cated was mostly triphenylphosphine oxide. A 0.190-g portion of this material was subjected to preparative TLC on silica gel, using 1:4 ether–hexane three times, to afford 0.012 g (36%) of cholest-4-en-3-one, mp 69–73° (lit.[28] mp 81–82°), identified by ir spectrum. From the preparative TLC there was also obtained 0.016 g of a mixture of cholestan-3-one and cholest-1-en-3-one.

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Registry No.—1, 31236-91-6; 2, 3588-80-5; palladium tetrakis(triphenylphosphine), 14421-01-3.

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Complex Formation Between Potassium Acetate and a Simple Triol

Ronald E. Hackler

Agricultural Organic Chemistry, Lilly Research Laboratories, Greenfield, Indiana 46140

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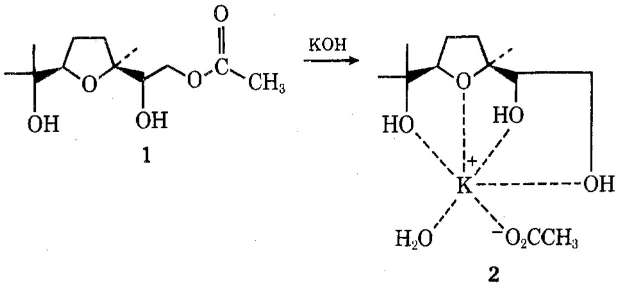
Complexes of organic compounds with metal ions have been known and studied for many years, but alkali metal ions have not been prominent in these studies until recently. The crown ethers[1] have been in the forefront of research on alkali metal ion complexes, and the first crown ethers have spawned a host of related compounds.[2,3] Other organic compounds[4–7] have shown a more limited capacity for complexing with alkali metal ions, and a number of naturally occurring polyether antibiotics[8–10] have shown remarkable selectivity for specific ions.

Most of the polyether molecules have a systematic configuration of ether, carbonyl, hydroxyl, and/or carboxyl groups that hold the ion in place, while the rest of the molecule serves to shield the ion, and give the overall complex more lipophilic character. X-Ray analysis of the structures of these complexes shows that often six ligand atoms are used in holding sodium and potassium ions. Six is not a magic number, but seems to be the frequent compromise between steric and electrostatic factors. An increasing number of ligands gives a more diffuse electrostatic interaction, but this is countered by the steric requirement of the ligands and their need to approach within a given distance of the ion.[11] The ligand atoms are frequently separated by two-carbon bridges. These consistent elements of structure[12] have made it possible to devise new compounds that show the capacity to complex, and this in part explains the proliferation of activity in this area.

We have observed a potassium acetate complex **2** involving a very small organic compound that has little more than the necessary elements of structure of the polyether ionophores. The four oxygen atoms in the triol have the characteristic two-carbon separations, with a water molecule and the acetate ion apparently functioning as additional ligands. The synthesis of 1 has been previously reported[13] using a neutral permanganate oxidation of geranyl acetate. These workers hydrolyzed 1 to the free triol using a fractional amount of potassium hydroxide. Our use of 1 equiv of potassium hydroxide permitted the isolation of **2**.



The presence of the water molecule is clearly noted in the ^1H NMR spectrum and confirmed by the microanalysis. It is assumed to be present only to give maximum steric and electrostatic stability to the complex. No attempt was made to remove the water. When the ^1H NMR sample is exchanged with D_2O, the spectrum reverts to that of the triol, which can be recovered from the chloroform solution.

The complex **2** could also be formed by addition of potassium acetate to the free triol. No complex formation could be detected between sodium acetate and the triol. It should be noted that there are only seven oxygens as possible ligands in this complex. The mole of water would seem to be necessary, although this has not been definitively shown. The acetate ion apparently functions similarly to the intramolecular carboxyl group in some ionophorous antibiotics.[9-10]

Experimental Section

Preparation of the Complex 2 by Hydrolysis. The acetate **1** (5 g, mp 107–108°) was treated with 1 equiv of potassium hydroxide in 1:1 $MeOH-H_2O$ (30 ml) at room temperature overnight. The solvents were removed under vacuum, $CHCl_3$ was added, and the solution was filtered. Removal of the $CHCl_3$ under vacuum gave an oil which could be crystallized by dissolving in a minimum volume of MeOH, adding five volumes of ether, and cooling. The complex separated slowly as flocculent, white crystals, mp 53–56° (2 g). Addition of a larger volume of ether caused separation of potassium acetate. The complex could be recrystallized from $CHCl_3$–ether, mp 56–58°. The free triol could be obtained from the first mother liquors and had mp 98–99°.

The complex **2** has ^1H NMR ($CDCl_3$) δ 4.91, s (5 H), 3.65, m (4 H), 1.92, broad s (7 H), 1.24, s (3 H), 1.13, s (3 H), and 1.08, s (3 H). D_2O exchange causes decomposition of the complex as shown by removal of the absorption at δ 4.91, decrease of the integration for the peak at δ 1.92 to four protons, and reversion of the spectrum to that of the triol: δ 3.8, sharpened multiplet (4 H), 1.4–2.4, multiplet (4 H), 1.27, s (3 H), 1.18, s (3 H), and 1.09, s (3 H). Titration of the complex gave a pK_a of 4.55 and a mol wt of 322. The calculated mol wt is 320. Combustion Anal. Calcd for $C_{12}H_{25}KO_7$: C, 44.98; H, 7.86. Found: C, 45.04; H, 7.67. Atomic Absorption Anal. Calcd: K, 12.2. Found: K, 11.7.

Formation of the Complex 2 from the Triol. The parent triol (5.01 g, 25 mmol), potassium acetate (2.45 g, 25 mmol), and water (0.45 ml) were stirred in MeOH (50 ml) until everything went into solution (about 20 min). The solvent was removed under vacuum, MeOH (10 ml) was added, and after filtration, ether (50 ml) was added. The solution was cooled for 24 hr at −25°, and white crystals (2.5 g) were collected, mp 55–57°.

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Registry No.—**1**, 4031-49-6; **2**, 56050-93-2; potassium hydroxide, 1310-58-3; *cis*-tetrahydro-α^2-(hydroxymethyl)-$2\alpha,\alpha^5,\alpha^5$-trimethyl-$2\beta,5\beta$-furandimethanol, 4031-50-9; potassium acetate, 127-08-2.

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The Carbon–Nitrogen Rotational Barrier as a Stereochemical Probe of Benzamidoximes

Alessandro Dondoni,* Lodovico Lunazzi,* Patrizia Giorgianni, and Dante Macciantelli

Istituto di Chimica Organica, Università, Bologna, Italy, and Laboratorio del C. N. R., Ozzano E., Bologna, Italy

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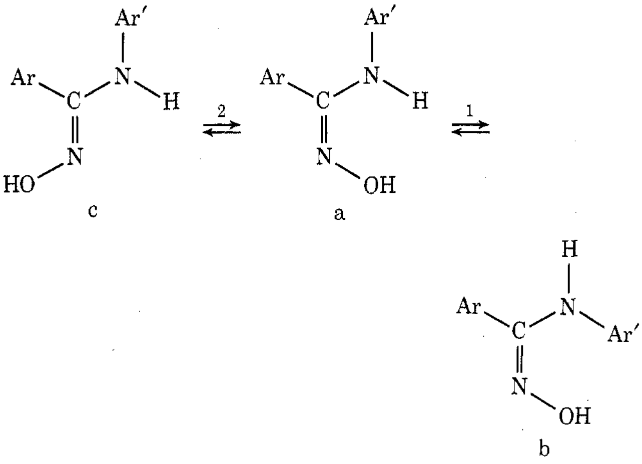
The stereochemistry of benzamidoximes has been recently investigated by electric dipole moment measurements and NMR spectroscopy.[1] The results of these two independent experimental approaches were complementary and conclusive enough to support the existence of the amino oxime tautomeric structure as well as the *Z* configuration on the C=N bond (structure a and b). However, a further point which remained to be clarified concerns the nature of the two isomers observed in the NMR spectra of some compounds. In principle the two species could derive either from restricted rotation around the amidic bond (equilibrium 1) which creates a barrier for the a ⇄ b transformation, or from inversion around the oximino bond (equilibrium 2); it has been already suggested that the first model should apply.[1]



In order to provide further evidence in favor of this interpretation, we have measured the activation parameters for the reversible conversion of these isomers, since it was thought that a quantitative estimate of the energy involved in this process could discriminate between the two possibilities. In fact it is well known that the rotational barriers around the amidic bond amount[2] to 15–24 kcal mol^{-1} in different environments, whereas the inversion of the carbon-nitrogen double bond of oximes[3] and related compounds[4] should require a much larger energy since syn–anti thermal isomerization is difficult and isomers can be separated.[5]

Among the compounds previously examined,[1] those bearing ortho methyl groups in Ar gave NMR spectra indicating the presence of two isomers whereas only one species was observed for Ar = Ar′ = Ph. We have therefore selected compounds **1** (Ar = $3,5-Cl_2-2,4,6-Me_3C_6$; Ar′ = Ph) and **2** (Ar = $2-MeC_6H_4$; Ar′ = Ph) and their NMR spectra were recorded at various temperatures. Ortho-methyl substituted benzamidoximes were suitable for a line-shape study since, owing to the lacking of exchange at room temperature, the methyl groups give enough separated sharp singlets. The same nonequivalence was observed also for the amidic and hydroxylic protons, which, however, were less reliable for this study since they can be involved in intra- and intermolecular exchange phenomena. The signals of