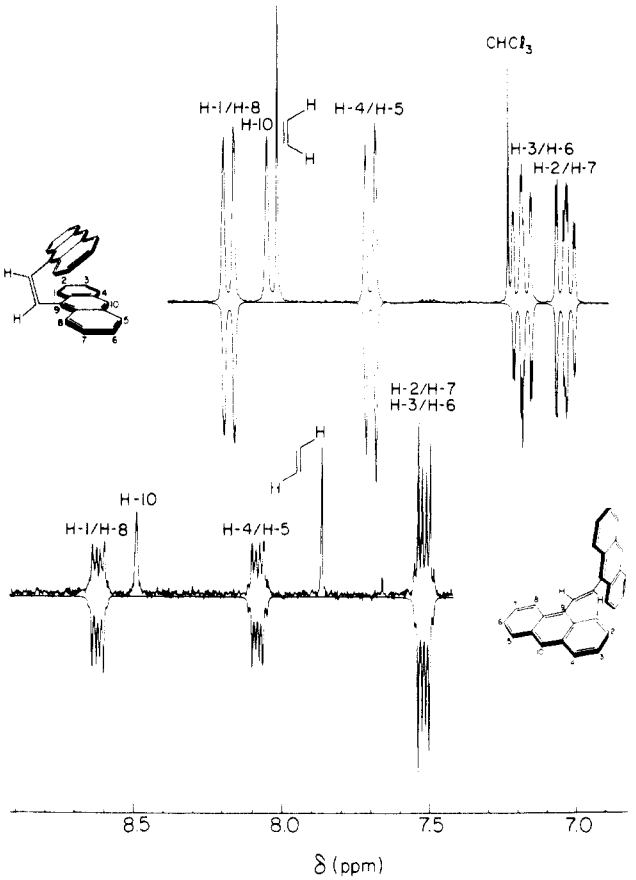

Figure 1. 250-MHz ^{1}H NMR spectra of (*Z*)-1,2-di-9-anthrylethene (**1**, top) and (*E*)-1,2-di-9-anthrylethene (**2**, bottom). Spin-simulated spectra are presented in inverted form for ease of visual matching with the experimentally observed spectra. The simulated spectra do not include the uncoupled 10-anthryl and ethene protons which appear as singlets in the observed spectra.

Table I. Parameters for Simulated ^{1}H NMR Spectra of 1 and 2

δ	1	2	J	1	2
δ_1	8.21	8.63	$J_{1,2}$	8.79	7.91
δ_2	7.07	7.53	$J_{1,3}$	1.35	1.91
δ_3	7.21	7.53	$J_{1,4}$	0.65	0.49
δ_4	8.21	8.09	$J_{2,3}$	6.63	6.32
			$J_{2,4}$	1.00	0.48
			$J_{3,4}$	8.55	8.30

[a] Chemical shifts (δ) relative to tetramethylsilane, in ppm. Coupling constants (J) in hertz. Subscripts refer to numbered positions on the anthracene ring (Figure 1).

sistent with unrestricted rotation on the NMR time scale.[4]

On the assumption of unrestricted rotation, the protons on either side of each anthryl ring in both **1** and **2** are pairwise related by symmetry and are therefore magnetically equivalent (H-1/H-8, H-2/H-7, H-3/H-6, H-4/H-5). The ABCD anthryl spin systems of both compounds are accordingly described by four chemical shifts and six coupling constants (Table I). The simulated spectra closely match the experimentally observed spectra (Figure 1),[5] and the striking difference in the appearance of the spectra of **1** and **2** is thus wholly accounted for by differences in the spectral parameters.[6]

Acknowledgment. We thank Silvio Biali for helpful discussions and the National Science Foundation (CHE-8510067) for support of this work.

Registry No. (*Z*)-1,2-Di-9-anthrylethene, 3162-57-0; (*E*)-1,2-di-9-anthrylethene, 3849-11-4.

(4) An X-ray structure of **2** throws no light on the problem of internal mobility. See: Becker, H.-D.; Engelhardt, L. M.; Hansen, L.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1329. However, examination of a CPK model suggests that the anthryl ring flip in **2** should be fairly unrestricted.

(5) Data for the analysis of the ^{1}H NMR spectra were obtained from $CDCl_3$ solutions of **1** and **2** on a Bruker WM 250 spectrometer. Spin simulations were performed by use of the Bruker PANIC simulation program.

(6) The ^{1}H NMR spectrum of **2** at 388 K showed no evidence of coalescence or line broadening. The change in the general shape of the spectrum at that temperature is due to changes in the chemical shifts of the anthryl protons.

Convenient Synthesis of Hex-1-enopyran-3-uloses: Selective Oxidation of Allylic Alcohols Using Pyridinium Dichromate†

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Hexenuloses have played a major role in carbohydrate chemistry as described in recent reviews.[1-4] Diversely protected hex-1-enopyran-3-uloses are of particular interest, because 1,4 additions allow functionalization and/or chain extension at the anomeric carbon, and their synthetic utility prompted a search for convenient methods of preparation. Earlier reports include the synthesis of a 4,6-benzylidene derivative of enone **1b**[5] and, more recently,[6c] another route to differently protected hex-1-enopyran-3-uloses from D-glucal via acetonation–oxidation or selective protection of primary hydroxyl followed by selective oxidation of the allylic alcohol. In both cases the overall yields were in the range of 20–25%. A more straightforward synthesis of enone **1b** was reported by Tronchet[7] who used Fetizon's reagent[8] to selectively oxidize D-glucal **1a** [After this work was submitted, preparation of compound **1c** from tri-*O*-acetyl-D-glucal (five steps, 35% overall yield) was reported: Fetizon, M.; Duc Do Khac; Nguyen Dinh Tho *Tetrahedron Lett.* **1986**, *27*, 1777.], but with this procedure, which requires a huge excess of reagent,[9] the glucal was not completely oxidized and purification by column chromatography was needed, resulting in low yields.

Because of the drawbacks of these methods, we decided to explore the synthetic utility of our recently developed rapid and high yield pyridinium dichromate (PDC) oxidation procedure[10] for selective oxidation of unprotected glycals. We report herein the results of our study.

D-Glucal **1a** was chosen as the model compound, since it is easily prepared from commercially available tri-*O*-acetyl-D-glucal.

The procedure which had given very good results with saturated carbohydrates, namely PDC in CH_2Cl_2 in the presence of anhydrous acetic acid (AcOH) and molecular

† Dedicated to Professor C. L. Stevens, Wayne State University, Detroit, MI.

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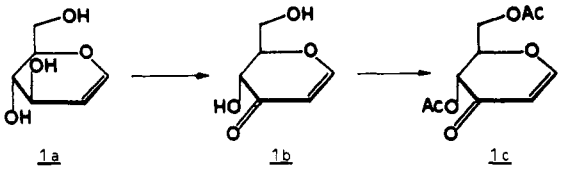


1a 1b 1c

sieve,[10,11] was not satisfactory because the reaction was too fast and many spots were observed in TLC within a few minutes. Omission of either of the additives (or both) resulted in very little transformation even after long reaction times, illustrating their synergistic effect.[10] The problem was attributed to the nature of the solvent, and after a number of trials ethyl acetate (EtOAc) was selected and molecular sieve powder, which caused nonselective oxidation (Table I, entry 1), omitted.

The advantage of EtOAc is due not only to solubility reasons, because even with soluble allylic alcohols the reaction proceeds better in EtOAc than in CH_2Cl_2.[12] In addition, the resulting Cr(III) species is less soluble in EtOAc; hence, after completion of the reaction the heterogeneous mixture can be filtered through a sintered-glass funnel, yielding a fine powder of chromium salts, and there is thus no need for adding Celite to the reaction mixture as a dispersing agent.

However, addition of AcOH was necessary to ensure smooth and complete reaction. Since AcOH acts also as a cosolvent for the glucal, reactions can be performed in a rather large range of concentrations (6–25 mL of EtOAc/mmol) without affecting the yield (entries 2, 3, and 5).

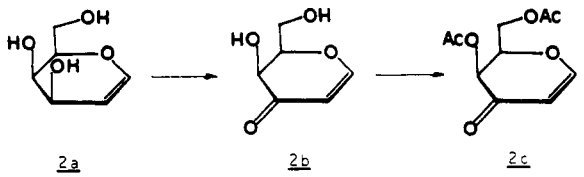
Although a two-electron change was claimed for pyridinium chlorochromate (PCC) oxidation of alcohols,[13] we have demonstrated the formation of Cr(III) species in PDC oxidation.[11] Nevertheless, we prefer to use at least 1 mol equiv of PDC to maintain a reasonable reaction time at room temperature.

To ensure reproducibility of the reaction (time, yield) it is important to use *anhydrous* glucal. If necessary, traces of water can be removed by prior drying of an EtOAc solution of glucal over activated molecular sieve beads.

Thus, the above described procedure allows the transformation of D-glucal **1a** to enone diol **1b** in a reproducible way in about 50% yield (see Table I).

We looked for any Cr(III)-complexed enone diol by subjecting the recovered brown Cr(III) residue to our novel oxalate technique[14] in EtOAc as described for the purification of **1b** in the Experimental Section. In the event, TLC analysis did not reveal the presence of any detectable organic compound. The complexation of Cr(III) by oxalate was verified by dissolving a small amount of the solid in water to give the characteristic violet color.[11] It is likely that about half of the D-glucal was transformed to an EtOAc-insoluble product due to competitive oxidation, presumably of the primary hydroxyl.

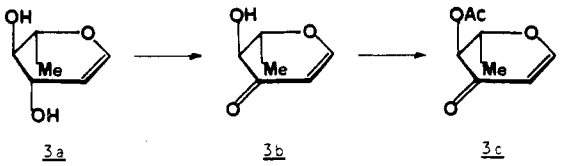
With the D-galactal **2a** the yields of enone diol **2b** (and hence its acetylated derivative **2c**) were routinely lower (≃40%, entry 8). This could be due to the presence of



2a 2b 2c

the pseudoaxial hydroxyl at C-4 in **2a**, which is likely oxidized more rapidly than the C-4 equatorial hydroxyl of **1a**. This difference of reactivity due to conformational effects is well-known in Cr(VI)-mediated oxidations[15] and was already observed by us in the oxidation of epimeric 4-*tert*-butylcyclohexanols with the same oxidant.[10]

In the case of L-rhamnal **3a** where there is no primary or secondary axial hydroxyl susceptible to competititve oxidation, the selectivity is good and the yield is significantly higher (entry 9).



3a 3b 3c

Although **1a** and **2a** gave lower yields than **3a** it should be mentioned that the reactions were clean, the respective enone diols being the major organic products detected by TLC (intense UV absorption).

The enone diols were then acetylated in nearly quantitative yield. By the recommended procedure, epimerization was not observed in the preparation of **1c** and **3c**, the crude products being respectively 99.5 and 100% pure by VPC. But some epimerization was detected (TLC or VPC) when 4-(*N*,*N*-Dimethylamino)pyridine was used for acetylation (or benzoylation[12]) or when the acetylated enones were kept in prolonged contact with pyridine and/or AcOH in the absence of solvent during workup. This problem was crucial with **2c** in which the C-4 acetoxy group is pseudoaxial. [Epimerization was not detected by TLC in the crude enone diol **2b**.] In this case, even under the mildest conditions, the minimum amount of observed epimerization was 5–7%, as measured by VPC. Flash chromatography removed the contaminating **1c** from **2c**, which was finally >99.5% pure.

Properties of the known products (**1b**, **3b**, **3c**) were identical with those reported in the literature. Structures of previously unreported products were supported by elemental analysis and IR and ^1H NMR spectra. Significantly, the $^3J_{4,5}$ coupling constant was large (13 Hz) in **1c** and smaller (6 Hz) in **2c**, in agreement with the proposed structures.

Our procedure offers a convenient alternative route to the sensitive title enuloses and is characterized by the operational simplicity, coupled with the ready availability

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Table I. Results of Oxidation of Glycals with PDC

entry	glycal (mmol)	EtOAc, mL	PDC, mmol	AcOH, mL	time, h	product (% yield[a] from glycal)
1[b]	**1a** (1)	10	1	0.3		many spots after 15 min **1c** (15)[c]
2	**1a** (5)	125	5	1	16	**1c** (52)[c]
3	**1a** (5)	125	5	1	16	**1c** (48)[d]
4	**1a** (5)	30	3.75	1	22	**1b** (21) + **1c** (22)[e]
5	**1a** (2)	12	1 + 1.2	0.2	18	**1c** (55)[c]
6	**1a** (10)	100	10	2	15	**1b** (52)
7	**2a** (2)	40	2	0.4	17[f]	**2b** (not determined)
8	**2a** (3.5)	70	3.5	0.7	8[f]	**2c** (40)[c]
9	**3a** (4.2)	90	4.2	0.9	12	**3b** (84) → **3c** (94)[d]

[a] Isolated yield. [b] In the presence of 350 mg of activated 3-Å molecular sieve powder.[11] [c] Acetylation without isolation of enone diol, followed by flash chromatography. [d] Isolation of enone diol, followed by acetylation and flash chromatography. [e] After acetylation of mother liquor and flash chromatography. [f] Since **2a** is not completely dissolved at the beginning, the reaction time is variable.

of the starting glycals and reagents. Hence, it compares favorably with known procedures.

The advantages and limitations of MnO_2 have been well documented by Fraser-Reid's group.[1,6] Using MnO_2, Paulsen and Bünsch[16] reported 64% yield of enone **3b** from the oxidation of **3a**, and for the same transformation Fetizon's method[8] afforded 59% yield.[17] Although PCC has been recently used for the selective oxidation of steroidal allylic alcohols,[18,19] we could not obtain satisfactory results with **1a** employing the suggested procedure. This could be due to the presence of primary hydroxyl in **1a** and also due to the known propensity of PCC to oxidize enol ethers to esters and lactones, a reaction that has been exploited on fully protected glycals.[20]

Incidentally, it is relevant to note the pseudoequatorial orientation of the allylic hydroxyl in all the three glycals studied by us. In the case of allylic alcohols it has been earlier remarked that the pseudoequatorial hydroxyl is the more reactive epimer in Cr(VI) oxidation of steroids[18] and also in MnO_2 oxidation of 4,6-acetal-protected glycals.[6c]

To our knowledge, this is the first instance of the application of PDC for preparatively useful oxidations of the allylic hydroxyl function of polyhydroxylated systems, and thus the role of PDC in synthetic methodology is further reinforced.

Experimental Section

General Methods. Optical rotations were measured in a Perkin-Elmer 141 polarimeter. IR spectra (film, KBr disk) were recorded on a Unicam SP3-300 spectrophotometer. ^1H NMR spectra were recorded at 90 MHz with a Varian EM-390 instrument, in $CDCl_3$, with Me_4Si as internal standard. Gas chromatography (VPC) was carried out with a 1 m 3% w/w phenyldiethanolaminesulfonate (PDEAS) on Chromosorb W AW DMCS column. Analytical TLC was performed on aluminum-precoated plates (E. Merck silica gel 60 F_{254}) using two solvent systems for elution: EtOAc alone (A); 2:3 EtOAc–cyclohexane (B). For flash chromatography E. Merck silica gel 60 (230–400 mesh) was used. Solvents were evaporated under reduced pressure in a rotary evaporator below 30 °C. PDC (Aldrich) was finely ground before use. Anhydrous AcOH (Prolabo) was used without purification. Reagent-grade EtOAc (Janssen) was distilled over PDC before use.

Preparation of Glycals 1a, 2a, and 3a. The glycals used in this study were prepared in the following way, which proved to be more efficient than the previously described procedures.[6c,21]

1,5-Anhydro-2-deoxy-D-*arabino*-hex-1-enitol (1a). To a solution of tri-*O*-acetyl-D-glucal (10 g, 36.7 mmol; Aldrich) in absolute methanol (100 mL) was added anion-exchange resin (1.5 g; Amberlite IRN-78, OH^- form). The solution was stirred at room temperature until completion of the reaction (≃15 h). After filtration and evaporation of the solvent, a thick syrup was obtained. The remaining traces of water were removed in vacuo in a desiccator containing KOH pellets: 4.91 g (≃100%) of crystalline title compound **1a**; R_f 0.23 (solvent A); mp 57–59 °C (lit.[21] mp 57–59 °C); $[\alpha]^{20}_D$ −10.2° (*c* 1.9, H_2O) [lit.[21] $[\alpha]^{20}_D$ −8° (*c* 1.9, H_2O)].

The same procedure was used to prepare the following glycals in quantitative yields, without need for purification.

1,5-Anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (2a): mp 83–84 °C (lit.[22] mp 100 °C); $[\alpha]^{20}_D$ −6.2° (*c* 2, H_2O) [lit.[22] $[\alpha]^{20}_D$ −6° (*c* 2, H_2O)].

1,5-Anhydro-2,6-dideoxy-L-*arabino*-hex-1-enitol (3a): mp 72–73 °C (lit.[21] mp 70–73 °C); $[\alpha]^{20}_D$ −21° (*c* 2, $CHCl_3$).

Typical Procedure for Oxidation. 1,5-Anhydro-2-deoxy-D-*erythro*-hex-1-en-3-ulose (1b) and Its 4,6-Di-*O*-acetyl 1c. The following preparation illustrates the typical procedure: finely ground PDC (3.76 g, 10 mmol) was added in one batch[23] to a stirred solution of glucal (1.46 g, 10 mmol) in EtOAc (100 mL) containing anhydrous AcOH (2 mL) at room temperature. The reaction was followed by TLC (solvent A). After completion (16 h), the mixture was filtered through a sintered-glass funnel and the chromium salts were washed with EtOAc (20 mL). At this point, **1b** can be isolated from the solution or directly acetylated to **1c**.

Isolation of 1b. The reddish brown filtrate was evaporated and azeotroped with toluene (3 × 10 mL) to remove traces of pyridine and AcOH. To the resulting dark brown residue was added CH_2Cl_2 (3 mL) followed by EtOAc (40 mL) to precipitate the Cr(III) species. The solution was then filtered through anhydrous Na_2SO_4, and the residue was rinsed with EtOAc. The brownish green filtrate was evaporated to yield 750 mg (52%) of **1b** as a viscous oil that gave sticky crystals from $CHCl_3$. An analytical sample was prepared in the following way. The crystals were dissolved in warm $CHCl_3$ (10 mL), stirred together with powdered oxalic acid dihydrate (504 mg, 4 mmol) and powdered ammonium oxalate monohydrate (568 mg, 4 mmol) for 1 h at room temperature, and filtered. The filtrate was then stirred for 30 min with powdered $NaHCO_3$ (840 mg, 10 mmol). After filtration through anhydrous Na_2SO_4, evaporation, and two recrystallizations from $CHCl_3$ pure **1b** (130 mg) was obtained as colorless fine needles: mp 87–88 °C (lit.[7] mp 86 °C); $[\alpha]^{20}_D$ 297.5° (*c* 1, H_2O) stable for at least 1 h [lit.[7] $[\alpha]^{20}_D$ 283° (*c* 0.8, H_2O)]; IR (KBr) 3400, 1665, 1590 cm^{-1}.

Direct Acetylation 1a → 1c. After oxidation of **1a** (10 mmol), the solution was concentrated to one-third of its volume, pyridine (2.6 mL, 30 mmol) and acetic anhydride (2 mL, 20 mmol) were added to the solution, and the mixture was left overnight. After disappearance of the enone diol followed by TLC (solvent A), the solution was evaporated and treated with toluene (3 × 20 mL; vide supra). The dark residue was then dissolved in CH_2Cl_2 (50 mL) and washed with 5% $NaHSO_4$ aqueous solution (50 mL) in

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order to eliminate any remaining traces of pyridine. Drying over anhydrous $MgSO_4$, filtration, and evaporation afforded a yellowish oil that was purified by flash chromatography (1:2 ether–petroleum ether); 1.23 g colorless oil (54% overall yield); R_f 0.59 (solvent B); retention time 7.7 min at 110 °C; $[\alpha]^{20}_D$ 255° (*c* 1, $CHCl_3$); IR (neat) 1745, 1685, 1600, 1370, 1230, 1040 cm^{-1}; ^1H NMR δ 7.32 (d, 1 H, H-1, $J_{1,2}$ = 6 Hz), 5.48 (d, 1 H, H-4, $J_{4,5}$ = 13 Hz), 5.43 (d, 1 H, H-2), 4.55 (dt, 1 H, H-5, $J_{5,6}$ = $J_{5,6'}$ = 4 Hz), 4.35 (d, 2 H, H-6,-6'), 2.10 (s, 3 H, CH_3COO), 2.04 (s, 3 H, CH_3COO). Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.61; H, 5.28.

From the other two glycals, compounds **2b**, **2c**, **3b**, and **3c** were prepared as described and characterized as follows:

1,5-Anhydro-2-deoxy-D-*threo*-hex-1-en-3-ulose (2b): white crystals; mp 106–107 °C; $[\alpha]^{20}_D$ 54° (*c* 0.9, H_2O); IR (KBr) 3400, 1665, 1600 cm^{-1}.

4,6-Di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*threo*-hex-1-en-3-ulose (2c): colorless oil; 50% overall yield; R_f 0.53 (solvent B); retention time 6.5 min at 110 °C; $[\alpha]^{20}_D$ 22.7° (*c* 0.5, $CHCl_3$); IR (neat) 1745, 1680, 1600, 1370, 1220, 1030cm^{-1}; ^1H NMR δ 7.30 (d, 1 H, H-1, $J_{1,2}$ = 6 Hz), 5.47 (d, 1 H, H-4, $J_{4,5}$ = 6 Hz), 5.25 (d, 1 H, H-2), 4.20–4.40 (m, 3 H, H-5,-6,-6'), 2.20 (s, 3 H, CH_3COO), 2.10 (s, 3 H, CH_3COO). Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.53; H, 5.38.

1,5-Anhydro-2,6-dideoxy-L-*erythro*-hex-1-en-3-ulose (3b). **3b** was easily isolated in 84% yield using toluene to precipitate the Cr(III) species. Filtration and evaporation of the solvent afforded crystals (subliming under vacuum) suitable for the next step without further purification: mp 92–93 °C (lit.[16] mp 86 °C); $[\alpha]^{20}_D$ −244° (*c* 3, MeOH) [lit.[16] $[\alpha]^{20}_D$ −288° (*c* 1.3, MeOH)]; IR (KBr) 1690, 1600, 1165, 1040, 955, 775, 720 cm^{-1}; ^1H NMR, in agreement with the data published by Paulsen and Bünsch.[16]

4-*O*-Acetyl-1,5-anhydro-2,6-dideoxy-L-*erythro*-hex-1-en-3-ulose (3c): white crystals; 94% yield from **3b**; mp 61–62 °C (lit.[16] mp 62 °C); $[\alpha]^{20}_D$ −272° (*c* 0.95, CH_2Cl_2) [lit.[16] $[\alpha]^{20}_D$ −277.9° (*c* 2.4, CH_2Cl_2)] after recrystallization from 2:1 ether–hexane; retention time 3 min at 75 °C.

Acknowledgment. The Centre National de la Recherche Scientifique is acknowledged for financial support and G. Fusey for expert technical assistance.

Communications

Extractability and Reactivity of OH^- in Low-Polarity Media under Phase-Transfer Catalysis Conditions: Dramatic Effect of the Aqueous Base Concentration

Summary: In the chlorobenzene–aqueous NaOH two-phase system, an increase in NaOH concentration from 15% to 50% produces both a decrease in the extractability and an enhancement in the reactivity of OH^- in the organic phase as quaternary ammonium hydroxide **1d**.

Sir: In a typical anion-promoted reaction carried on under phase-transfer catalysis (PTC) conditions (Scheme I), the catalytic efficiency is related to the concentration of anion Y^-, present in the organic phase associated with a quaternary cation Q^+ as Q^+Y^-.[1] It is expressed by the equilibrium constant of the liquid–liquid exchange reaction 1, defined as selectivity constant $K_{Y/X}^{sel}$ 2.[1,2]

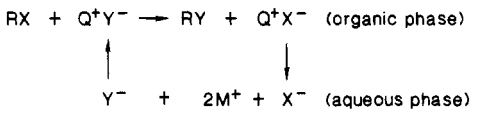
$$Q^+X^-_{org} + Y^-_{aq} \rightleftarrows Q^+Y^-_{org} + X^-_{aq} \quad (1)$$

$$K_{Y/X}^{sel} = \frac{[Q^+Y^-_{org}][X^-_{aq}]}{[Q^+X^-_{org}][Y^-_{aq}]} \quad (2)$$

$K_{Y/X}^{sel}$ values were extensively studied for a number of anions in different solvents. They mainly depend on the nature of the anions, the structure of the onium cation Q^+ and the solvent.[1-3] On the contrary, until now, little attention has been paid to the effect of inorganic aqueous phase composition on $K_{Y/X}^{sel}$.[4]

Here we report a particularly striking example of how the base concentration in the aqueous phase affects the selectivity coefficients of OH^-, extracted in the organic phase as quaternary hydroxide Q^+OH^-.[5] This effect is the opposite of that produced, under the same conditions, on the OH^- reactivity in the organic phase.

Scheme I



When a chlorobenzene solution of a tetrahexylammonium salt $(C_6H_{13})_4N^+X^-$ [X^- = Cl^- (**1a**), $MeSO_3^-$ (**1b**), Br^- (**1c**)] was equilibrated with an aqueous solution of 15% NaOH, a certain amount of OH^- was found in the organic phase associated with the quaternary cation Q^+, as $(C_6H_{13})_4N^+OH^-$ (**1d**).[9] At 60 °C the percent of extracted **1d** was 5%, 18%, and 28% for X^- = Br^-, $MeSO_3^-$, and Cl^-, respectively (Table I); it depends on the nature of the anion X^- and the order found ($Br^- < MeSO_3^- < Cl^-$) follows the well-known selectivity coefficients in low polarity media for these anions.[1-3] When the equilibrations were carried out at 25 °C the amount of extracted OH^- slightly diminished, but the selectivity order was unchanged (Table I).

Surprisingly, by increasing the base concentration in the aqueous phase (up to 50% aqueous NaOH) the extracta-

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(4) (a) Dermeik, S.; Sasson, Y. *J. Org. Chem.* **1985**, *50*, 879. (b) Yonovich-Weiss, M.; Sasson, Y. *Isr. J. Chem.* **1985**, *26*, 243.

(5) The knowledge of this effect is particularly interesting since important reactions promoted by alkaline hydroxides under liquid–liquid PTC conditions involve the OH^- extraction in the organic phase, e.g.: alkenes isomerization,[6] dehydrobromination reactions,[7] H/D exchanges in weak carbon acids.[8]

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(8) (a) Halpern, M.; Sasson, Y.; Rabinovitz, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 54. (b) Feldmann, D.; Halpern, M.; Rabinovitz, M. *J. Org. Chem.* **1985**, *50*, 1746 and references therein.

(9) The amount of OH^-, extracted in the organic phase as $(C_6H_{13})_4N^+OH^-$, was measured via acid/base titration according to a previously described procedure.[10]

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