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ALKYL SUBSTITUTED TETRAAZA-CYCLOALKANES: CARRIERS OF TRANSITION METAL IONS IN ORGANIC PHASE AND CATALYSTS OF ANION PROMOTED REACTIONS

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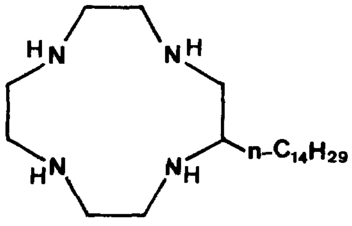
It is well known that cyclic molecular systems having oxygen[1] or oxygen and nitrogen[2] donor atoms in the ring are strongly complexing agents for alkali and alkaline earth metal ions. Therefore, when these are preferably soluble in organic phase (with the presence of a long alkylic chain), they can easily catalyze phase-transfer reactions promoted by anions[3,4].

Furthermore, cyclic tetraamines[5] at various ring radii have been known for a long time; more recently, polyaza-macrobicyclic systems[6].
These molecules (which do not contain a long hydrophobic chain, and are therefore strongly water soluble) complex the cations of various transition elements (Cu^{++}, Ni^{++}, Co^{+++}, Cr^{+++}, Rh^{+++}, etc.).

We now report the synthesis and the catalytic activity in some classical PT reactions, of cyclic alkyl substituted tetraamines; the latter transfer the cations of the transition elements in organic phase thus making possible the catalysis not only of the reactions in which the associated anions are involved, but also of those in which the cations might react.



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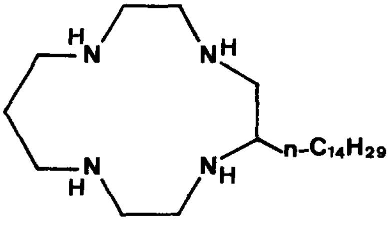

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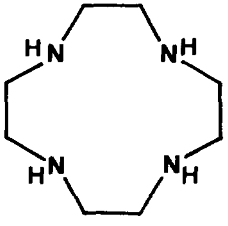

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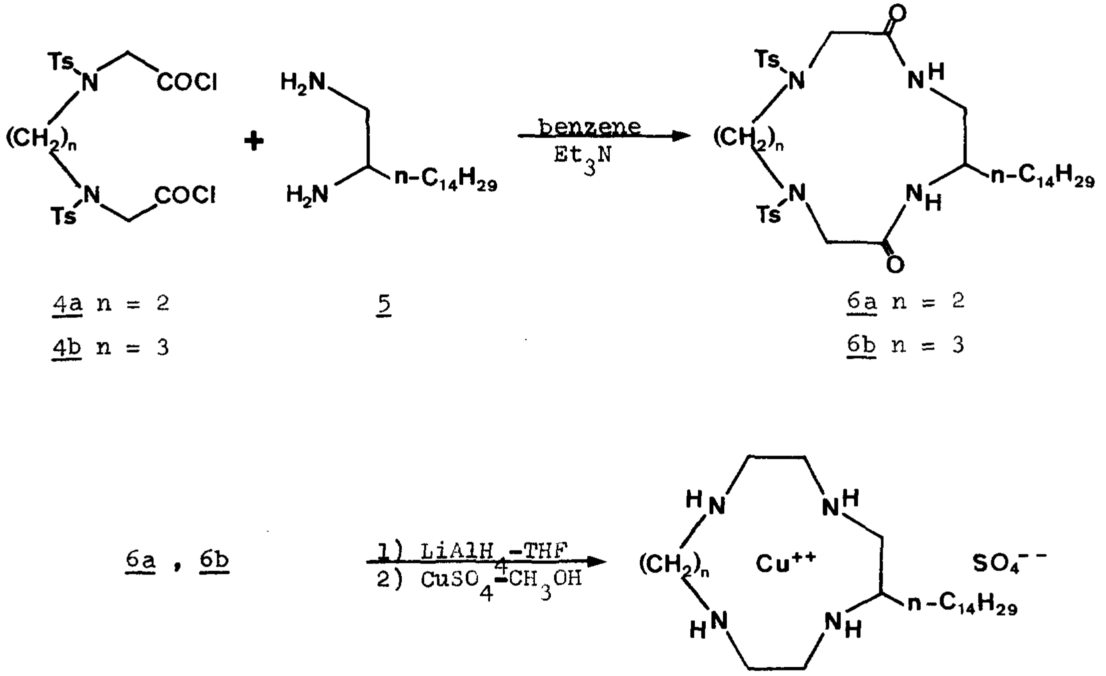
2-Tetradecyl-1,4,7,10-tetraaza-cyclododecane 1 and 2-Tetradecyl-1,4,7,11-tetraaza-cyclotridecane have been obtained according to the following reaction scheme:



4a n = 2
4b n = 3

5

6a n = 2
6b n = 3

1·$CuSO_4$ n = 2
2·$CuSO_4$ n = 3

The acyl chlorides 4a[5] and 4b[5] reacting with 1,2 diamino-n-hexadecane 5[7] in anhydrous benzene at high diluition[2] give a reaction mixture from which 6a (Y = 42%; m.p. 146-8°C) and 6b (Y = 43%; m.p. 170-2°C) are respectively separated by chromatography on silica gel (el. acetone-light petroleum 30:70).

6a and 6b by reduction with $LiAlH_4$ in refluxing THF for 4 days, give 1 and 2 which have been purified from the reaction mixture via their complexes with $CuSO_4$. Infact, stirring the methanolic solution of crude 1 or 2 with an excess of solid and anhydrous copper(II) sulphate, the solution rapidly becomes deep blue, as is characteristic in the case of copper(II) complexes with simple amines in water (it can be noticed that n-decylamine in the same conditions does not form the corresponding complex). After the residual $CuSO_4$ is filtered and the solvent removed, 1·$CuSO_4$ (Y = 60%; m.p. 200°C decomp.) and 2·$CuSO_4$ (Y =

65%; m.p. 185°C decomp.) are obtained by crystallization from CH_2Cl_2-Et_2O.

From their complexes with $CuSO_4$ 1 and 2 are set free by treating their solutions in CH_2Cl_2 with an excess of a potassium cyanide aqueous solution.

1 and 2 are non distillable viscous oils and have a high solubility in organic solvents (from n-pentane to methanol), a low one in water.

^{1}H NMR: 1 (δ,$CDCl_3$) 4.5-2.2(m,18H); 1.8-1.2(m,26H); 1.05-0.85(t,3H).
2 (δ,$CDCl_3$) 4.5-2.2(m,18H); 1.8-1.2(m,28H); 1.05-0.85(t,3H).

Similarly to the cyclic tetraamines without a long alkylic chain, 1 and 2 gives complexes with several transition metal ions (Fe^{+++}, Co^{+++}, Cr^{+++}, Ni^{++}, etc.) , but the latter are soluble in organic solvents and insoluble in water, in accordance with the hydrophilicity of the associated anions.

For example 1·$CuSO_4$ and 2·$CuSO_4$ are soluble in water too, in which they form micelles; adding water to a CH_2Cl_2 solution of these complexes and stirring, the blue colour is entirely transfered to the aqueous phase, but, by adding a salt with an anion less hydrophilic than $SO_4^=$ (such as $KClO_4$) the colour returns completely to the organic phase.

1·$CuSO_4$ and 2·$CuSO_4$ are stable in a wide pH range, thus showing the positive cyclic effect on the complexes' stability constants: they are stable from 2.0 to 9.0 pH; chloride derivatives 1·4HCl and 2·4HCl too, give, although more slowly, the corresponding $CuSO_4$ complexes in methanolic solution.

1 and 2 catalyze the PT reactions promoted by anions: the formation of quaternary ammonium salts in the course of the reactions shown in Table is not hypothesizable because all the reactions follow correct pseudo-first order kinetics. Though this would indicate that they also complex the alkali metal ions, their corresponding complexes have not been isolated.

Their metal transition complexes too catalyze PT reactions: in organic phase the complexed cation is present; i. e. in the conversion n-$C_8H_{17}Br$ $\longrightarrow$ n-$C_8H_{17}J$ the organic phase constantly remains a green colour, thus denoting not only that the copper is in organic phase (it is reducet to Cu(I) by J^- anion), but also that the cyclic tetraamines do not quaternarize.

It is noted that the macrocyclic tetraamine 3 does not catalyze this kind of reactions.

Organic reactions favoured by the transition metal cation in organic phase are object of study: oxidations and reductions induced by changes in the oxidation states of the cations so strongly complexed.

TABLE: Some PT Reactions Catalyzed by <u>1</u>, <u>2</u> and their Copper Complexes.

Substrate[a]	Catalyst[b]	Reagent	Product[c]	T(°C)	Time(h)	Yield(%)[d]
$n\text{-}C_8H_{17}Br$	<u>1</u>	KJ[e]	$n\text{-}C_8H_{17}J$	80	2.5	97
"	<u>2</u>	"	"	"	2.0	98
"	<u>1</u> $CuSO_4$	"	"	"	4.0	95
"	<u>2</u> $CuSO_4$	"	"	"	4.0	91
"	<u>3</u>	"	"	"	15.0	<1
$n\text{-}C_6H_{13}COCH_3$	<u>1</u>	$NaBH_4$[f]	$n\text{-}C_6H_{13}\underset{OH}{CH}CH_3$	25	6.5	95
"	<u>2</u>	"	"	"	3.0	95
"	<u>1</u> $CuSO_4$	"	"	"	4.0	90
"	<u>2</u> $CuSO_4$	"	"	"	2.0	97
"	<u>3</u>	"	"	"	20.0	~5

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a 2 mmol; b 0.05 molar equiv.; c the products were characterized by glc retention time and by NMR comparison with authentic samples; d by glc analysis; e KJ 5 mmol, water 0.70 ml; f $NaBH_4$ 3 mmol, benzene 0.80 ml, water 1.60 ml; during this reaction, Cu(II) is probably reduced to Cu(0) or to one of its hydrides, still remaining in organic phase: the reaction mixture appears dark but no precipitation occurs, and, after destroying the exceeding $NaBH_4$, the characteristic colour of the complexed Cu(II) appears again.

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