

A New Host Compound for the Selective Inclusion of Ethanol

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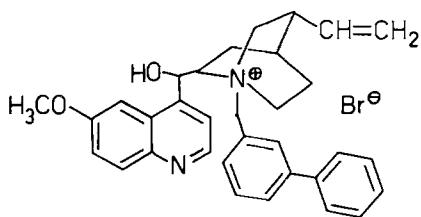
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Abstract. A new host compound of the onium salt type, *N*-(3-biphenylmethyl)quininium bromide (**1**), is described. This host compound shows an unusually high selectivity for the inclusion of ethanol. Using this clathrand, ethanol can be extracted from a variety of solvent mixtures. In most cases, a remarkable enrichment of the ethanol is observed. The following solvents in a mixture with ethanol remain in the mother liquid: methanol, *n*-propanol, *n*-hexane, pyridine.

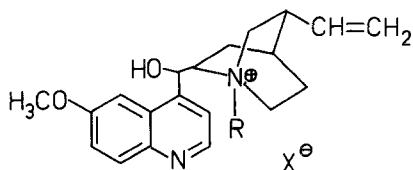
Key words: Alcohol inclusion, clathrate, clathrand, enrichment of ethanol, host/guest chemistry, inclusion, lattice inclusion, separation of solvents.

1. Introduction

As we have shown in a previous paper [1], *N*-benzylquininium chloride (**2**) and *N*-methylquininium iodide (**3**), like many other onium salts [2, 3], form lattice inclusion compounds [4, 5] with several low molecular weight guest compounds, in particular with a series of alcohols. In a search for even more selective host compounds for the inclusion of more important low molecular weight substances, we have found a new host of the onium type, *N*-(3-biphenylmethyl)quininium bromide (**1**). The selective inclusion of ethanol displayed by this host compound is remarkable. In this paper we report the separation of ethanol from various mixtures with methanol, pyridine, *n*-hexane and *n*-propanol.



1



2: R = CH₂-C₆H₅ X = Cl
3: R = CH₃ X = I

2. Experimental

2.1. PREPARATION OF 3-(BROMOMETHYL)BIPHENYL

3.00 g 3-methylbiphenyl (17.8 mmol) were dissolved in 10.0 ml of CCl_4 (dried over P_4O_{10}) and 3.17 g *N*-bromosuccinimide (17.8 mmol) and 0.10 g AIBN were added. The mixture was refluxed until the reaction started. In addition, refluxing was continued for 1 h. After cooling, the succinimide was filtered off and the solvent distilled off. The residue was recrystallized from ethanol: 1.8 g of colourless crystals (41% yield), m.p. 60–61°C. $^1\text{H-NMR}$ ($\text{CDCl}_3/\text{DMSO}-d_6$ 1:1): $\delta = 4.52$ (s, 2H, $\text{BrCH}_2\text{-Ar}$), 7,5 (m, 9H, Ar-H).

2.2. PREPARATION OF *N*-(3-BIPHENYLMETHYL)QUININIUM BROMIDE (1)

80 ml of acetone were refluxed under argon for 10 min. Under argon, 3.24 g quinine (7.30 mmol) were added. After solution, 1.80 g (7.30 mmol) 3-(bromomethyl)biphenyl were added and the solution was refluxed for an additional 45 min. For crystallization the solution was cooled in the refrigerator overnight (+4°C). The crystals were sucked off, recrystallized from ethanol and dried at 50°C/0.1 Torr for 1 h. Quantitative yield, m.p. 191°C. $\text{C}_{33}\text{H}_{35}\text{BrN}_2\text{O}_2$ (571.6). Calcd: N 4.90%; Found: N 4.80%.

2.3. PREPARATION OF THE CLATHRATES

The host compound (1) was recrystallized from three different mixtures containing ethanol, methanol, *n*-propanol, *n*-hexane and pyridine (see Table I). The test tubes containing the solutions were placed in a beaker with warm water allowing the solutions to cool very slowly to room temperature. After standing overnight at +4°C, the crystals were sucked off and washed with ether. To obtain the included solvent, the crystals were placed in the little flask of the distilling apparatus shown in Figure 1. The apparatus was evacuated and the flask heated to 50°C for 5–10 min. The solvent was condensed in the Teflon® tube. The Dewar flask was removed and after warming up to 0°C, the condensate was quickly collected in a GC syringe to prevent evaporation.

2.4. ANALYSIS BY GAS-CHROMATOGRAPHY

1 μl of distillate of each crystallization was measured two or three times. Also the original solutions were analyzed under the same conditions and the integrated spectra were evaluated. The operating conditions for GC analysis were: column: 2 m Carbowax 20 M, column

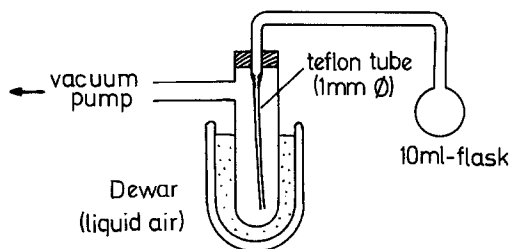


Fig. 1. Distilling apparatus used for small quantities of condensate. The distilled liquid is collected in the Teflon tube.

Table I. Solvent mixtures for recrystallization and guest substances enclosed

(a) Composition of solvent mixtures for recrystallization [weight %]		(b) Composition of included solvents [weight %, standard deviation in parenthesis]									
	Ethanol	Methanol	<i>n</i> -Propanol	<i>n</i> -Hexane	Pyridine		Ethanol	Methanol	<i>n</i> -Propanol	<i>n</i> -Hexane	Pyridine
I	9.8	22.1	22.4	18.4	27.3	I	71.4	15.5 (1.5)	5.33 (0.42)	5.21 (0.55)	2.57 (0.04)
II	29.5	17.3	17.5	14.4	21.3	II	85.4	5.20 (0.5)	3.38 (0.07)	3.08 (0.08)	2.90 (0.06)
III	49.4	12.4	12.6	10.3	15.3	III	90.3	2.11 (0.2)	2.77 (0.26)	2.94 (0.48)	1.88 (0.05)

temperature program: 1: 50°C for 8 min, 2: 100°C for 4 min, 3: 150°C for 4 min, heating rate between 1 and 2: 20°C/min, for 2 and 3: 30°C/min; injector temperature: 100°C; detector: FID, detector temperature: 190°C; carrier gas: N₂, flow rate 10 ml/min. The amount of methanol in the distillate was determined by ¹H-NMR spectroscopy because of insufficient separation from ethanol in GC.

3. Results and Discussion

N-(3-biphenylmethyl)quininium bromide (**1**) includes ethanol with high selectivity in its crystal lattice. The byproducts *n*-hexane, pyridine, *n*-propanol which are typical contaminations of ethanol, can be diminished by a factor of 0.1 to 0.38 by simply recrystallization. Ethanol is selectively and preferably extracted in the course of crystal formation with only small amounts of the byproduct(s). With the exception of methanol, the degree of purification of ethanol is not strongly dependent on the starting concentrations, so ethanol can be isolated from solvents with a great amount of impurities. Table I summarizes the composition of solutions and the results of the analyses. Table II shows the reducing factors of the impurities.

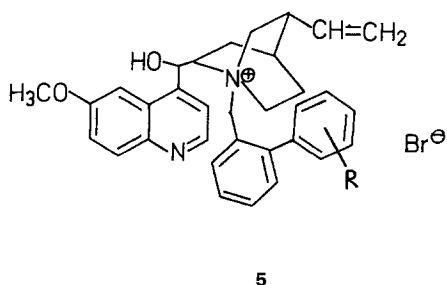
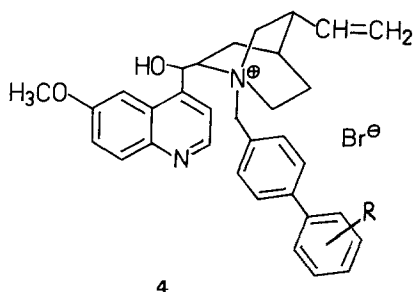
Table II. Reducing factors for the impurities^a [standard deviations in parenthesis]

Methanol	<i>n</i> -Propanol	<i>n</i> -Hexane	Pyridine
0.7 (0.07)	0.238 (0.079)	0.283 (0.105)	0.094 (0.014)
0.3 (0.03)	0.193 (0.021)	0.214 (0.027)	0.136 (0.019)
0.17 (0.02)	0.220 (0.093)	0.285 (0.162)	0.123 (0.028)

$$^a \text{ reducing factor} = \frac{\text{weight \% after clathration}}{\text{weight \% before clathration}}$$

From aqueous solution ethanol cannot be easily enriched by inclusion with (**1**). Water is also included to some extent in the course of the clathrate formation.

The results reported here encourage the search for even higher selective clathrands in the onium type series. Also, the separation of ethanol from water is of industrial and economic importance. It is to be expected that molecular structures similar to (**1**), but with modified side chains like (**4**) and (**5**), should lead the way to clathrands with modified guest selections. Investigations aimed at this are under way.



References

1. D. Worsch and F. Vögtle, *Naturwissenschaften* **71**, 423 (1984).
2. E. Weber, U. Müller, D. Worsch, F. Vögtle, A. Kirfel, and G. Will, *J.C.S., Chem. Commun.* 1578 (1985).
3. F. Vögtle, H.-G. Löhr, J. Franke, and D. Worsch, *Angew. Chem.* **97**, 721 (1985); *Int. Ed. Engl.* **24**, 727 (1985).
4. J. L. Atwood and J. E. D. Davies (eds.), *J. Incl. Phenom.* **1**, Nos. 1, 2 (1983); **2**, Nos. 1-4 (1984); **3**, Nos. 1-4 (1985).
5. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, *Inclusion Compounds*, vols. 1-3, Academic Press, London (1984).