1450, 1140, 1120, 1070, 1035, 1020 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.55 (m, 2 H), 3.9–3.65 (m, 4 H), 3.55–3.30 (m, 4 H), 2.55 (bt, J = 7, 2 H), 2.20 (bt, J = 7, 2 H), 1.90 (s, 3 H), 1.65–1.4 (m, 20 H); MS, *m/e* (relative intensity) 353 (M$^+$ – I, 22), 269 (31), 185 (37), 149 (40), 85 (75), 53 (100); HRMS calcd for $C_{21}H_{37}O_4$ 353.2691, found 353.2696.

5,6-Dimethyl-5-decene-1,10-diol Bis(tetrahydropyranyl ether) (5). In a flask was placed tetrakis(triphenylphosphine)-palladium (0.140 g, 0.116 mmol) under N$_2$. A solution of the above iodo diether (0.96 g, 2 mmol) in freshly distilled benzene (35 mL) was added, and the mixture stirred at room temperature for 30 min. Three equivalents of methylmagnesium iodide in ether were injected into the flash with a syringe over 12 h. After aqueous workup, chromatography on alumina (activity III) eluting with ether–petroleum ether (1:9) gave **5** (0.602 g, 80%): colorless oil; IR (neat) 2940, 2860, 1455, 1440, 1350, 1140, 1120, 1070, 1035 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.55 (t, J = 3.75, 2 H), 3.85–3.70 (m, 4 H), 3.50–3.33 (m, 4 H), 2.02 (t, J = 7.5, 4 H), 1.59 (s, 6 H) 1.8–1.4 (m, 20 H); MS, *m/e* (relative intensity) 368 (M$^+$, 5), 200 (8.2), 167 (3.2), 149 (20), 85 (100); HRMS calcd for $C_{22}H_{40}O_4$ 368.2927, found 368.2928.

5,6-Dimethyl-5-decene-1,10-diol. To a solution of **5** (0.60 g, 1.6 mmol) in methanol (1 mL) was added *p*-toluenesulfonic acid (5 mg) at 0 °C. The temperature was allowed to rise to room temperature, the reaction mixture was stirred for 12 h, and potassium carbonate (0.5 g) was added. Chromatography on silica gel with ether as eluent gave the desired diol (0.31 g, 97%): colorless oil; IR (neat) 3320, 2930, 2860, 1450, 1360, 1060, 1035 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.63 (t, J = 6.1, 4 H), 2.03 (t, J = 7.5, 4 H), 1.60 (s, 6 H), 1.6–1.35 (m, 8 H); MS, *m/e* 200 (relative intensity) (M$^+$, 14), 192 (9), 149 (16), 55 (100); HRMS calcd for $C_{12}H_{24}O_2$ 200.1776, found 200.1780. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.58, H, 11.88.

5,6-Dimethyl-5-decene-1,10-diol Dimesylate. To a solution of the enediol (0.20 g, 1.0 mmol) in freshly distilled methylene chloride (10 mL) at 0 °C were added under N$_2$ triethylamine (0.303 g, 3.0 mmol) and then methanesulfonyl chloride (0.286 g, 2.5 mmol) via syringe within 5 min. The mixture was stirred for 15 min at 0 °C and then worked up with cold water to give the crude dimesylate, pure by TLC and ^{1}H NMR (0.345 g, 96%): colorless oil; IR (neat) 3020, 2940, 2860, 1380, 1170, 990, 930 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 4.20 (t, J = 7, 4 H), 2.95 (s, 6 H), 2.00 (t, J = 7, 4 H), 1.60 (s, 6 H), 1.7–1.4 (m, 8 H).

1,10-Dibromo-5,6-dimethyl-5-decene (6). In a round-bottomed flask were placed the dimesylate (0.32 g, 0.90 mmol), lithium bromide (0.39 g, 4.5 mmol), and freshly distilled DMF (10 mL). The flask was continuously purged with a flow of N$_2$ and the mixture heated to 70 °C for 1 h. The resulting solution was worked up with water and the crude product chromatographed on silica with ether–petroleum ether (1:9) as eluent to give **6** (0.272 g, 93%): colorless liquid; IR (neat) 2960, 2945, 2860, 1455, 1445, 1250 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.40 (t, J = 6.8, 4 H), 2.01 (t, J = 7.5, 4 H), 1.82 (quin, J = 7, 4 H), 1.60 (s, 6 H), 1.47 (quin, J = 7, 4 H).

7,8-Dimethyltetradec-7-ene-1,13-diyne (7). In a round-bottomed flask were placed under N$_2$ lithium acetylide–ethylenediamine complex (0.276 g, 3 mmol) and freshly distilled Me$_2$SO (2 mL). To this slurry was added the dibromide **6** (0.245 g, 0.75 mmol) in Me$_2$SO (2 mL) at 10 °C within 5 min. The mixture was stirred under N$_2$ for 2.5 h at room temperature, then quenched with cold water, and worked up. The crude compound was chromatographed on silica gel with ether–petroleum ether (1:9) as eluent to give enediyne **7** (0.145 g, 95%): colorless oil; IR (neat) 3300, 2940, 2860, 2120, 1455, 1440 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 2.18 (td, J = 7, 2.7, 4 H), 2.00 (t, J = 7, 4 H), 1.92 (t, J = 2.7, 2 H), 1.60 (s, 6 H), 1.53–1.43 (m, 8 H); MS, *m/e* (relative intensity) 216 (M$^+$, 8), 201 (8.3), 164 (25), 145 (11), 84 (100); HRMS calcd for $C_{16}H_{24}$ 216.1879, found 216.1882.

(η^5-Cyclopentadienyl)(8a,9,10,10a-η^4-*endo*,*endo*-*cis*-1,2,3,4,4a,4b,5,6,7,8-decahydro-4a,4b-dimethylphenanthrene)cobalt (8). A degassed solution of **7** (38.9 mg, 0.18 mmol) in *m*-xylene (20 mL) was heated to 120 °C and irradiated (visible light, GE-ENH, 250 W) in the presence of CpCo(CO)$_2$ (36 mg, 0.20 mmol). After 1.5 h the solvent was removed in vacuo (0.05 torr) and the residue chromatographed on alumina (activity II) under N$_2$ with degassed hexane as eluent to give the complex **8** (37 mg, 60%): red orange oil; ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 4.57 (s, 2 H), 4.50 (s, 5 H), 2.4–1.75 (m, 6 H), 1.65 (m, 4 H), 1.45–1.25 (m, 4 H), 1.21 (s, 6 H), 1.00 (m, 4 H); MS, *m/e* (relative intensity) 340 (M$^+$, 88), 325 (10), 310 (14), 272 (39), 216 (41), 201 (94), 187 (13), 173 (42), 159 (100); HRMS calcd for $C_{21}H_{29}Co$ 340.1601, found 340.1593.

***cis*-1,2,3,4,4a,4b,5,6,7,8-Decahydro-4a,4b-dimethylphenanthrene (9).** The cobalt complex **8** (36 mg, 0.11 mmol) was filtered through silica gel (10 g) with degassed hexane as eluent under N$_2$ to give the free ligand **9** (14 mg, 61%): viscous, colorless oil; IR (neat) 3030, 2920, 2860, 1650, 1600 cm^{-1}; ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 5.55 (s, 2 H), 2.37 (ddd, J = 4.7, 13.1, 2 H), 2.18 (ddd, J = 1.5, 3, 13, 2 H), 1.82 (bd, J = 11, 2 H) 1.75–1.25 (m, 10 H), 1.02 (s, 6 H); MS, *m/e* (relative intensity) 216 (M$^+$, 60), 201 (84), 187 (27), 159 (100); HRMS calcd for $C_{16}H_{24}$ 216.1877, found 216.1874.

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Registry No. **1**, 1720-37-2; **2**, 92937-82-1; **3**, 92937-83-2; **4**, 92937-84-3; **4**·2THP, 92937-89-8; **5**, 92937-85-4; **6**, 92937-86-5; **7**, 92937-87-6; **8**, 92957-39-6; **9**, 92937-88-7; Cp$_2$ZrCl$_2$, 1291-32-3; (CH$_3$)$_3$Al, 75-24-1; (Ph$_3$P)$_4$Pd, 14221-01-3; CH$_3$MgI, 917-64-6; LiC≡CH, 1111-64-4; CpCo(CO)$_2$, 12078-25-0; 4-bromobutanol tetrahydropyranyl ether, 31608-22-7; dihydropyran, 110-87-2; 5,6-dimethyl-5-decene-1,10-diol, 92937-90-1; 5,6-dimethyl-5-decene-1,10-diol dimesylate, 92937-91-2; ethylenediamine, 107-15-3.

Reaction of Bis(2,4-dinitrophenyl) Phosphate with Hydrophobic Ammonium Ions

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The overall hydrolysis of diaryl phosphates is a two-step reaction,[1] and reaction of bis(2,4-dinitrophenyl) phosphate (bis-2,4-DNPP) in aqueous alkali is shown in Scheme I.[2]

The first step involves nucleophilic attack upon the phosphoryl group and the second step is spontaneous heterolysis, which is written as generating short-lived metaphosphate ion.[1-5]

Both steps of the reaction are speeded by cationic micelles which assist attack of OH$^-$ by bringing the reactants into close proximity and assist spontaneous dephosphorylation by exerting a medium effect.[6]

Functional micelles which contain nucleophilic groups are effective reagents in deacylation, dephosphorylation, and nucleophilic addition and substitution.[7-10] Nonmi-

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Scheme I

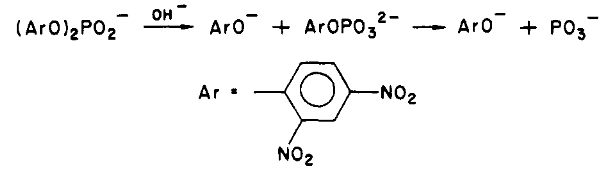


Table I. Interaction of 1 and Bis-2,4-DNPP[a]

10^4[1], M	*A*	10^4[1], M	*A*
	0.101	5.0	0.162
0.5	0.115	7.0	0.171
1.0	0.124	10.0	0.176
2.5	0.146		

[a] At 25.0 °C, 7 × 10^{-6} M bis-2,4-DNPP in H_2O:MeCN (90:10, v/v), pH 4.

cellizing, hydrophobic ammonium ions, e.g., tri-*n*-octylalkylammonium salts, effectively speed deacylation by functional surfactants and dephosphorylation by arylimidazolide ions.[11,12] The state of aggregation of these hydrophobic ammonium ions is not known, although aggregates, if formed, are probably very small.[13] However, rate enhancements are often large,[11,12] although rate constants for reagents bound to the ammonium ions seem to be similar to those at a micellar surface.[12]

The present work largely concerns the reaction of tri-*n*-octyl(2-hydroxyethyl)ammonium mesylate (1) with

$$\underset{\mathbf{1}}{(C_8H_{17})_3N^+CH_2CH_2OH\ X^-} \xrightarrow{OH^-} \underset{\mathbf{2}}{(C_8H_{17})_3N^+CH_2CH_2O^-}$$

$$X = MeSO_3$$

bis(2,4-dinitrophenyl) phosphate at high pH where the alkoxide species 2 is an effective nucleophile. Coulombic binding between an anionic phosphate ester and the hydrophobic ammonium ions should be important in these systems.

We used the mesylate because it is more soluble than the bromide in aqueous solvents.[12,14] We also examined reaction of the hydroxyethyl surfactant 3 with bis(2,4-dinitrophenyl) phosphate.

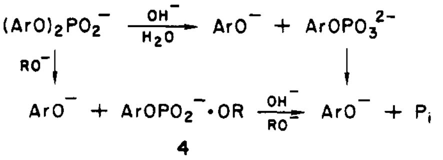
$$\underset{\mathbf{3}}{C_{16}H_{33}N^+Me_2CH_2CH_2OH\ Br^-}$$

Micelles of 3 and related surfactants are effective nucleophiles at high pH and react readily with phosphate esters.[8,10]

Results

The first-order rate constants for attack of OH^- upon bis-2,4-DNPP in dilute NaOH are similar in water and H_2O:MeCN (80:20, v/v) at 25 °C. The values of 10^6k_ψ, s^{-1}, in 10^{-3} and 10^{-2} M NaOH are respectively 2.2 (3.1) and 33 (32). Values in parentheses are for reaction in water.[2]

Scheme II[a]



[a] $R = (C_8H_{17})_3N^+CH_2CH_2O$; $Ar = 2,4\text{-}(NO_2)_2C_6H_3$.

Table II. Reaction in 1[a]

10^2[1], M	10^4k_ψ, s^{-1}	10^2[1], M	10^4k_ψ, s^{-1}
	0.33	2.0	1.77
0.1	0.43	3.0	2.37
0.2	0.60	4.0	2.47
0.3	0.65	5.0	2.46
0.4	0.79	6.0	2.44
0.5	0.84	7.0	2.39
1.0	1.50	8.0	2.38

[a] At 25.0 °C with 0.01 M NaOH in H_2O:MeCN (80:20, v/v).

Table III. Reaction in Micellized 3[a]

10^3[3], M	10^4k_ψ, s^{-1}	10^3[3], M	10^4k_ψ, s^{-1}
0.1	0.62 (6.7)	2.0	1.10 (10.1)
0.3	1.28 (9.3)	4.0	1.07 (8.9)
0.5	1.83 (9.9)	6.0	0.92 (5.9)
0.7	1.31 (10.6)	8.0	(5.8)
1.0	1.17 (11.3)		

[a] At 25.0 °C and 0.001 M NaOH. Values in parentheses are for reaction in 0.01 M NaOH.

Solutions of monoanionic bis-2,4-DNPP have absorbance at <320 nm with a shoulder at 280 nm (log ε 4.5). Addition of 1 in initially neutral or at pH 4 or in alkaline H_2O:MeCN (90:10, v/v) gives an immediate increase in absorbance at 290–310 nm. At pH 4 there is no further spectral change over several hours, but in 10^{-3} M NaOH absorbance steadily decreases at <320 nm and increases at higher wavelengths as 2,4-dinitrophenoxide ion (λ_{max} at 350 and 400 nm) is formed, and there is an isosbestic point at 322 nm. The effect of 1 upon the absorbance at 290 nm is shown in Table I.

The association constant K_s between bis-2,4-DNPP and 1 can be calculated from the variation of absorbance *A* at 290 nm and [1] from eq 1, where A_0 is absorbance of

$$A = (A_0 - A)/K_s[1] + A_0\epsilon_c/e_s \qquad (1)$$

substrate S and ϵ_c and ϵ_s are respectively extinction coefficients of the complex and bis-2,4-DNPP. A plot of *A* against $(A_0 - A)/[1]$ is linear, consistent with the assumed 1:1 binding, and the association constant $K_s = 3 \times 10^3$ M^{-1}.

Possible reactions of bis-2,4-DNPP in solutions of 1 at high pH are shown in Scheme II.

Scheme II does not include attack of alkoxide ion upon the 2,4-dinitrophenyl group because no 2,4-dinitrophenyl ether of 1 was detected, and this ether decomposes slowly under the reaction conditions.[14]

The first-formed product is the diester 4 because initial reaction generates only 1 mol of 2,4-dinitrophenoxide ion and the second mole is generated only slowly (Experimental Section). Thus the reaction which we follow is attack by alkoxide zwitterion 2 upon the phosphoryl group of the bis ester. This reaction is faster than attack by OH^- and H_2O, and hydrophobic ammonium ions akin to 1 do not speed attack of OH^- upon relatively hydrophilic substrates.[11-13] The final product, inorganic phosphate, is

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Table IV[a]

[choline], M	[cholinate], M	10^4k_ψ,[b] s^{-1}
0.2	0.068	4.25
0.3	0.078	4.33

[a] In water at 25.0 °C and 0.1 M NaOH. [b] In aqueous 0.1 M NaOH, $k_\psi = 3.2 \times 10^{-4}$ s^{-1}.[2]

formed relatively slowly, and only the first step of reaction is followed kinetically.

First-order rate constants k_ψ for reaction in solutions of 1 are in Table II at 0.01 M NaOH in H_2O:MeCN (80:20, v/v). They reach a plateau with increasing [1], and the rate enhancement, by a factor of ca. 7, is much smaller than that for dephosphorylation of *p*-nitrophenyl diphenyl phosphate by 1 under similar conditions.[14]

The reaction of bis-2,4-DNPP with 1 is speeded by an increase in the water content of the solvent and in H_2O:MeCN (90:10, v/v), and 0.001 M NaOH 10^4k_ψ = 2.85 and 5.51 s^{-1} in 0.001 and 0.003 M 1, respectively. We could only use dilute 1 in this solvent.

Rate constants in solutions of the hydroxyethyl surfactant 3 are in Table III. They go through maxima with increasing [surfactant] as is general for bimolecular reactions speeded by ionic micelles, and addition of NaOH increases the rate because of increased deprotonation of the hydroxyl group of **3**.[8,10,15]

Reaction of bis-2,4-DNPP in aqueous NaOH is slightly speeded by choline chloride, probably because of nucleophilic attack by cholinate zwitterion (Table IV). The pK_a of choline is 12.8,[16] and neglecting any salt effect of choline chloride, the second-order rate constant for reaction of cholinate zwitterion with bis-2,4-DNPP monoanion is 4.7 × 10^{-3} M^{-1} s^{-1}. The corresponding second-order rate constant for reaction of OH^- is 3.2 × 10^{-3} M^{-1} s^{-1}.[2] Cholinate[17] and other alkoxide ions of similar basicity are generally better nucleophiles than OH^- toward nonionic and cationic electrophiles by factors larger than observed here.[19] There is no indication that the quaternary ammonium center speeds attack upon the anionic substrate.

Reaction of bis-2,4-DNPP in solutions of 1 is speeded by an increase in the concentration of hydroxide ion (Figure 1). This behavior is general for other reactions involving nucleophilic attack by alkoxide moieties in 1 or analogous micellized surfactants.[8,10,15,20]

For a given concentration of functional surfactant, or hydrophobic ammonium ion, rate constants typically do not increase linearly with [OH^-], so that we can calculate apparent acid, or base, dissociation constants for these systems.[10]

We assume that a change in the extent of acid dissociation of 1 will not affect either substrate binding or reactivity of bound substrate so that

$$k_\psi = k'[OH^-]/(K_b + [OH^-]) \qquad (2)$$

where K_b is an apparent base dissociation constant and

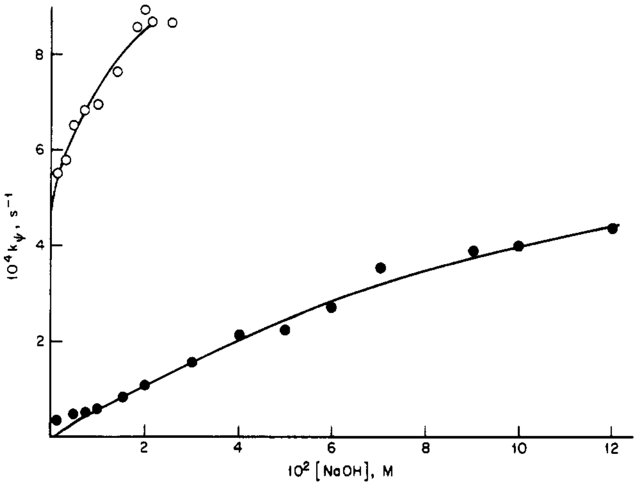

Figure 1. Reaction of bis-2,4-DNPP in 0.003 M 1. (○) H_2O:MeCN (90:10, v/v); (●) H_2O:MeCN (80:20, v/v). The curve for reaction in H_2O:MeCN (80:20 v/v) is predicted.

k' is a first-order rate constant which is a function of [1] and solvent composition. Equation 2 neglects minor contributions of reactions of unbound substrate and predicts that a plot of $1/k_\psi$ against $1/[OH^-]$ will be linear. The predicted linear plot was obtained for reaction in H_2O:MeCN (80:20, v/v) for [OH^-] > 0.01 M, and $k' = 10^{-3}$ s^{-1} and K_b = 0.16. The plot in Figure 1 is calculated from eq 2 and these parameters, and the agreement is satisfactory except at the lowest [OH^-]. We could not fit the data for reaction in H_2O:MeCN (90:10, v/v) to a linear reciprocal plot based on eq 2, and there appears to be some random scatter in the data, probably because of solubility problems with higher [NaOH].

Our value of pK_b = 0.8(app) for reaction of bis-2,4-DNPP is very similar to values calculated for reactions of *p*-nitrophenyl diphenyl phosphate and 2,4-dinitrochlorobenzene in solutions of 1.[14]

Discussion

Reaction of bis-2,4-DNPP with micelles of the hydroxyethyl functionalized surfactant (**3**) follows the pattern typically observed for bimolecular reactions and k_ψ goes through maxima with increasing [surfactant] (Table III).

An approximate value of the second-order rate constant k_M for reaction of bound substrate with the alkoxide moiety of micellized 3 can be calculated from k_ψ (Table III) and the apparent pK_a of the micellized surfactant, which from other results is ca. 12.3.[10,21] The calculation assumes that substrate is extensively micellar bound at the rate maxima.[22]

The second-order rate constant k_M is written in terms of nucleophile concentration as a mole ratio of micellized alkoxide ion (R^+O^-) to total surfactant.[8,15a] On the assumption that substrate is fully micellar bound the overall rate constant k_ψ is given by eq 3.[24]

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(22) Substrate is generally not fully bound at the rate maximum in a bimolecular reaction,[23] so that our assumption of complete substrate binding leads to an underestimation of the rate constant in the micellar pseudophase. The binding constant K_s is approximately 1500 M^{-1} in micellized cetyltrimethylammonium bromide,[8b] and if a similar value applies to micellized 3 substrate will be approximately 75% bound at the rate maxima (Table II).

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$$k_\psi = k_M[R^+O^-]/([R^+O^-] + [R^+OH]) \qquad (3)$$

The values of k_ψ were for 5×10^{-4} M **3** in 0.001 M NaOH, and 10^{-3} M **3** in 0.01 M NaOH, and from an apparent pK_b = 1.7 for micellized **3** values of $[R^+O^-]/([R^+O^-] + [R^+OH])$ are 0.05 and 0.33, respectively, which gives $10^3k_M = 3.6$ and 3.3 s^{-1}, respectively, for reaction with the alkoxide derivative of **3**.

A similar calculation can be made for reaction with **1** in H_2O:MeCN (80:20, v/v) where we assume that the value of $k_\psi \approx 2.5 \times 10^{-4}$ s^{-1} corresponds to reaction of fully bound substrate (Table II). In this solvent pK_b = 0.8(app) so that application of eq 2 gives $k_M \approx 4 \times 10^{-3}$ s^{-1} for reaction of **2** and 0.01 M NaOH.

These comparisons show that k_M is very similar in the aqueous micelles of **3** and in the nonmicellizing hydrophobic ammonium ion (**1**) in H_2O:MeCN (80:20 v/v), despite the difference in solvent composition. Similar values of k_M have been found for reactions in micelles and in hydrophobic ammonium ions.[14]

The second-order rate constants k_M, s^{-1}, cannot be compared directly with second-order rate constants k_W, M^{-1} s^{-1}, in water because of the difference in dimensions.[8,25] The concentration expressed as mole ratio can be converted into molarity in the micellar pseudophase, assuming that reaction occurs in the micellar Stern layer whose assumed molar volume is 0.14 L.[26] The second-order rate constant k_2^m, M^{-1} s^{-1}, is given by[8,25] (eq 4) and values of k_2^m can be compared with those of k_W in water.

$$k_2^m = 0.14k_M \qquad (4)$$

For reaction of bis-2,4-DNPP in micelles of **3**, $k_M \approx 3.5 \times 10^{-3}$ s^{-1} and $k_2^m \approx 5 \times 10^{-4}$ M^{-1} s^{-1}. The second-order rate constant for reaction of cholinate zwitterion in water is 4.7×10^{-3} M^{-1} s^{-1}, neglecting the salt effect of choline chloride. The second-order rate constant for reaction of OH^- with bis-2,4-DNPP in water is ca. 3×10^{-3} M^{-1} s^{-1},[2] so that the second-order rate constant for reaction of bis-2,4-DNPP with the alkoxide moiety in micelles of **4** is somewhat lower than the second-order rate constants for reactions of hydroxide ion and cholinate zwitterion in water.[28] In dephosphorylations of *p*-nitrophenyl diphenyl phosphate in cationic micelles nucleophilicity in the micellar pseudophase is typically similar to but lower than that in water.[15a,29] The overall rate enhancement in these and other bimolecular reactions mediated by colloidal aggregates is generally due to the bringing together of the reagents, rather than to enhanced reactivity of the nucleophile, for example. In reactions of monoanionic bis-2,4-DNPP substrate binding to the cationic aggregate is strengthened by coulombic attractions.

Experimental Section

Materials. Bis(2,4-dinitrophenyl) phosphate was prepared as the pyridine salt, mp 157–158 °C (lit. mp 156–157 °C).[2] Preparation of the ammonium salts has been described,[14] and purification of the other reagents was by standard methods.

Kinetics. Formation of 2,4-dinitrophenoxide ion was followed spectrophotometrically at 25.0 °C in Gilford or Beckman spectrophotometers with 7×10^{-6} M substrate. The integrated first-order rate constants k_ψ are in reciprocal seconds.

Reaction Products. Reaction of bis-2,4-DNPP in solutions of **1** in H_2O:MeCN (90:10 and 80:20, v/v) and 0.001–0.01 M NaOH gave release of equimolar 2,4-dinitrophenoxide ion, and the second mole of phenoxide ion was released slowly.

Reaction of 5×10^{-4} M bis-2,4-DNPP in aqueous 0.08 M **3** and 10^{-3} M NaOH also gave release of equimolar 2,4-dinitrophenoxide ion. The cationic surfactant plus its phosphorylated derivative was precipitated by addition of $NaClO_4$. The precipitate was washed (H_2O) and then dissolved in EtOH. This solution absorbed at 290 nm (shoulder) but not in the visible region. The second mole of phenoxide ion was released quantitatively over a period of several days after addition of 0.1 M NaOH.

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Registry No. 1, 92642-02-9; 2, 92642-03-0; 3, 20917-32-2; 4, 93254-09-2; choline chloride, 67-48-1.

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[25] Bunton, C. A.; Carrasco, N.; Huang, S. K.; Paik, C. H.; Romsted, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 5420.

[26] A larger volume element of reaction is sometimes assumed which leads to a larger value of k_2^m, but the various estimates are within a factor of approximately 2.[7b,27]

[27] Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. In ref 23, p 489. Chaimovich, H.; Aleixo, R. M. V.; Cuccovia, I. M.; Zanette, D.; Quina, F. H. In ref 7c, p 949.

[28] Our estimated second-order rate constant for reaction of cholinate zwitterion in water may be too low, because cholinate is generally a better nucleophile than OH^-. The underestimation is probably due to a negative salt effect of choline chloride.

[29] Bunton, C. A. *Pure Appl. Chem.* **1977**, *49*, 969.

Fluorination of 1,3-Dienes with Xenon Difluoride and (Difluoroiodo)Benzene

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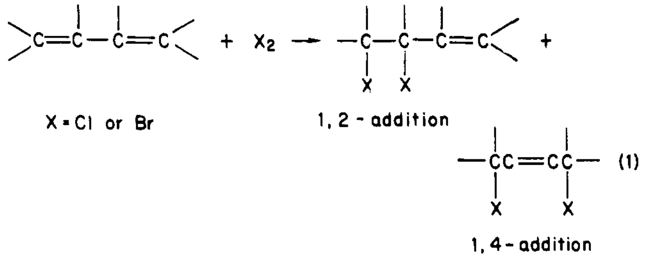
Ionic fluorinations of alkenes with xenon difluoride (XeF_2)[1a] and (difluoroiodo)benzene ($C_6H_5IF_2$)[2] have previously been reported. More recently, Shackelford[1b] described the photochemical reaction and we[1c] reported on the photochemical and molecule-induced homolysis reactions of XeF_2 with alkenes. In this study we report on the ionic reaction[3] of XeF_2 andd$C_6H_5IF_2$ with butadiene (**1**), 2,3-dimethyl-1,3-butadiene (**2**), and *cis*- and *trans*-1,3-pentadiene (**3c** and **3t**). This report presents the first fluorination of a 1,3-diene.

Halogenation of 1,3-dienes gives both 1,2- and 1,4-addition products (eq 1). Reactions of bromine (and to a



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[1] (a) Filler, R. *Isr. J. Chem.* **1979**, *17*, 71–79. Shackelford, S. A. *J. Org. Chem.* **1979**, *44*, 3485. Gregorcic, A.; Zupan, M. *Ibid.* **1979**, *44*, 4120, 1255, and references therein. (b) Hildreth, R. A.; Druelinger, M. L.; Shackelford, S. A. *Tetrahedron Lett.* **1982**, *23*, 1159. (c) Shellhamer, D. F.; Ragains, M. L.; Gipe, B. T.; Heasley, V. L.; Heasley, G. E. *J. Fluorine Chem.* **1982**, *20*, 13.

[2] Patrick, T. B.; Scheibel, J. J.; Hall, W. E.; Lee, Y. H. *J. Org. Chem.* **1980**, *45*, 4492. Carpenter, W. *Ibid.* **1966**, *31*, 2688. Garvey, B. S.; Halley, L. F.; Allen, C. F. *J. Am. Chem. Soc.* **1937**, *59*, 1827. Dimroth, O.; Bockemueller, W. *Chem. Ber.* **1931**, *64*, 522.

[3] One reviewer suggested that we include a discussion of a radical cation. A radical cation mechanism has been reported for the XeF_2 reactions with aromatics by Filler.[1a] Zupan suggests, but gives no evidence for, an ion radical intermediate on the reaction pathway for reaction of XeF_2 with alkenes [Zupan, M.; Pollak, A. *J. Org. Chem.* **1977**, *42*, 1559). A radical cation mechanism seems quite possible, but our data does not discriminate between an ionic or radical cation pathway.

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