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COMPLEXATION OF OLEFINIC ALCOHOLS WITH AQUEOUS SILVER ION

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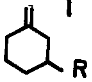
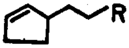
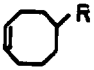
Recently, in the course of some synthetic work in the cyclooctene system, we noted that cis-4-cycloocten-1-one was much less easily extracted from ether into aqueous silver nitrate than the corresponding alcohol. Measurement of the equilibrium constants[2] for complex formation for several cyclooctene derivatives (Table I) showed that while the unsaturated ketone and alcohol were each better than cis-cyclooctene in coordinating ability, the alcohol was a strikingly superior ligand. Investigation of a series of acyclic, terminally unsaturated alcohols (Table I) indicated that the equilibrium complex is largest when the double bond is in a Δ^4 relationship to the hydroxyl group, but a Δ^3 (homoallylic) or Δ^6 relationship also gives rise to a relatively stable complex. Conversion of the hydroxyl group to acetate or methoxyl drastically decreases the stability of the complex. Also, secondary hydroxyls appear to have a smaller effect.

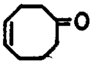
Although silver normally does not coordinate strongly with oxygen,[3] the best explanation for enhancement in complexation constant (10^3- fold in some cases) would appear to be direct bonding of the hydroxyl oxygen to silver. The alternative, hydrogen bonding of the hydroxyl to a water molecule coordinated with silver, seems unlikely in view of the small effect of acetate or methoxyl groups. The decrease in coordinating ability on changing the hydroxyl group to methoxyl is what one would expect for direct bonding of the oxygen to silver.[4] The nmr spectrum (60 MHz) of the 4-penten-1-ol complex in 10% CD_3OD-90% D_2O has the triplet due to the protons on C-1 shifted 10 Hz downfield relative to that of the free alcohol in the same solvent.

The stoichiometry of the complex was shown, by measurement of the equilibrium constant at various concentrations of silver nitrate and 4-pentenol, to be 1:1. The usual linear geometry of

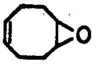
Table I

Equilibrium Constants[a] for Silver Ion Complexation of Olefin Derivatives at 25°

	K, l/mole	K, l/mole	K, l/mole	K, l/mole
	R = H	R = OAc	R = OH	R = OCH_3
	---	0.35	12[b], 22[c]	---
	---	0.31	26	---
	---	0.44	51	0.34
	0.095[b]	0.15	29	0.10
	---	<0.1	8.2	---
	---	<0.1	<0.1	---
	---	0.07	25	---
	0.096[d]	<0.1	19	---
	0.119[d,e]	<0.1	38	---
	0.005[d]	<0.1	29	---

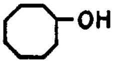


= 1.30



= 0.10

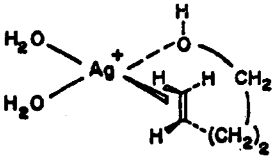
<0.1



<0.1

[a] See ref. 2 for definition of K. Reproducibility is ca. 10%. [b] S. Winstein and H.J. Lucas, J. Amer. Chem. Soc., 60,836(1938). [c] F.R. Hartley and L.M. Venanzi, J.Chem.Soc. (A), 333(1967). This is the equilibrium constant for olefin in water solution. [d] J.G. Traynham and J.R.Olechowski, J.Amer.Chem.Soc., 81, 571(1959). [e] Value for cyclopentene.

dicoordinate Ag(I) species,[3] is clearly not possible in this case. Conceivably, the 6 1/2-membered ring imposed by the hydroxyolefin ligand forces the silver into a roughly tetrahedral arrangement, similar to its 8-hydroxyquinoline complex,[3] with loosely held water molecules occupying the other positions:



The enhancement has obvious utility. Franzus and coworkers, noting that syn-7-acetoxy-2-norbornene formed a 10-fold more stable silver complex than the anti isomer, were able to use this small difference to separate efficiently the two isomers.[5] In synthesizing the methyl ethers of 4-penten-1-ol and 5-hexen-1-ol (by reaction of the alkoxides with methyl iodide) traces of unreacted alcohol were removed completely from the crude alkenyl ethers by simply washing an ether solution of the crude product once with aqueous silver nitrate.

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REFERENCES

1. Fellow of the Alfred P. Sloan Foundation, 1968-70.
2. The equilibrium constants were measured by equilibrating, at 25° CCl_4 solutions of the olefin with 1.0 M aqueous silver nitrate and determining the loss of olefin from the CCl_4 phase by gas chromatography. The solubility of the free olefin in the aqueous phase was determined similarly by equilibrating CCl_4 solutions of the olefins with 1.0 M KNO_3 solution. The constant for complexation was determined as:

$$K = \frac{[\text{complex}]_{H_2O}}{[\text{olefin}]_{CCl_4}\quad[Ag^+]_{H_2O}}$$

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4. R.W. Parry and R.N. Keller, "The Chemistry of The Coordination Compounds," (J.C. Bailar, Jr., and D.H. Busch, Eds.), Reinhold, New York, New York, 1956, p 123.
5. B. Franzus, W.C. Baird, Jr., E.I. Snyder, and J.H. Surridge, J. Org. Chem., **32**, 2845(1967).