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; $[\alpha]^{20}_{\mathrm{D}}$ 255° (*c* 1, $CHCl_3$); IR (neat) 1745, 1685, 1600, 1370, 1230, 1040 $cm^{-1}$; $^1H$ NMR $\delta$ 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; $[\alpha]^{20}_{\mathrm{D}}$ 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; $[\alpha]^{20}_{\mathrm{D}}$ 22.7° (*c* 0.5, $CHCl_3$); IR (neat) 1745, 1680, 1600, 1370, 1220, 1030$cm^{-1}$; $^1H$ NMR $\delta$ 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); $[\alpha]^{20}_{\mathrm{D}}$ −244° (*c* 3, MeOH) [lit.[16] $[\alpha]^{20}_{\mathrm{D}}$ −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); $[\alpha]^{20}_{\mathrm{D}}$ −272° (*c* 0.95, $CH_2Cl_2$) [lit.[16] $[\alpha]^{20}_{\mathrm{D}}$ −277.9° (*c* 2.4, $CH_2Cl_2$)] after recrystallization from 2:1 ether–hexane; retention time 3 min at 75 °C.

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# 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]

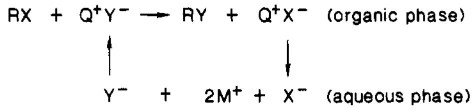
$$Q^+X^-{}_{org} + Y^-{}_{aq} \rightleftarrows Q^+Y^-{}_{org} + X^-{}_{aq} \tag{1}$$

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

$K_{Y/X}{}^{sel}$ 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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[1] (a) Starks, C. M.; Liotta, C. In *Phase-Transfer Catalysis: Principles and Techniques*; Academic: New York, 1978. (b) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147. (c) Dehmlow, E. V.; Dehmlow, S. S. In *Phase-Transfer Catalysis*, 2nd ed.; Verlag-Chemie: Weinheim, Germany, 1983.

[2] Gordon, J. E.; Kutina, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 3903.

[3] Brandstrom, A. *Adv. Phys. Org. Chem.* **1977**, *15*, 267.

[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]

[6] Halpern, M.; Sasson, Y.; Rabinovitz, M. *J. Org. Chem.* **1983**, *48*, 1022.

[7] Halpern, M.; Sasson, Y.; Rabinovitz, M. *J. Org. Chem.* **1984**, *49*, 2011 and references therein.

[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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**Table I. Extractability of $OH^-$ in the Organic Phase as $(C_6H_{13})_4N^+OH^-$ with Tetrahexylammonium Salts 1a–c in Chlorobenzene–Aqueous NaOH Two-Phase Systems[a] at 25 and 60 °C**

| $(C_6H_{13})_4N^+X^-$ | | | extractability of **1d**,[b] % | | | |
|---|---|---|---|---|---|---|
| compd | $X^-$ | $T$, °C | 15% NaOH | 30% NaOH | 40% NaOH | 50% NaOH |
| **1a** | $Cl^-$ | 25 | 19 | 13 | 10 | 8 |
| | | 60 | 28 | 22 | 17 | 10 (48)[c] |
| **1b** | $MeSO_3^-$ | 25 | 14 | 5 | 3 | 3 |
| | | 60 | 18 | 12 | 6 | 4 (33)[c] |
| **1c** | $Br^-$ | 25 | 2.5 | 1.5 | | $\leq 0.5$ |
| | | 60 | 5 | 4 | 3 | $\leq 1$ (9)[c] |

[a] 40 mL of a chlorobenzene solution of **1a–c** ($4 \times 10^{-2}$ M) and 40 mL of an aqueous solution of NaOH (15–50% w/w). [b] Evaluated via acid–base titration of the organic phase.[10] Percent expressed as $[Q^+OH^-]/([Q^+X^-] + [Q^+OH^-]) \times 100$, $Q^+ = (C_6H_{13})_4N^+$. Average of at least three determinations. [c] Values obtained from the selectivity constants, $K_{OH/X}^{sel}$, evaluated in the system PhCl–15% aqueous NaOH (see Table II).

**Table II. Effect of the Aqueous Base Concentration on Both the Selectivity Constants $K_{OH/X}^{sel}$ (X = Cl, $MeSO_3$, Br) and Decomposition Percent (Hofmann Elimination) of Quaternary Salts 1a–c in Chlorobenzene–Aqueous NaOH Two-Phase Systems,[a] at 60 °C**

| | **1a** | | **1b** | | **1c** | |
|---|---|---|---|---|---|---|
| NaOH, % | $10^5 K_{OH/Cl}$[b] | dec after 2 h, %[c] | $10^5 K_{OH/MeSO_3}$[b] | dec after 7 h, %[c] | $10^5 K_{OH/Br}$[b] | dec after 7 h, %[c] |
| 15 | 91 | 2 | 33 | 7 | 2.2 | 1 |
| 30 | 25 | 17 | 6.5 | 36 | 0.67 | 15 |
| 40 | 9.3 | 76 | 1.0 | 65 | 0.25 | |
| 50 | 2.2 | 100 | 0.33 | 94 | 0.02 | 40 |

[a] For reaction conditions see footnote *a*, Table I. [b] Calculated values according to the equilibrium constant 2, see text. [c] Percents evaluated by following the disappearance of quaternary salt.

bility of $OH^-$ was found to diminish (2.4–5 times) for all the anions. The percent of quaternary hydroxide **1d** found at 60 °C in the system PhCl–50% aqueous NaOH (10%, 4%, and $\leqslant$ 1% for $Cl^-$, $MeSO_3^-$, and $Br^-$, respectively)[9] is noticeably lower than that expected by a mass effect on the equilibrium 1 (i.e., 48%, 33%, and 9%)[11] (Table I). $K_{OH/X}^{sel}$ values so obtained dramatically diminish in the same sense (41, 100, and 110 times for $Cl^-$, $MeSO_3^-$, and $Br^-$, respectively) (Table II).

It is well-known[1,10] that, under PTC conditions in the presence of strongly alkaline aqueous solutions, lipophilic quaternary ammonium salts such as **1a–c** undergo Hofmann decomposition via $OH^-$ extraction in the organic phase.[10] Degradation measurements, carried out in the PhCl–aqueous NaOH two-phase system at 60 °C, show that the decomposition extent[12] of **1a–c** is strongly enhanced by increasing the base concentration from 15% to 50% (Table II). These data are in striking contrast with the effect of aqueous base concentration on selectivity constants $K_{OH/X}^{sel}$. As shown in Table II, the highest degradation rates are indeed observed in the PhCl–50% aqueous NaOH system, where the lowest values of extracted $OH^-$ are found.

This apparent discrepancy can be explained on the basis of the different hydration state of the hydroxide ion transferred in the organic phase at various aqueous base concentrations.

Indeed we found[13] that by increasing the aqueous NaOH concentration from 15% to 50% the specific hydration of $(C_6H_{13})_4N^+OH^-$ (**1d**) dissolved in chlorobenzene is progressively reduced from 11 to 3.5 molecules of water.[14] The higher anion destabilization, due to the lower hydration, produced dramatic enhancements of $OH^-$ reactivity (up to $10^4$ times)[13] and is likely the main reason for its reduced extractability in the organic phase.

These results, to the best of our knowledge, provide the first quantitative evaluation of the effect produced by the aqueous base concentration both on the selectivity coefficients $K_{OH/X}^{sel}$ and reactivity of $OH^-$ under liquid–liquid PTC conditions.

**Registry No.** $OH^-$, 14280-30-9; $(CH_3(CH_2)_5)_4N^+Cl^-$, 5922-92-9; $(CH_3(CH_2)_5)_4N^+Br^-$, 4328-13-6; $(CH_3(CH_2)_5)_4N^+CH_3SO_3^-$, 105140-20-3.

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*Received May 2, 1986*

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[10] Landini, D.; Maia, A.; Rampoldi, A. *J. Org. Chem.* **1986**, *51*, 3187.

[11] These data are calculated by the selectivity constants evaluted in the system PhCl–15% aqueous NaOH (see Table II).

[12] Unfortunately, it was impossible to determine the decomposition rate constants due to the complexity of the system.

[13] Landini, D.; Maia, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1041.

[14] The specific hydration of $(C_6H_{13})_4N^+OH^-$ was determined by Karl Fischer analysis of the organic phase following a previously described procedure.[13]

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## Discorhabdin C, a Highly Cytotoxic Pigment from a Sponge of the Genus *Latrunculia*

*Summary:* The cytotoxic sponge pigment discorhabdin C (1) was shown, by a single-crystal X-ray diffraction study, to contain a new tetracyclic iminoquinone chromophore with a spiro 2,6-dibromocyclohexadienone.

*Sir:* The strong cytotoxicity of extracts from various sponges of the genus *Latrunculia* du Bocage was detected in our wide-scale screening of New Zealand's marine invertebrates for antiviral and antitumor activity.[1] Bioassay-directed analysis of one such extract led to the isolation of a compound named discorhabdin C (1).[2] This compound, the major pigment of the red-brown sponge, is toxic

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[1] Presented in part at the PAC CHEM 84 Congress, Honolulu, HI, Dec., 1984.

[2] One characteristic of the family Latrunculiidae Topsent is the possession of discorhabd microscleres: Bergquist, P. R. *Sponges*; Hutchinson: London, 1978.