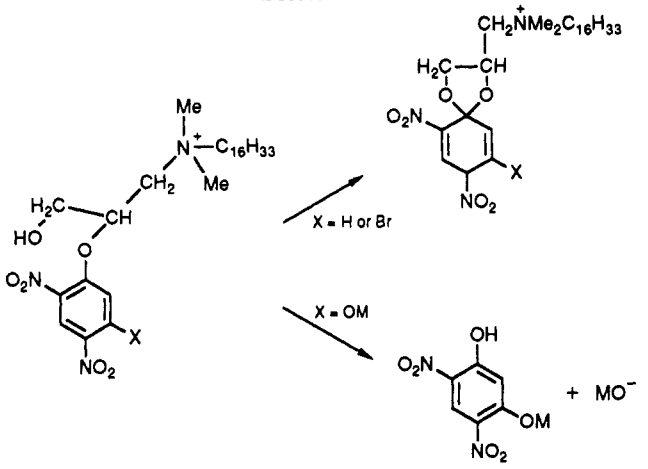
Scheme II



pound 4 with the fluoro group replaced by a bromo group is produced. This compound is less sterically crowded than the dimicellar ether 6 and the intramolecular reaction leading to the corresponding Meisenheimer complex should be favored compared to reaction with hydroxide ion. This is confirmed by the rapid production of a strong absorbance at 480 nm (A = 0.8).

The Meisenheimer complex formed from BrDNFB decomposed slowly at 30 °C in a reaction that had a slightly less than first-order dependence on the hydroxide ion concentration. This is typical of second-order reactions carried out under pseudo-first-order conditions in the presence of micelles.[7,8]

The rate constants for this reaction are in Table Ib. Since these rate constants for the decomposition of the Meisenheimer complex depend on the hydroxide concentration, we conclude that ring opening of the Meisenheimer complex to form the aryl micellar ether is fast and the decomposition of the micellar ether is the rate-determining step, as is the case for DNFB.[3]

Experimental Section

Materials. (a) Substrates. DFDNB (1, Aldrich) and BrDNFB (Alfred Bader Library of Rare Chemicals/Aldrich) were commercially available. 5-Fluoro-2,4-dinitrophenol (2), mp 78–80 °C (lit.[9] mp 80 °C) was prepared from DFDNB (1) by treatment with a solution containing 0.5 M NaOH at reflux temperature for 2 h. The reaction solution was cooled to room temperature, extracted with Et_2O (3 × 50 mL) to remove residual 1 and then acidified with dilute HCl. This solution was then extracted again with Et_2O (3 × 50 mL). The extract was dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallized (EtOH/water) to give 2, which was pure by TLC (SiO_2/2:1 petroleum ether–$CHCl_3$).

(b) Detergents. CTAB was commercially available (BDH), while CHEDAB,[10] CHPDAB,[10] 2-OHCTAB,[10] and CDHPDAB[3] were prepared as previously described.

CTAB was purified by the method of Mukerjee and Mysels.[11] Distilled water was further purified by a Millipore system to achieve a resistivity of at least 10 MΩ cm^{-1}.

Kinetics. Stock solutions (0.01 M) of the substrates were prepared in HPLC-grade acetonitrile. Stock solutions of NaOH (0.5 M) and the detergents (20 mM) were prepared in purified water. Rate measurements were carried out at the temperatures indicated in the tables in a cuvette kept at constant temperature in the cell compartment of a Varian 635 UV–vis spectrophotometer. Solutions for kinetic studies were prepared by mixing appropriate volumes of NaOH and detergent with dilution as required. The mixed solutions were placed into cuvettes and allowed 30 min in the constant temperature cell holder of a Varian 635 UV–vis spectrophotometer to reach thermal equilibrium. The temperature within the cuvette was measured with a Jenco Thermistor thermometer. Then, a sample of the stock solution of the required substrate (20 μL) was added and the contents were mixed thoroughly to initiate the reaction. The rate of change of absorbance at the desired wavelength (see tables) was followed by means of a National VP 6511 A X-T recorder. Reactions were followed to infinity (10 half-lives) where possible or, alternatively for very slow reactions or for consecutive reactions, an infinity value was calculated by using a computer program designed to give the best straight-line fit to data collected over at least 2 half-lives. Good agreement was obtained between rate constants and infinity measurements obtained by the two methods. Rate constants were all obtained in duplicate and average results (within ±2%) are presented in the tables.

All reactions were first studied using an X-Y recorder to determine the spectral changes occurring during the reaction. Substrate solution (20 μL) was added to the desired detergent/NaOH mixture in a cuvette, and the reaction mixture was scanned between 550–250 nm at appropriate time intervals.

Abbreviations. DNFB, 2,4-dinitrofluorobenzene; CTAB, cetyltrimethylammonium bromide; CHEDAB, cetyl(2-hydroxyethyl)dimethylammonium bromide; 2-OH-CTAB, (2-hydroxycetyl)trimethylammonium bromide; CDHPDAB, cetyl(2,3-dihydroxypropyl)dimethylammonium bromide; DFDNB, 1,5-difluoro-2,4-dinitrobenzene; BrDNFB, 5-bromo-2,4-dinitrofluorobenzene; CHPDAB, cetyl(2-hydroxypropyl)dimethylammonium bromide.

Registry No. DFDNB, 327-92-4.

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Phosphonium Ions Rather Than Phosphenium Ions from the Reaction of Secondary Phosphines with Trityl Cation

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Introduction

Phosphenium and nitrenium ions ($R_2P:^+$ and $R_2N:^+$) are isoelectronic with silylenes and carbenes ($R_2Si:$ and $R_2C:$) but possess the positive charge of silylenium and carbenium ions (R_3Si^+ and R_3C^+). All of these species have only a sextet of valence electrons and hence possess an empty p orbital. The two neutral species and the nitrenium ion are generally regarded as reactive intermediates, available for study only on a brief time scale. Carbenium ions have been known as stable species for decades, and silylenium ions also have been found to be long-lived under selected conditions of solvent.[1] Phosphenium ions were reported as stable species in solution during the 1970s.[2] Essentially all reported examples of phosphenium ions have at least one heteroatom, usually nitrogen, directly attached to phosphorus.

The most common method for preparation of phosphenium ions is chloride abstraction from chloro-

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phosphines with aluminum chloride, eq 1. We have found[1]

$$R_2\ddot{P}Cl + AlCl_3 \rightarrow R_2P{:}^+\ AlCl_4^- \quad (1)$$

that hydride abstraction from silanes[3] is the most successful method for the production of silylenium ions, eq 2. Consequently, we have carried out studies to examine

$$R_3SiH + Ph_3C^+\ ClO_4^- \rightarrow R_3Si^+\ ClO_4^- + Ph_3CH \quad (2)$$

whether secondary phosphines can react with trityl via hydride abstraction to form phosphenium ions eq 3. In

$$R_2\ddot{P}H + Ph_3C^+\ ClO_4^- \rightarrow R_2P{:}^+\ ClO_4^- + Ph_3CH \quad (3)$$

particular, we wanted to use this method to form phosphenium ions with alkyl or aryl substituents rather than the usual heteroatom substituents. We report herein that trityl reacts entirely with the lone pair rather than with the hydride of the phosphines, so that the quaternized phosphonium ion is formed.

Results and Discussion

In order to confirm that our analytical methods could detect and characterize the same species that previous workers have claimed to be phosphenium ions, we carried out the reaction of eq 1 with bis(diisopropylamino)-chlorophosphine at −78 °C in dichloromethane (0.2 M). The reaction mixture became light yellow when warmed to room temperature. The ^{31}P spectrum showed a sharp singlet at δ 313, and the ^{27}Al spectrum showed a singlet at δ 102.9 (line width 11.5 Hz), in agreement with the literature.[2]

We carried out the hydride abstraction reaction of eq 3 with the same substrate (R = diisopropylamino). In dichloromethane, acetonitrile, or sulfolane, the resonances of starting material disappeared but none of the resonances expected for the phosphenium ion appeared. The ^{31}P spectrum contained several peaks.

Because the amino groups have alternative sites of nucleophilicity (the amino nitrogens) that could react with the trityl cation, we carried out the same reaction with the simpler substrate, diphenylphosphine. Reaction with trityl perchlorate in dichloromethane did not lead to formation of Ph_3CH (eq 3). The phosphine hydride resonance at δ 5.23 (J_{P-H} = 219 Hz) disappeared and was replaced with a new doublet at δ 9.22 (J_{P-H} = 504 Hz). In the ^{31}P spectrum, the doublet of starting material at δ −39.6 was replaced cleanly by a new doublet at δ 13.1 (J_{P-H} = 504 Hz). In sulfolane, the results were the same, except that the ^{31}P doublet of product was centered at δ 16.2. A very small amount of diphenylphosphine oxide from reaction with residual water also was observed.

The resonance position and the one-bond P–H coupling of the product are consistent with a phosphonium ion formed by quaternization of the phosphine by reaction of the trityl cation at the phosphorus lone pair site, eq 4. The

$$Ar_2\ddot{P}H + Ph_3C^+\ ClO_4^- \rightarrow Ar_2\overset{+}{P}HCPh_3\ ClO_4^- \quad (4)$$

product mixture was quenched with water, and the organics were extracted with hexane. Mass spectral analysis of the hexane extracts indicated that the major products were Ph_3COH (from reaction of water with excess trityl cation), Ph_3CH, Ph_2CO, and $Ph_2P(O)CPh_3$. The last product could be formed by the process of eq 5.

The phosphonium structure was confirmed by isolation and characterization of the tetrafluoroborate salt. For

$$Ph_2PH + Ph_3C^+\ ClO_4^- \longrightarrow Ph_2\overset{+}{P}HCPh_3\ ClO_4^- \xrightarrow{H_2O} Ph_2P(H)(OH)CPh_3 \xrightarrow{[O]} Ph_2P(O)CPh_3 \quad (5)$$

purposes of purification, it was deemed that BF_4^- would be safer than ClO_4^-. Reaction of diphenylphosphine with trityl tetrafluoroborate in dichloromethane at −78 °C and evaporation of the solvent produced a white solid. The ^1H doublet at δ 8.95 (J_{P-H} = 508 Hz) and the ^{31}P doublet at δ 13.56 (J_{P-H} = 508 Hz) corresponded well with the perchlorate product. The mass spectral parent peak from the solid was at 429 ($Ph_2(Ph_3C)PH^+$). The ^{11}B spectrum contained a singlet at δ −1.21 (trityl tetrafluoroborate was at δ −1.55). Finally, elemental analysis confirmed the structure $Ph_2P^+HCPh_3\ BF_4^-$.

In order to decrease the ability of the phosphine to complex with trityl, we prepared substrates with bulkier aryl groups. Dimesitylphosphine and bis(2,4,6-triisopropylphenyl)phosphine were prepared by reduction of the corresponding halophosphines. Reaction of mesitylmagnesium bromide with trichlorophosphine according to literature procedures gave a mixture of the chloro- and bromophosphines, which were converted to the hydride with lithium aluminum hydride.[4] The ^{31}P spectrum of the hydride showed a singlet at δ −91.2 (J_{P-H} = 232 Hz), which disappeared on reaction with trityl perchlorate in CD_2Cl_2 and was replaced with a singlet of δ 22.7 (J_{P-H} = 494 Hz). The new product was assigned the structure $Mes_2(Ph_3C)P^+H\ ClO_4^-$ by analogy with the phenyl system. Therefore, the increased bulk of mesityl compared with phenyl failed to alter the mode of reactivity.

To increase the aryl bulk further, we prepared bis-(2,4,6-triisopropylphenyl)phosphine by the same procedure. This material was not obtained in pure form, as the ^{31}P spectrum contained two impurities along with the resonance of the hydride (δ −100.8, J_{P-H} = 231 Hz). The impurities did not impede the reaction with trityl perchlorate, as the starting hydride peaks were replaced by a doublet at δ 24.1 (J_{P-H} = 510 Hz), due presumably to $Ar_2(Ph_3C)P^+H$. Although we did not carry out a rigorous structure proof, this value of J_{P-H} is diagnostic of a phosphonium ion. Efforts were made to prepare bis-(2,4,6-tri-*tert*-butylphenyl)phosphine without success.

In all cases examined, the secondary phosphine appeared to react with trityl perchlorate at the phosphine lone pair, eq 4. Apparently the nucleophilicity of the phosphorus lone pair is considerably greater than that of the phosphine hydride, so that the P–H bond remains intact. The higher electronegativity of phosphorus than silicon, by 0.2–0.3 unit on either the Allred–Rochow or Pauling scales, renders the P–H bond less polar than the Si–H bond, so that the phosphine hydride is less nucleophilic.

Experimental Section

Trityl perchlorate was prepared as previously reported.[1] NMR spectra were recorded on JEOL FX-270 and Varian VXR-400 spectrometers at ambient temperatures. Chemical shifts are reported downfield from 85% phosphoric acid for ^{31}P and from aluminum chloride for ^{27}Al. Dichloromethane was dried over CaH_2. All reactions were carried out under N_2, and solutions were transferred entirely by syringe techniques in the inert atmosphere.

Bis(diisopropylamino)phosphine. Diisopropylamine was allowed to react with trichlorophosphine according the method of King and Sundaram.[5] Bis(diisopropylamino)chlorophosphine

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was obtained in 42% yield (mp 94–98 °C; lit.[5] mp 96–98 °C). The chlorophosphine was reduced with $LiAlH_4$ in 64% yield to give bis(diisopropylamino)phosphine (bp 76–79 °C (0.4 mmHg); lit.[5] bp 83–85 °C (0.5 mmHg). The chlorophosphine also was converted to the analogous phosphenium tetrachloroaluminate according to the method of Cowley et al.[6]

Dimesitylhalophosphine. Magnesium (70 mmol) and 10 mL of tetrahydrofuran (THF) were placed into a 100-mL, three-necked flask equipped with a magnetic stirrer, a condenser, and an addition funnel. Mesityl bromide (58 mmol) in 50 mL of THF was added slowly, at such a rate as to keep the reaction mixture at a gentle reflux. The mixture was allowed to reflux for 1 h upon completion of the addition. In a separate 250-mL, three-necked flask was placed PCl_3 (29 mmol) in 65 mL of THF, and the Grignard reagent was added via an addition funnel, with the reaction mixture cooled to −78 °C under an N_2 atmosphere. The mixture was stirred at room temperature overnight. The solvent was removed by distillation, and the product was extracted with hexane. Distillation of the extracts gave a light yellow liquid that solidified overnight (87% based on a 1:1 mixture of chloride and bromide): bp 180–195 °C (0.3 mmHg).

Dimesitylphosphine. Dimesitylhalophosphine (25 mmol) and 50 mL of THF were placed in a 100-mL, three-necked flask. At −78 °C, 10 mmol of $LiAlH_4$ was added slowly with rapid stirring. The mixture was stirred overnight at room temperature, the solvent was removed by rotary evaporation, and the product was extracted with hexane. Evaporation of the hexane gave a light yellow solid, which was recrystallized from hexane to give a colorless solid (68%, mp 89–91 °C): ^1H NMR (CD_2Cl_2) δ 2.24 (s, 6 H), 2.25 (s, 12 H), 5.25 (d, 1 H, J_{P-H} = 232 Hz), 6.83 (s, 4 H); ^{31}P NMR (CD_2Cl_2) δ −91.3 (d, J_{P-H} = 232 Hz); IR (Nujol) 2492 (m) cm^{-1}; MS m/z 270 (M^+, 98.8).

Bis(2,4,6-triisopropylphenyl)phosphine was prepared in the same fashion as dimesitylphosphine but was not obtained in pure form.

Reaction of Phosphine with Trityl Perchlorate. The example of reaction with bis(diisopropylamino)phosphine is given. Stock solutions (0.1 M) were prepared from 0.1142 g (0.49 mmol) of bis(diisopropylamino)phosphine in 5 mL of CH_2Cl_2 and from 0.43 g (1.25 mmol) of trityl perchlorate in 12.5 mL of CH_2Cl_2. In an oven-dried, 10-mL NMR tube were placed 2 mL of CH_2Cl_2 and 1 mL of the 0.1 M stock solution of trityl perchlorate (0.1 mmol). At −78 °C, 1 mL of the phosphine solution (0.1 mmol) was added to the NMR tube under N_2. The resulting concentration was 0.025 M. The NMR tube was allowed to warm to room temperature with occasional shaking. The color of the mixture changed from yellowish brown to light yellow. After 3 h at room temperature, NMR spectra were recorded.

Reaction of Diphenylphosphine with Trityl Tetrafluoroborate. Trityl tetrafluoroborate (19.3 mmol) and CH_2Cl_2 (40 mL) were placed into a 100-mL, three-necked flask equipped with a magnetic stirrer and under N_2. Diphenylphosphine (19.3 mmol) in CH_2Cl_2 (20 mL) was added slowly to the flask at −78 °C with stirring. The mixture decolorized and a white solid appeared. The mixture was stirred overnight at room temperature. The solvent was evaporated, and the resulting white solid was washed five times with hexane and dried overnight under reduced pressure to give 8.92 g (90%) of diphenyl(triphenylmethyl)-phosphonium tetrafluoroborate: ^1H NMR (CD_2Cl_2) δ 7.19–7.28 (m, 10 H), 7.41–7.48 (m, 12 H), 7.68–7.73 (m, 3 H), 8.95 (d, 1 H, J_{P-H} = 508 Hz); ^{31}P NMR (CD_2Cl_2) δ 13.56 (d, J_{P-H} = 508 Hz); ^{11}B NMR (CD_2Cl_2) −1.21 (s) (trityl tetrafluoroborate was used as an external standard at δ −1.55); IR (Nujol) 2420 (w) cm^{-1}; MS m/z 429 ($Ph_2(Ph_3C)HP^+$, 75), 244 (Ph_3C^+, 100). Anal. Calcd for $C_{31}H_{28}BF_4P$: C, 72.11; H, 5.08; P, 6.00. Found: C, 71.95; H, 5.06; P, 5.70.

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Registry No. $(i\text{-Pr})_2NPN(Pr\text{-}i)_2^+ \cdot AlCl_4^-$, 68880-45-5; bis(diisopropylamino)chlorophosphine, 56183-63-2; bis(diisopropylamino)phosphine, 86660-77-7; mesityl bromide, 576-83-0; dimesitylbromophosphine, 86280-09-3; dimesitylchlorophosphine, 67950-05-4; dimesitylphosphine, 1732-66-7; bis(2,4,6-triisopropylphenyl)phosphine, 135665-28-0; diphenylphosphine, 829-85-6; diphenyl(triphenylmethyl)phosphonium tetrafluoroborate, 135665-30-4.

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N-Fluoropyridinium Pyridine Heptafluorodiborate: A Useful Fluorinating Agent

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The development of electrophilic fluorinating agents has been the subject of intense investigation by a number of research groups.[1] Most recently, *N*-fluoropyridinium triflates[2] and *N*-fluorosulfonamides[3] have been introduced as stable effective reagents with a wide range of strengths for the selective preparation of fluorine-containing molecules. These reagents, however, have the unfortunate disadvantages of tedious preparation and high cost in large-scale applications.

As part of our ongoing interest in fluorine chemistry, we report the ability of *N*-fluoropyridinium pyridine heptafluorodiborate (NFPy) (1) to react with enol compounds, under mild conditions, to selectively transfer fluorine to the reactive sites of organic compounds (Table I). NFPy is a cream colored crystalline solid, with an empirical formula of $C_5H_5NF(C_5H_5N)B_2F_7$, conveniently prepared by the reaction of fluorine with pyridine–boron trifluoride complex as described by Van Der Puy et al.[4] Treatment of enol acetates with 1 in refluxing acetonitrile gives α-fluoro ketones in good yields. Exposure of 1-acetoxy-4-*tert*-butylcyclohexene to NFPy affords a 62% yield of *cis*-/*trans*-2-fluoro-4-*tert*-butylcyclohexanone in a 3:1 ratio (entry 1). Similarly, the enol acetates derived from 17-keto steroids upon reaction with 1 yield high α/β ratios of the corresponding 16-fluoro steroids (entry 3).

Fluorine can be introduced selectively into the 6-position of steroids by employing their dienol acetates. For example, treatment of 3,5-androstadiene-3,17β-diol diacetate with 1 in acetontrile affords 6-fluorotestosterone acetate (entries 4 and 5). In all the reactions studied, fluorination occured at the terminus of the conjugated system and no complications were observed by the presence of carbonyl groups.

For steroids with two reactive sites of conjugated and nonconjugated enol acetates, NFPy showed a preference in fluorinating the terminus of the conjugated vinyl esters

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