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Registry No. (±)-1, 71899-16-6; **10**, 22954-83-2; **11**, 55130-14-8; **12**, 92958-26-4; **15**, 92958-27-5; **16**, 76946-39-9; **17**, 92958-28-6; **18**, 92958-29-7; trichloroacetyl chloride, 76-02-8.

Nucleophilic Reactivity of Anions Associated with a Lipophilic Proton Cryptate, $[H^+\subset(1.1.1,C_{14})]$

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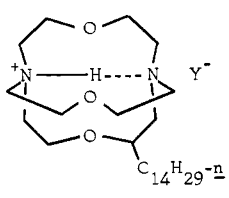
The reactivity of an ion pair A^+X^- in a condensed phase reaches the highest values when at least two fundamental conditions are achieved: (1) a good solubility in non-polar media; (2) a large cation–anion separation.[1] These conditions are especially fulfilled by onium quaternary salts, bearing long and/or bulky alkyl chains,[1] and by multidentate ligands which surround metal cations giving rise to lipophilic macrocations.[2] Within the latter species, lipophilic cryptates are of particular interest, since they probably represent the best model of "solvent-separated ion pair".[3,4]

In a series of papers we have studied the anionic reactivity of lipophilic cryptates[3,5,6] compared with that of quaternary onium salts[7,8] and complexed crown ethers.[4]

We have also reported[9] the synthesis of $[H^+\subset(1.1.1,C_{14})]Y^-$ cryptates **1**, following a route which directly affords the proton cryptated species. It was shown by Lehn[10] that the unsubstituted [1.1.1] cryptand **2** is capable of selectively binding one or two protons inside its intramolecular cavity. Whereas one proton can be removed from the dicationic species, it is practically impossible to remove the last proton from the one-proton cryptate.[10] Cryptates **1** are readily soluble in non-polar media. Since the anionic reactivity of cryptates is independent of the nature of metal cation, which only affects[11] the stability constant of the complex, it was interesting to know about the reactivity of the anions associated with the "unique" species of a lipophilic proton cryptate.



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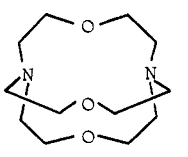

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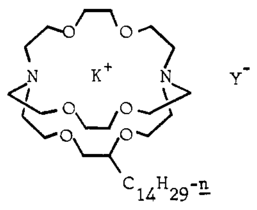

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Results and Discussion

Rates of displacement of the methanesulfonic group in *n*-octyl methanesulfonate by a series of anions (Cl^-, Br^-, I^-, N_3^-) associated with the cation $[H^+\subset(1.1.1,C_{14})]$ have been measured in anhydrous chlorobenzene at 60 °C (eq 1).

$$n\text{-}C_8H_{17}OSO_2Me + [H^+\subset(1.1.1,C_{14})]Y^- \xrightarrow[60\ ^\circ C]{PhCl} n\text{-}C_8H_{17}Y + [H^+\subset(1.1.1,C_{14})]MeSO_3^- \quad (1)$$

a, Y = Cl; **b**, Y = Br; **c**, Y = I; **d**, Y = N_3; **e**, Y = ClO_4

The same reactions were studied by using tetraoctylammonium salts **4** as a source of anions. In all cases

$$\underset{\mathbf{4}}{(n\text{-}C_8H_{17})_4N^+Y^-} \qquad \underset{\mathbf{5}}{n\text{-}C_{16}H_{33}P^+Bu_3Y^-}$$

comparable amounts of substrate [(2–6) × 10^{-2} M] and nucleophile [(0.8–2.4) × 10^{-2} M] were used. The rates were measured by potentiometric titration of the nucleophile. Under these conditions reactions follow a second-order kinetic equation (eq 2) up to at least 80% conversion.

$$\text{rate} = k[\text{substrate}][\text{cryptate}] \qquad (2)$$

Rate constants are reported in Table I together with those, previously measured under the same conditions, for $[K^+\subset(2.2.2,C_{14})]Y^-$ cryptates **3** and hexadecyltributylphosphonium salts **5**. Results indicate that the reactivity of anions associated with $[H^+\subset(1.1.1,C_{14})]$ cation is high and comparable with the reactivities measured in the presence of the best anionic activators (quaternary salts and metal cryptates).

All the attempts for obtaining the free ligand from the proton cryptates failed. For example, when **1c** was treated with $NaBH_4$ and $LiAlH_4$ in tetrahydrofuran (THF), anion exchange and decomposition of the cryptate were observed, respectively;[9b] nor was it possible to remove the proton when a toluene solution of **1c** was stirred for several days in the presence of 50% aqueous NaOH. In other words, the proton included into the ligand $[1.1.1,C_{14}]$ behaves as an ordinary cryptated metal cation.

The smaller size and the higher charge localization of **1** compared with that of **3** is likely responsible for its anionic reactivity (1.5–3.5 times less, depending on the anion) (Table I). Compared with bulky tetraoctylammonium salts **4**, cryptates **1** represent a more rigid and a less hindered system. Indeed, these factors, altogether,

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Table I. Second-Order Rate Constants for Nucleophilic Substitutions of Methanesulfonate by Anions Y^- Associated with $[H^+\subset(1.1.1,C_{14})]$, $[K^+\subset(2.2.2,C_{14})]$, $(C_8H_{17})_4N^+$, or $C_{16}H_{33}P^+Bu_3$, in Anhydrous Chlorobenzene at 60 °C

	10^2k,[a] $M^{-1}\,s^{-1}$			
Y^-	$[H^+\subset(1.1.1,C_{14})]Y^-$ [b]	$[K^+\subset(2.2.2,C_{14})]Y^-$ [c]	$(C_8H_{17})_4N^+Y^-$ [b]	$C_{16}H_{33}P^+Bu_3Y^-$ [d]
Cl^-	1.9	5.1	3.7	2.0
Br^-	1.1	3.7	2.0	0.81
I^-	0.60	0.87	0.68	0.30
N_3^-	7.0	15.0	15.6	7.0

[a] The rate constants are computer generated by using a least-square analysis and are the average of at least two runs. [b] [substrate] = 2–6 × 10^{-2} M; [nucleophile] = 0.8–2.4 × 10^{-2} M. [c] Data from ref 3. [d] Data from ref 7.

allow a stronger cation–anion interaction within the ion pair, hence a lower reactivity of **1** compared with those of **3** and **4**. In any case, anion activation by cryptates **1** is roughly comparable with that of the largely used quaternary phosphonium salts **5**.

As a conclusion, attachment of an aliphatic chain to $[H^+\subset(1.1.1)]$ cryptate results in a "unique example" of protonated tertiary amine, which behaves, in all of the essential aspects, like a tetralkylammonium or -phosphonium cation, and it is capable to impart to the anions a high nucleophilic reactivity.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian EM-390 90-MHz spectrometer with tetramethylsilane as internal standard. Potentiometric titrations were carried out with a Metrohm Titroprocessor E636 using silver and calomel electrodes, the latter isolated with a potassium sulfate bridge.

Materials and Solvents. *n*-Octyl methanesulfonate, bp 112–114 °C (2 mm), $n^{20}{}_D$ 1.4398, was prepared according to the literature [lit.[12] bp 110–114 °C (2 mm), $n^{20}{}_D$ 1.4392]. Quaternary ammonium salts **4a–d** were obtained from the commercially available tetraoctylammonium perchlorate (**4e**) by exchange with the appropriate anion, according to a previously described procedure.[13] Many of these salts are hygroscopic and must be stored in a desiccator. The $[H^+\subset(1.1.1,C_{14})]I^-$ cryptate (**1c**), mp 65–67 °C, was synthetized as previously reported.[11a] Cryptates **1a**,**b**,**d** were prepared from the corresponding perchlorate **1e** by exchange with the appropriate anion as follows: to a solution of **1e** (1 mmol) in methanol (15 mL) a solution of potassium salt (1.1 mmol) in methanol (100 mL) was added and stirred for 15 min. The precipitated $KClO_4$ was filtered and the solvent evaporated. The residue was taken up in CH_2Cl_2 and filtered again to remove traces of inorganic salts, and the solvent was evaporated. The overall sequence was repeated (at least 2 times), until a ≥95% exchange value was reached (potentiometric titration with 0.01 N silver nitrate of the nucleophile). The cryptates **1a**,**b**,**d** were carefully dried under vacuum at 1 mm at 50 °C and used for kinetic measurements without further purification. The $[H^+\subset(1.1.1,C_{14})]ClO_4^-$ cryptate (**1e**) was obtained by stirring a CH_2Cl_2 solution (100 mL) of the corresponding iodide **1c** (5 mmol) with an aqueous solution (50 mL) of $NaClO_4$ (20 mmol) for 30 min. The aqueous phase was substituted by a fresh solution of $NaClO_4$ and the procedure was repeated (at least 3 times) until the I^-/ClO_4^- exchange was complete (potentiometric titration of iodide). The organic phase was evaporated to give **1e**, mp 66–68 °C (hexane). Anal. Calcd for $C_{26}H_{53}ClN_2O_7$: C, 57.70; H, 9.87; N, 5.17. Found: C, 57.55; H, 10.00; N, 5.03. Chlorobenzene was carefully purified and dried by standard methods[14] and stored over molecular sieves. Karl Fischer titration showed a water content ≤40 ppm.

Kinetic Measurements. At zero time a standardized solution (10 mL) of substrate [(10–30) × 10^{-2} M] was added to a standardized solution (40 mL) of cryptate $[H^+\subset(1.1.1,C_{14})]Y^-$ or quaternary salt [(1–3) × 10^{-2} M] in a 100-mL flask thermostated at 60 ± 0.1 °C. Samples (2–5 mL) withdrawn periodically were quenched in ice-cold MeOH (50 mL), and the unreacted nucleophile was determined by potentiometric titration with 0.01 N silver nitrate. From the equation $1/([B_0] - [A_0]) \ln ([BA_0]/[AB_0]) = kt$, where [A] = [substrate] and [B] = [nucleophile] or vice versa, the second-order rate constants were calculated by using a least-squares computer program. All rates involved at least nine samplings and gave correlation coefficients ≥0.996.

Attempt at Deprotonation of $[H^+\subset(1.1.1,C_{14})]I^-$ (1c). A heterogeneous mixture of a deuteriotoluene solution (3 mL) of **1c** (300 mg) and 50% aqueous NaOH (1 mL) was stirred at room temperature for 5 days. ^1H NMR (C_7D_8) analysis of the organic phase showed that **1c** was unchanged: δ 8.8 (br s, 1 H, $\gt N^+$–H).

Registry No. **1a**, 92958-32-2; **1b**, 92958-33-3; **1c**, 92958-34-4; **1d**, 92958-35-5; **1e**, 92958-36-6; $(n\text{-}C_8H_{17})OSO_2CH_3$, 16156-52-8; $(n\text{-}C_8H_{17})_4N^+Cl^-$, 3125-07-3; $(n\text{-}C_8H_{17})_4N^+Br^-$, 14866-33-2; $(n\text{-}C_8H_{17})_4N^+I^-$, 16829-91-7; $(n\text{-}C_8H_{17})_4N^+N_3^-$, 81389-83-5.

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Synthesis and Photolysis of *S*-Methyl *S*-Alkenyl Dithiocarbonates in the Monoterpene Series

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The use of xanthate derivatives in organic synthesis continues to provoke interest particularly in carbohydrate chemistry as reflected in the recent reports on reductive,[1,2] thermal,[3-6] and photolytic reactions.[5,7-9] Surprisingly, the literature provides few examples of transformations of dithiocarbonates and particularly of unsaturated ones.[10] In connection with our preceding investigations into the allylic rearrangements of terpenic substrates,[11] we herein report the synthesis and photolysis of dithiocarbonates derived from myrtenol (**1**). *trans*-Pinocarveol (**2**) and perillyl alcohol (**3**).

Xanthation of **1**, **2**, and **3** in Me_2SO gave the crude xanthates **4**, **5**, and **6**, respectively. Xanthate **5** was spontaneously transformed into dithiocarbonate **8**, whereas xanthates **4** and **6** required silica gel chromatography or thermolysis at 85 °C in Me_2SO for their [3.3] sigmatropic rearrangement into dithiocarbonates **7** and **9**.[12-15] Pho-

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