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$AlCl_3$-Catalyzed Dichlorophosphorylation of Saturated Hydrocarbons with PCl_3 in Methylene Chloride Solution[1]

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$AlCl_3$-catalyzed dichlorophosphorylation of saturated hydrocarbons has been carried out with PCl_3 in CH_2Cl_2 solutions. Whereas polycycloalkylphosphonic acid dichlorides were obtained in 40–64% yields, monocyclic and acyclic hydrocarbons gave only poor (10–20%) yields of their phosphorylated derivatives under identical reaction conditions. A mechanism involving alkyl(cyaloalkyl) cation formation from the starting hydrocarbons via hydride abstraction by the polarized methylene chloride–aluminum chloride complex $ClCH_2^{\delta+}{-}Cl \rightarrow {}^{\delta-}AlCl_3$ is proposed, followed by alkylation of PCl_3 to the corresponding alkyl(cycloalkyl)trichlorophosphonium ions and through the hydrolysis the dichlorophosphorylated products.

Introduction

The rapid free-radical chain reaction of alkanes with phosphorus trichloride and oxygen gives alkylphosphoryl dichlorides.[2] Yields of the reaction, however, are generally low (15–25%) with most of the phosphorus trichloride oxidized to phosphorus oxychloride. Interested in substitution of saturated hydrocarbons, we decided to explore the possibility of expectedly more selective ionic dichlorophosphorylation of alkanes and cycloalkanes.

Aluminum chloride catalyzed phosphorylation of aromatic hydrocarbons with PCl_3 has been extensively studied,[3] and dichlorophosphine derivatives of aromatics,[4a] alkylaromatics[4b] haloaromatics,[4c] and various other substituted aromatics[5] are obtained in good yield. Phosphorylated organic polymers[6] such as polystyrene have also been prepared with PCl_3 in the presence of $AlCl_3$ and hydrocarbon solvent. However, no related Friedel–Crafts phosphorylation of aliphatic hydrocarbons has been reported.

The $AlCl_3$-catalyzed reaction of alkyl halides or polyhalogenated alkanes with PCl_3 is known as the Clay reaction.[7a,b] While this is not a Friedel–Crafts reaction in its usual sense, it does have similarities. Thus, when halogenated alkanes are reacted with PCl_3 and $AlCl_3$, the resulting 1:1:1 molar complex yields phosphonic acid dichlorides upon workup with H_2O. The complexes formed in the reaction appear to be similar to those formed in the Friedel–Crafts reaction of PCl_3 with aromatic derivatives. The formation of the initial complex has been depicted as shown in eq 1. Partial hydrolysis of the complex results in conversion to $[RP(O)Cl]^+[AlCl_4]^-$, which gives the final product (upon further hydrolysis).

$$RCl + AlCl_3 + PCl_3 \rightleftharpoons [RPCl_3]^+[AlCl_4]^- \xrightarrow{H_2O} RP(O)Cl_2 \quad (1)$$

Chloroalkanes and dichloroalkanes are also phosphorylated using PCl_3 in presence of $AlCl_3$.[8] Whereas 1,2-dichloroethane affords poor yields,[8c] methyl chloride[8a,b] and dimethylsilacyclobutane[8d] gave high yields of dichlorophosphorylated products upon reaction with $PCl_3/AlCl_3$ systems.

The $AlBr_3$-catalyzed reaction of 1-bromoadamantane with PCl_3 affords 1-adamantylphosphonic acid dichloride in high yield.[9] Similarly 2-bromoadamantane with $PBr_3/AlBr_3$ gave exclusively 1-adamantylphosphonic acid dibromide. The reaction with PCl_3–$AlBr_3$ gives a mixture of bis(2-adamantyl)phosphinic acid chloride and bromide together with 1-adamantyl- and 2-adamantylphosphinic acid chloride.[10] Attempts to react adamantane with $AlBr_3/PCl_3$ system under reflux did not afford the corresponding phosphorylated derivatives.[9]

High-temperature direct phosphorylation of lower alkanes, including methane, was reported in the gas phase, presumably under free-radical conditions. Upon heating methane or ethane at 500–700 °C with PCl_3, the corresponding dichlorophosphines were obtained in high yield. Gas-phase phosphorylation of hydrocarbons was also carried out under similar conditions using $COCl_2$ as catalyst,[12] but only poor yields of the phosphorylated products were obtained.

Results and Discussion

Our continuing studies of the electrophilic functionalization of saturated hydrocarbons led us to investigate the

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(1) Synthetic Methods and Reactions. Part 147. For Part 146, see: Olah, G. A.; Wu, A.; Forooq, O.; Prakash, G. K. S. *J. Org. Chem.*, in press.

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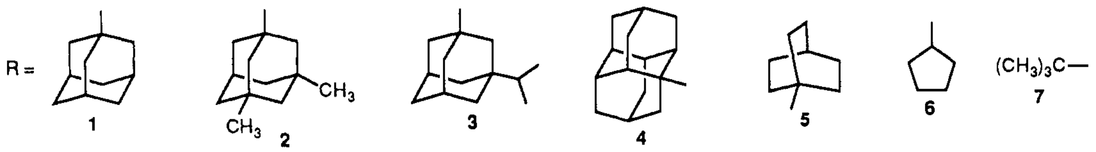
Table I. Dichlorophosphorylation of Saturated Hydrocarbons

$$RH \xrightarrow[\text{reflux}]{PCl_3,\ AlCl_3,\ CH_2Cl_2} RPOCl_2$$



hydrocarbon RH	$AlCl_3$:PCl_3:RH (molar ratio)	reaction time, h	reaction temp	% yield[a] of phosphorylated compounds	IR (cm^{-1}) >P=O
1	1.3:1.1:1	16	reflux	64	1265
2	1.3:1.1:1	18	reflux	46	1275
3	1.3:1.1:1	20	rt[b]	40	1270
4	1.3:1.1:1	17	reflux	60	1280
5	1.3:1.1:1	21	reflux	20	1250
6	1.3:1.1:1	22	reflux	18	1260
7	1.3:1.1:1	24	rt[b]	10	1270

[a] Isolated yield. [b] Room temperature.

phosphorylation of saturated hydrocarbons. Here we report that $AlCl_3$-catalyzed reaction of polycycloaliphatic hydrocarbon with PCl_3 in CH_2Cl_2 solution gives dichlorophosphorylated derivatives in generally satisfactory yields.

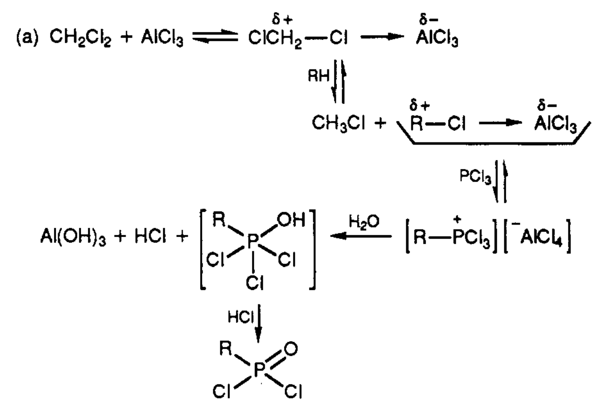
When PCl_3–$AlCl_3$, an effective phosphorylating agent for aromatic hydrocarbons,[2-5] was reacted with adamantane in methylene chloride solution under reflux, 1-adamantylphosphinic acid dichloride was obtained in 64% yield (Table I). Even at room temperature the reaction took place, albeit slower. Alkyladamantanes and diamantanes reacted similarly, giving 40–60% yields. At the same time bicyclic, monocyclic, or acyclic hydrocarbons gave only poor (10–20%) yield of phosphorylated products (Table I).

With respect to the mechanism of the reaction, the interaction of $AlCl_3$ with PX_3 (X = F, Cl) has been investigated.[15] $AlCl_3$ reacts with PF_3 to form the F_3P–$AlCl_3$ complex (a stable compound) having an ethane-like structure involving a P–Al bond. No identifiable compound was found in the reaction of $AlCl_3$ with PCl_3 at room temperature. $AlCl_3$ is insoluble in PCl_3 at room temperature, but at 130 °C about 2.5 mol % of $AlCl_3$ dissolves in PCl_3, forming the $AlCl_3$–PCl_3 complex.[16] On cooling to room temperature, only trace amounts of the complex could be identified. The failure of PCl_3 to more strongly bond with $AlCl_3$ was attributed to the larger size of chlorides which leads to chloride–chloride repulsions.[16]

Since CH_2Cl_2 in presence of $AlCl_3$ effects aromatic substitution,[13,14] we studied the reaction of CH_2Cl_2–$AlCl_3$ complex, in the presence and absence of PCl_3, with aliphatic hydrocarbons. When a mixture of $AlCl_3$ and adamantane in CH_2Cl_2 is stirred at room temperature for a prolonged period of time (24 h) in a closed system, CH_3Cl together with some methane was identified by GC. Similar gaseous products were not formed during shorter reaction times (i.e. 4 h). Formation of gaseous products was accelerated by refluxing the reaction mixture at atmospheric pressure or by heating in a pressure autoclave.

When a $AlCl_3$–CH_2Cl_2 mixture, in a sealed NMR tube, was analyzed by ^{13}C NMR with occasional Vortex mixing, no deshielding of the methylene carbon, characteristic of the donor–acceptor complex, was observed, and no formation (even after 7 days) of bis(chloromethyl)chloronium ion was suggested by the data. The latter halonium ion, however, has been observed with SbF_5 in SO_2ClF solution.[17] Formation of CH_3Cl and CH_4 in the reaction of $AlCl_3$–CH_2Cl_2 with adamantane (or other saturated hydrocarbons), together with the known reaction of $AlCl_3$–CH_2Cl_2 with aromatics, strongly suggests the intermediate formation of a polarized donor–acceptor complex, albeit in low concentration, which rapidly exchanges on the NMR time scale.

Scheme I



The mechanism of the phosphorylation reaction of saturated tertiary aliphatic (cycloaliphatic) hydrocarbons is suggested to involve the polarized $ClCH_2^{\delta+}$–$Cl \rightarrow {}^{\delta-}AlCl_3$ complex interacting with a tertiary C–H bond. The resultant formation, via hydrogen abstraction of an intermediate carbocation (or polarized alkyl halide $AlCl_3$ complex), leads to a tertiary alkyl(cycloalkyl) chloride, which then alkylates PCl_3 (Scheme I) to yield the corresponding alkyltrichlorophosphonium ion and by its hydrolysis the dichlorophosphorylated products.

The complexation of CH_2Cl_2 with SbF_5 has been previously investigated under stable ion conditions.[11] Hydride abstraction from hydrocarbons by (chloromethyl)chloronium ion giving carbocations is accompanied by formation of CH_3Cl, CH_3F, and CH_4. Use of SbF_5 in the present investigation gave no phosphorylated products presumably because of the strong complexation of PCl_3 with SbF_5. This observation, together with the fact that $AlCl_3$–PCl_3 effects aromatic substitution, suggests the intermediacy of at least a polarized electrophilic $Cl_2P^{\delta+}Cl$–

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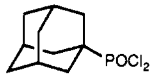
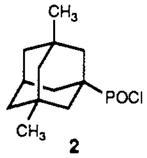
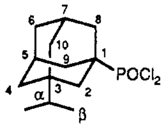
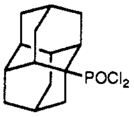
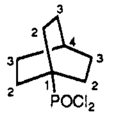
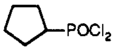
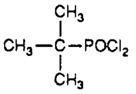
Table II. GC–MS and ^{13}C and ^{31}P NMR Spectral Data of Phosphorylated Compounds

compound	GC–MS	$\delta_{^{13}C}$[a] (J_{C-P})	$\delta_{^{31}P}$[a]
 **1**	253 (~0.1), 252 (~0.1), 136 (38), 135 (100), 119 (5), 118 (4), 117 (8)	C_1 48.42 (^1J = 82.4 Hz), C_2 35.24 (^2J = 3 Hz), C_3 27.34 (^3J = 15.4 Hz), C_4 34.79 (^4J = 4 Hz)	65.11
 **2**	164 (14), 163 (100), 148 (2), 147 (5), 135 (2), 119 (5), 118 (2), 117 (3)	C_1 50.17 (^1J = 87.3 Hz), C_2 42.15 (J = 3.5 Hz), C_8 40.80 (J = 4.2 Hz), C_3 50.00 (J = 3.1 Hz), C_7 28.74 (J = 16.9 Hz), C_6 31.04 (J = 15.8 Hz), C_{10} 33.72 (J = 4.0 Hz), CH_3 30.15	61.22
 **3**	150 (3), 149 (30), 135 (100), 119 (2), 118 (2), 117 (3)	C_1 49.30 (J = 87.3 Hz), 37.43 (J = 2.5 Hz), 36.49 (J = 4.2 Hz), 35.40 (J = 2.8 Hz), 34.92, 34.62 (J = 3.8 Hz), 27.85 (J = 15.9 Hz), C_α 37.24, C_β 16.05	61.60
 **4**	188 (15), 187 (100), 145 (5), 131 (8), 119 (1), 117 (3)	C_1 46.90 (^1J = 89.4 Hz), 37.21, 37.15, 36.69, 36.37, 35.963, 35.91, 35.87, 35.80, 24.95	62.27
 **5**	228 (1), 226 (2), 118 (6), 117 (10), 109 (100)	47.52 (J 3.2 Hz), 37.44 (J = 3.5 Hz), 34.07 (J = 8.4 Hz), 25.71 (J = 9.6 Hz)	62.17
 **6**	145 (72), 119 (14), 118, 69 (100), 68 (66), 67 (48), 47 (33)	C_1 50.76 (^1J = 96.6 Hz), C_2 27.76 (^2J = 2.4 Hz), C_3 26.37 (^3J = 13.4 Hz)	55.08
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-POCl_2$ **7**	176 (1), 174 (2), 119 (3), 117 (9), 57 (100.0)	C_1 45.52 (^1J = 68.4 Hz), C_2 24.11	64.96

[a] ^{13}C NMR spectra (50 MHz) were recorded using tetramethylsilane as internal standard; ^{31}P NMR spectra (81 MHz) were recorded using H_3PO_4 as external standard.

$^{\delta-}AlCl_3$ species in equilibrium with PCl_3. Whereas a stable bis(dialkylamino)-substitutd phosphenium ion was obtained from the corresponding chloride with $AlCl_3$ in CH_2Cl_2, to date there is no evidence for the long-lived existence of $^+PCl_2$ (as well as $^+PF_2$) in the condensed phase.[16,18] Although halogen substituents should be capable of conjugatively stabilizing phosphenium ions by conjugation, they probably have insufficient π-donor character to impart the necessary thermodynamic stabilization, unless the phosphonium ion contains strongly electron-donating ligands, including transition-metal moieties. Consequently PX_3 (X = Cl, F) with $AlCl_3$ gives only donor–acceptor complexes[16] rather than the dichlorophosphenium ion $^+PCl_2$. This ion, however, has been identified in the mass spectrum of PCl_3 as the most abundant positive ion.[19] ^{31}P NMR studies gave no indication for the $^+PCl_2$ ion in PCl_3–$AlCl_3$/CH_2Cl_2.

No evidence was obtained in the present study that a polarized $Cl_2^{\delta+}P–Cl \rightarrow Al^{\delta-}Cl_3$ complex (or undetectable PCl_2^+ ion) would directly substitute adamantane (or other hydrocarbons) via C–H bond insertion involving a pentacoordinate carbonium ion intermediate. Although Lewis acids, including $AlCl_3$, are capable of abstracting hydride from hydrocarbons (involving the protic conjugate acids), when adamantane and $AlCl_3$ was refluxed in 1,1,2-trichlorotrifluoroethane (Freon-113), instead of CH_2Cl_2, solution, only ~2% of 1-adamantylphosphonic acid dichloride was obtained. This reaction also gave extremely poor yields in other solvents. Thus carbocation formation fom adamantane (or other tertiary hydrocarbons) by reaction with $AlCl_3$ (i.e., $AlCl_3$–H_2O) followed by alkylation of PCl_3 is possible but appears to be only a minor contribution toward the phosphorylation reaction in CH_2Cl_2 solution. However, CH_2Cl_2 through its polarized complex with $AlCl_3$, i.e. $ClCH_2^{\delta+}\cdots Cl \rightarrow {}^{\delta-}AlCl_3$ strongly assists the reaction.

Experimental Section

Phosphorus trichloride (Aldrich) and aluminum trichloride (Fluka) were analytical grade reagents of highest purity. Cyclopentane, adamantane, and 1,3-dimethyladamantane were obtained from Aldrich. 1-Isopropyladamantane,[20] bicyclo[2.2.2]octane, and diamantane[21,22] were prepared as reported. Dichloromethane was dried over P_2O_5 under reflux and distilled.

Gas chromatographic analyses were obtained on a Varian (Model 3700) gas chromatograph using a quartz silica capillary column coated with DB-1. Mass spectroscopic analysis was performed on a Finnigan Mat Model 700 GC–MS spectrometer. ^{13}C and ^{31}P NMR spectra were recorded on a Varian-200 MHz

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(VXR-200) superconducting NMR spectrometer.

General Procedure for Preparation of Alkylphosphonic Acid Dichloride. To a suspension of hydrocarbon (10.0 mmol), aluminum chloride (1.72 g, 13.0 mmol), and dry dichloromethane (25 mL) was slowly added a 2 M solution of phosphorus trichloride in dichloromethane (5.5 mL, 11.0 mmol) with stirring under nitrogen atmosphere at 0 °C (ice bath) during a period of 10 min. After the addition of phosphorus trichloride had been completed, the ice bath was removed and the reaction mixture was heated to reflux for the stipulated time (Table I) and cooled, and then a 10% aqueous solution of hydrochloric acid was slowly added. After the addition of hydrochloric acid to the reaction mixture, stirring was continued for another 0.5 h. Normal workup and extraction was carried out with dichloromethane (5 mL $\times$ 3), and the combined organic layer was dried over anhydrous magnesium sulfate; evaporation in vacuo afforded the crude products, which could be purified via column chromatography on silica gel (hexane and dichloromethane as eluents) to give the corresponding alkylphosphonic acid dichlorides.

1-Adamantylphosphonic Acid Dichloride (1). The reaction of adamantane (1.36 g, 10.0 mmol), $AlCl_3$, and PCl_3 in the ratio provided in Table I gave 1. All the spectral data were consistent with the literature values.[9]

(3,5-Dimethyladamantyl)phosphonic Acid Dichloride (2). The reaction of 1,3-dimethyladamantane (1.6 g, 10 mmol), $AlCl_3$, and PCl_3 gave 2 as colorless crystals, mp 78.5–80.2 °C. $C_{12}H_{19}POCl_2$ Calcd: C, 51.24; H, 6.77; P, 11.03. Found: C, 50.88; H, 6.52; P, 10.93.

(3-Isopropyladamantyl)phosphonic Acid Dichloride (3). The reaction of 1-isopropyladamantane (1.78 g, 10.0 mmol), $AlCl_3$, and PCl_3 gave 3 as a colorless liquid, bp 141–142 °C (1.0 mm). $C_{13}H_{21}POCl_2$ Calcd: C, 52.91; H, 7.12. Found: C, 53.12; H, 7.09.

3-Diamantylphosphonic Acid Dichloride (4). The reaction of diamantane[22] (1.88 g, 10.0 mmol), $AlCl_3$, and PCl_3 gave 4 as colorless crystals, mp 288–289 °C. $C_{14}H_{19}POCl_2$ Calcd: C, 55.11; H, 6.23; P, 10.16; Cl, 23.28. Found: C, 54.88; H, 6.40; P, 10.55; Cl, 23.52.

1-Bicyclo[2.2.2]octylphosphonic Acid Dichloride (5). The reaction of bicyclo[2.2.2]octane (1.10 g, 10.0 mol), $AlCl_3$, and PCl_3 gave 5 as a colorless liquid, bp 69–70 °C (1.0 mm). $C_8H_{13}POCl_2$ Calcd: C, 42.32; H, 5.73. Found: C, 42.55; H, 5.61.

Cyclopentylphosphonic Acid Dichloride (6). From the reaction of cyclopentane (0.7 g, 10.0 mmol), $AlCl_3$, and PCl_3 was obtained 6. All spectral data were consistent with the literature values.[23]

***tert*-Butylphosphonic Acid Dichloride (7).** The reaction of condensed isobutane (0.58 g, 10.0 mmol), $AlCl_3$, and PCl_3 in a closed vessel gave 7 as a colorless liquid, bp 45–46 °C (30 mm). $C_4H_9POCl_2$ Calcd: C, 27.63; H, 5.14; Cl, 40.57. Found: C, 27.88; H, 5.09; Cl, 40.19.

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Difunctionalized 4-Nitroisoxazoles as Dienophiles in Diels–Alder Reactions[1]

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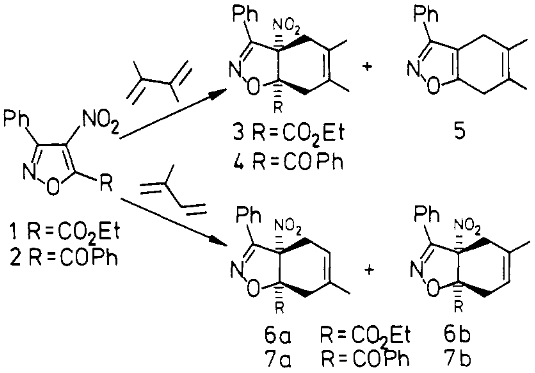
[2 + 4] Cycloadditions of the nitroisoxazoles 1 and 2 with 2,3-dimethylbuta-1,3-diene afforded the bicyclic derivatives 3 and 4 in good yields; the regio- and stereochemical pattern of the reactions of the same compounds with isoprene and cyclohexa-1,3-diene, respectively, was investigated. The structures of the new compounds were established on the basis of spectroscopic and chemical data.

A great deal of work carried out over a century[2] well established for the isoxazole ring a peculiar and versatile reactivity that appears very attractive both from a mechanistic viewpoint and for synthetic purposes. Despite that, the possibility of employing "aromatic" derivatives of this system as dienophiles remained unexplored until ethyl 4-nitro-3-phenylisoxazole-5-carboxylate (1) was found to react with 2,3-dimethylbuta-1,3-diene (DMB) in toluene at 110 °C to give the cycloadduct 3 in good yields together with a small amount of the dihydro-1,2-benzisoxazole 5[1] (Scheme I).

In an effort to expand the scope of this new [2 + 4] cycloaddition process in the isoxazole series, we now report the behavior of the corresponding nitro ketone 2, recently obtained in our laboratory,[3] with the same reagent, as well as the reactivity of compounds 1 and 2 toward isoprene and cyclohexa-1,3-diene, respectively.

Scheme I



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(1) For a preliminary communication on a part of this work, see: Nesi, R.; Giomi, D.; Papaleo, S.; Quartara, L. *J. Chem. Soc., Chem. Commun.* **1986**, 1536.

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(3) Nesi, R.; Giomi, D.; Papaleo, S.; Bracci, S.; Dapporto, P. *Synthesis* **1988**, 884.