent to that of authentic 2-chlorooctane.

Conversion of 1-Iodo-2-phenylethane to 1-Chloro-2-phenylethane. A solution of 1-iodo-2-phenylethane (2.35 g, 10.1 mmol) in dichloromethane (8 ml) was added by syringe to a solution of molybdenum(V) chloride (4.25 g, 15.6 mmol) in methylene chloride (7 ml) contained in a 25-ml, dried flask equipped with Teflon-coated stirrer bar and capped with a rubber septum. The resulting mixture was stirred for 2 hr at room temperature before cautiously adding water (1 ml). The organic layer was separated, dried ($MgSO_4$), and passed through a short column of alumina. Analysis of the eluent indicated a 60% yield of 1-chloro-2-phenylethane. The infrared spectrum and retention time of sample collected from GLC was equivalent to that of authentic 1-chloro-2-phenylethane.

Conversion of 1,3-Dibromobutane to 1-Bromo-3-chlorobutane. Molybdenum(V) chloride (1.27 g, 4.66 mmol) was placed in a 25-ml, flame-dried flask equipped with a Teflon-coated stirrer bar and capped with a rubber septum. Dichloromethane (3 ml) was added by syringe followed by a solution of 1,3-dibromobutane (1.80 g, 8.32 mmol) in dichloromethane (2 ml). After stirring for 10 hr at room temperature, the reaction mixture was cautiously hydrolyzed with water (1 ml) and the organic layer was dried and passed through a short column of alumina. Analysis of the eluent by GLC indicated the major product (66%) to be 1-bromo-3-chlorobutane: M^+ *m/e* 170; ir (CS_2) 803 cm^{-1} [s, ν(C–Cl)]; ^1H NMR (CCl_4) δ 4.18 (sextet, 1 H), 3.49 (t, 2 H), 2.13 (quart, 2 H), 1.55 (d, 3 H).

Conversion of 1,1-Difluorocyclohexane to 1,1-Dichlorocyclohexane. Molybdenum(V) chloride (1.69 g, 6.20 mmol) was placed in a 25-ml, flame-dried flask equipped with Teflon-coated stirrer bar and capped with a rubber septum. Dichloromethane (3 ml) was added by syringe followed by a similar addition of a solution of 1,1-difluorocyclohexane in methylene chloride (3 ml). After 5 hr and a work-up similar to that described above, the reaction mixture was analyzed by GLC. The principal product (31%) as revealed by its retention time, mass, and infrared spectra, was 1,1-dichlorocyclohexane.[21]

Registry No.—$MoCl_5$, 10241-05-1.

References and Notes

(1) (a) Supported by the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) Exxon Summer Research Fellow, 1974.
(2) (a) C. K. Ingold, *Q. Rev., Chem. Soc.*, **11**, 1 (1957). (b) Of much more limited use is halogen exchange by free-radical processes; see G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", Macmillan, New York, N.Y., 1964, pp 308–313.
(3) Typical solvents include acetone,[4] ethanol,[5] or dimethylformamide.[6]
(4) H. B. Hass and H. C. Hoffman, *J. Am. Chem. Soc.*, **63**, 1233 (1941); M. S. Newman and R. D. Closson, *ibid.*, **66**, 1553 (1944); P. Coad et al., *J. Org. Chem.*, **28**, 218 (1963); M. Barash and J. M. Osbond, *J. Chem. Soc.*, 2157 (1959).
(5) L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651 (1930).
(6) J. F. Bunnett and R. M. Connor, *J. Org. Chem.*, **23**, 305 (1958).
(7) Cf. C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses", Wiley-Interscience, New York, N.Y., 1970, p 339.
(8) Exchange of bromide or iodide for fluoride can sometimes be carried out by displacement procedures[9] but is more commonly and efficiently performed by reaction with mercury(II) or silver(I) fluoride.[10]
(9) A. I. Vogel, J. Leicester, and W. A. T. Macey, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 525.
(10) J. San Filippo, Jr., and L. J. Romano, *J. Org. Chem.*, **40**, 782 (1975), and references cited therein.
(11) For a discussion of the factors governing the displacement of fluorine bonded to an alkyl carbon, see W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, pp 43–46.
(12) Aluminum and boron trichloride have been used to affect the interchange of chlorine for fluorine in certain perfluoro compounds at elevated temperatures: Kh. R. Raver, A. B. Bruker, and L. Z. Soborovskii, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 2347 (1960).
(13) J. San Filippo, Jr., and L. J. Romano, *J. Org. Chem.*, **40**, 1514 (1975).
(14) Under similar conditions, optically active 2-fluorooctane[13] (α^{20}_{589} −9.44°, 95% optically pure) is 11% racemized by $MoCl_5$ in 1 hr.
(15) Solvolysis studies of 2-phenylethyl dervatives have shown that 1,2-aryl migration proceeds concomitantly with ionization: W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 5919 (1972), and references cited therein.
(16) The interchange of chloride or bromide for fluoride using mercury(II) fluoride also proceeds through the intermediacy of carbonium ions;[10] however, in contrast to the stereochemistry of chloride interchange using molybdenum(V) chloride, the reaction of (−)-(*R*)-2-bromooctane with mercury(II) fluoride in pentane at 25° yields (+)-(*S*)-2-fluorooctane (α^{20}_{589} 4.65°, 47% optical purity), indicating that reaction has occurred with a 74% net *inversion* of configuration. Neither optically active 2-bromonor 2-fluorooctane suffers any racemization under these conditions.[17]
(17) J. San Filippo, Jr., and L. Romano, unpublished results.
(18) Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were determined with a Varian T-60 NMR spectrometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute product yields were calculated from peak areas using internal standard techniques with response factors obtained from authentic samples. Dichloromethane was distilled from phosphorus pentoxide immediately prior to use. GLC analysis were determined on a 20 ft × 0.25 in. column of 7.5% SE-30 on Gas-Chrom Z. All reactions and transfers of solids and liquids were performed under a nitrogen atmosphere. Unless otherwise indicated, starting halides and authentic product samples were obtained from commercial sources.
(19) A. J. Leffler and R. Penque, *Inorg. Synth.*, **12**, 187 (1970). Molybdenum(V) chloride is also available from several commercial sources.
(20) F. Mathey and J. Bensoam, *Tetrahedron*, **27**, 3965 (1972).
(21) B. Carroll, D. G. Kubler, H. W. Davis, and A. M. Whaley, *J. Am. Chem. Soc.*, **73**, 5382 (1951).

Introduction of *N*-Vinyl Group into Tautomeric Heterocycles by the Exchange Reaction

Josef Pitha

Laboratory of Molecular Aging, National Institutes of Health, National Institute of Child Health and Human Development, Gerontology Research Center, Baltimore City Hospitals, Baltimore, Maryland 21224

Received June 25, 1975

Vinyl exchange between vinyl acetate and a nitrogen heterocyclic compound is a valuable one-step preparation of *N*-vinyl heterocycles, and thus is important in the synthesis of polymers.[1] The reaction is acid catalyzed and is believed to proceed through two successive equilibria[1] as shown in eq 1.

$$\text{HetN–H} + CH_3COOCH{=}CH_2 + Hg(OCOCH_3)_2 \rightleftarrows \text{HetN}(CH_3COO)CHCH_2HgOCOCH_3 + CH_3COOH \rightleftarrows \text{HetN–CH}{=}CH_2 + CH_3COOH + Hg(OCOCH_3)_2 \quad (1)$$

Use of this reaction brings two problems—it is not clear which of the possible isomeric *N*-vinyl compounds may be formed and the isolation of the product is often tedious. In this work we focus on both these problems.

In many cases several isomeric *N*-vinyl derivatives could arise from a single heterocycle; nevertheless, in all examples described to date, only one isomer has been isolated. In the pyrimidine series, of the two possible (1 or 3) isomers, only the 1-vinyl compounds were obtained. The following compounds were investigated: 4-ethoxy-2-pyrimidinone (yield of vinyl derivative 55%),[2] 2-ethoxy-4-pyrimidinone (yield 10%),[3] 2,4-bis(trimethylsiloxy)pyrimidine (yield 40%),[4] and 2-trimethylsiloxy-4-trimethylsilylaminopyrimidine (yield 21%).[4] In the purine series, of the four possible isomers (1, 3, 7, and 9) only the 9-vinyl compounds were formed. The following compounds were studied: 6-chloropurine (yield 70%),[2] 2,6-dichloropurine (yield 80%),[2] adenine (yield 2%),[5] and 6-benzoyladenine (yield 65%).[5]

In surprising contrast, two major products and one minor one were formed when purine was used in the vinyl exchange reaction. The major products, obtained in approximately equal yields, were hydrogenated, compared with the known *N*-ethylpurines,[6-8] and identified as 7-vinylpurine and 9-vinylpurine. When the vinyl exchange reaction was used on theophylline (1,3-dimethyl-2,6-purinedione), only one product was formed. This was 7-vinyltheophylline, previously synthesized by another method.[9,10] The position of the vinyl group was further confirmed by hydrogenation of this compound to the known 7-ethyltheophylline.[11]

Considerable data have been collected on the direction of alkylation and acylation of purine derivatives;[12] the position of vinylation and the position of alkylations or acylation do not seem to correspond. On the other hand, a reasonable correlation is obtained between the position of the tautomeric hydrogen atom in the parent heterocycle and the position of vinyl substitution. All the purine derivatives investigated to date are either 7H or 9H tautomers. In purine, both 7H and 9H tautomers have the same stability;[12-16] in theophylline the 7H tautomer is favored[17,18] while in adenine,[13,19] 6-chloropurine,[18] and 2,6-dihloropurine[18] the 9H tautomers are favored. The position of the proton in the most stable tautomeric form is also taken by the vinyl group in this reaction. 2-Ethoxy-4-pyrimidinone exists in nonpolar solutions as the 3H tautomer, while in polar solutions both forms are present.[3] In this particular compound, however, positions 1 and 3 are very different sterically and this may override other factors in the vinylation reaction.

We investigated the possibility that the position of the vinyl group in the product is determined by the relative thermodynamic stability of the product, but found that this is not the case. When purine is used in the vinyl exchange reaction, approximately the same amounts of 7- and 9-vinylpurine are obtained. When pure 7- and 9-vinyl derivatives were used in the vinyl exchange reaction no isomerization was noticed. Apparently equilibria as given by eq 1, for all the isomeric *N*-vinyl compounds, are not established under the mild conditions used. Thus the ratio of isomeric vinyl derivatives is apparently kinetically controlled.

Isolation of the products from the vinyl exchange reaction is a tedious process because vinyl acetate forms decomposition products which appear to form emulsions and interfere with extractive isolation. We now find that simple filtration of the reaction mixture through a short column of activated alumina gives directly a colorless solution of the *N*-vinyl compound in vinyl acetate; the catalysts, the unreacted starting material, and the decomposition products are much more strongly adsorbed than the product. This labor-saving procedure furthermore improves the yields considerably. Thus, 1-vinyl-4-ethoxy-2-pyrimidinone was obtained in 70% instead of the previously obtained 55% yields.[2]

Experimental Section

Melting points were determined on a hot stage and are not corrected; ultraviolet spectra were measured in a Cary 15 spectrophotometer in phosphate buffer (0.15 *M* NaCl, 0.01 *M* sodium phosphate, pH 7.3), and infrared spectra in a Beckman IR12 spectrophotometer. All products, before any identification operation, were sublimed in vacuo (0.1 mm).

Vinylation Reactions. To a suspension of 0.5 g of mercuric acetate in 150 ml of vinyl acetate (stabilized, practical grade) contained in a glass pressure flask was added a solution of 0.1 ml of sulfuric acid in 2 ml of ethyl acetate. After a solution was formed, 1–1.5 g of the heterocyclic compound was added and nitrogen was bubbled through the suspension for 10 min. Thereafter, the closed flask was kept for 3–4 days at 40°C (water bath). The red-brown reaction mixture was then filtered through neutral activated alumina (100 ml was used for 4 g of starting compound) in a separatory funnel. The alumina was washed with 100 ml of ethyl acetate and the slightly yellow filtrate was evaporated in vacuo to yield a crystalline product.

A. Purine. The product from the vinylation of 4 g of purine was recrystallized from ethyl acetate to yield pure 7-vinylpurine (925 mg): mp 137–138°; uv λ_{max} 225 nm (ϵ 4000), 260 (6000), 274 (shoulder). Anal. Calcd for $C_7H_6N_4$: C, 57.53; H, 4.14; N, 38.34. Found: 57.25; H, 4.03; N, 38.51. The mother liquors were concentrated in vacuo and applied to six preparative thin layer chromatography plates (PLC silica gel 60F-254, E. Merck, Darmstadt: 2 mm layer with the fluorescent indicator) and developed by ethyl acetate. Three main bands were observed with the following colors under uv light: violet (R_f 0.9), violet (R_f 0.6), blue (R_f 0.3). Extraction with ethyl acetate of the blue band yielded more 7-vinylpurine (total 1225 mg, 25%). The violet (R_f 0.9) band on extraction yielded a small amount of material which darkened rapidly in air and therefore could not be satisfactorily identified. It may be noted that 1-ethylpurine, unlike all its isomers, was found to be unstable.[6] The violet (R_f 0.6) band on extraction yielded 9-vinylpurine which after recrystallization from ethyl acetate had mp 113°; λ_{max} 219 nm (ϵ 15000), 263 (5000); yield 22% (1050 mg). Anal. Calcd for $C_7H_6N_4$: C, 57.53; H, 4.14; N, 38.34. Found: C, 57.50; H, 4.06; N, 38.29. The 7 and 9 isomers may be identified by ir bands at 600 and 635 cm^{-1} (KBr pellet), respectively. Each of these peaks are unique for each respective isomer.

B. Theophylline. Vinylation of theophylline (4 g) yielded only one product which after recrystallization from benzene had mp 177–178°, yield 75% (3.4 g) (lit.[9] mp 173–174°; lit.[10] 176–177°).

Hydrogenation of Vinyl Derivatives. The vinyl derivative (25 mg) was dissolved in water, 25 mg of Pd (10%) on C was added, and the mixture was stirred in a hydrogen atmosphere at atmospheric pressure and room temperature for 5 hr. The mixture was clarified by filtration with filtration aid (Hyflo Super Cel, Fisher Scientific Co., Fair Lawn, N.J.) and evaporated in vacuo and the residue was sublimed in vacuo. 7-Ethylpurine was identified by mp 102–104° and uv spectra: λ_{max} 267 nm (pH 7) and 258 (1 *N* HCl) [lit.[6] mp 107°, uv spectra λ_{max} 267 nm (pH 7) and 258 (pH 1)]. 9-Ethylpurine was identified by its ir spectrum in CCl_4 (identical with previously obtained material[2]). 7-Ethyltheophylline was identified by mp 154–155° (lit.[11] mp 154°).

Equilibration of 7- or 9-Vinylpurines. Purified isomer (10 mg) was treated in the same way as described under Vinylation Reaction. Only the starting isomers were detected by thin layer chromatography (silica gel Eastman sheet 6060 with fluorescent indicator, developed by ethyl acetate). To ascertain that the catalytic components were still fully active, a sample of purine (10 mg) was added to either reaction mixture. After 4 days at 40°C both 7- and 9-vinylpurines were in either reaction mixture.

Acknowledgments. The author wishes to thank Drs. C. H. Robinson and R. B. Brundrett for helpful comments.

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.

References and Notes

(1) H. Lüssi, *Chimia*, **21**, 82 (1967).
(2) J. Pitha and P. O. P. Ts'o, *J. Org. Chem.*, **33**, 1341 (1968).
(3) J. Pitha, *J. Org. Chem.*, **35**, 903 (1970).
(4) H. Kaye and S. H. Chang, *Tetrahedron*, **26**, 1369 (1970).
(5) H. Kaye, J. *Polym. Sci., Part B*, **7**, 1 (1969).
(6) R. Balsiger, A. L. Fikes, T. P. Johnston, and J. A. Montgomery, *J. Org. Chem.*, **26**, 3446 (1961).
(7) J. A. Montgomery and C. Temple, *J. Am. Chem. Soc.*, **79**, 5232 (1957).
(8) H. Bredereck, F. Effenberger, and G. Rainer, *Justus Liebigs Ann. Chem.*, **673**, 82 (1964).
(9) F. Cacace, G. Fabrizi, and M. Ziffero, *Ann. Chim. (Rome)*, **46**, 91 (1956); *Chem. Abstr.*, **50**, 12071 (1956).
(10) K. Kondo, H. Iwasaki, N. Veda, and K. Takemoto, *Makromol. Chem.*, **125**, 298 (1969).
(11) E. Schmidt and F. Schwabe, *Arch. Pharm. (Weinheim, Ger.)*, **245**, 312 (1907).
(12) J. H. Lister in "The Chemistry of Heterocyclic Compounds", A. Weissberger and E. C. Taylor, Ed., Wiley-Interscience, New York, N.Y., 1971.
(13) B. Pullman and A. Pullman, *Adv. Heterocycl. Chem.*, **13**, 77–156 (1971).
(14) B. Pullman, H. Berthod, F. Bergmann, Z. Neiman, H. Weiler-Feinchenfeld, and E. D. Bergman, *Tetrahedron*, **26**, 1483 (1970).
(15) D. G. Watson, R. M. Sweet, and R. E. Marsh, *Acta Crystallogr.*, **19**, 573 (1965).
(16) A. Novak and A. Lautie, *Nature (London)*, **216**, 1202 (1967).
(17) D. J. Sutor, *Acta Crystallogr.*, **11**, 83 (1958).
(18) H. W. Feilchenfeld and E. D. Bergmann, *Isr. J. Chem.*, **6**, 823 (1968).
(19) E. D. Bergmann, H. W. Feizchenfeld, and Z. Neiman, *J. Chem. Soc. B*, 1334 (1970).

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

Hadassa Rosin and Meir Asscher*

Department of Plastics Research, The Weizmann Institute of Science Rehovot, Israel

Received March 17, 1975

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.

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

$$CuCl + CCl_3POCl_2 \rightleftharpoons CuCl + \cdot CCl_2POCl_2 \quad (b)$$

$$C{=}C + \cdot CCl_2POCl_2 \longrightarrow C{-}C{-}Cl_2POCl_2 \quad \text{propagation} \quad (c)$$

$$CuCl_2 + \cdot C{-}C{-}CCl_2POCl_2 \longrightarrow CuCl + Cl{-}C{-}C{-}CCl_2POCl_2 \quad (d)$$

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] [δ 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: δ 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