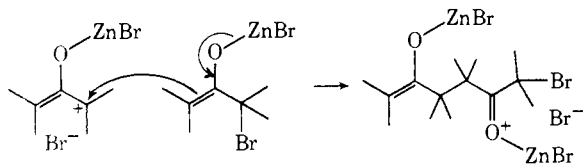
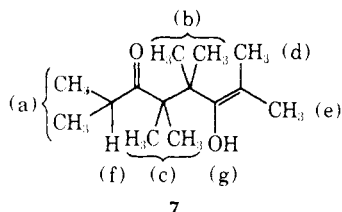


procedure insofar as attempted cross-coupling (**1** with **3**, **1** with **4**) was not successful and afforded only those 1,4-diketones which had already been obtained by self-dimerization. However, whereas treatment of isopropyl methyl ketone with diacetylperoxide gave exclusively dimer **3c**^{4a,c} as we have confirmed by analytical glc, our reaction produced all three possible isomers and the distribution of dimers could be influenced by the solvent and reducing agent.⁶ Further, the dimerization described here is considered to be ionic rather than free radical and visualized to involve the combination of zinc oxyallyl^{3c} and zinc enolate (Scheme I).

Scheme I



Thus, coupling of 2,4-dibromo-2,4-dimethyl-3-pentanone (**1**) in *N*-deuterio-*N*-methylformamide yielded the 2,7-dideuterio analog (52%) of 3,6-octanedione **1a**, implicating the solvent as the proton source. By recording consecutive nmr spectra immediately after removal of solvent pentane, it was possible to identify the trialkylated enol **7** as the direct precursor of 3,6-octanedione **1a** in the postulated reaction sequence.



After *ca.* 10 min at 25° the enol⁸ had disappeared completely and **1a** was formed as the final product.

Acknowledgments. We thank the Science Research Council, the Dr. Carl Duisberg-Stiftung, and Schering A. G., Berlin, for support of this work.

(6) By using NaI in acetonitrile, the most crowded diketone **3c** was formed exclusively in addition to some 3-bromo-3-methyl-2-butanone: R. Chidgey, unpublished.

(7) Pmr δ (TMS) (a) 0.95 (d, $J \sim 8$ Hz, 6 H), (b) 1.00 (s, 6 H), (c) 1.10 (s, 6 H), (d) 1.56 (s, 3 H), (e) 1.60 (s, 3 H), (f) 2.80 (sept, $J \sim 8$ Hz, 1 H) (g) 7.15 ppm (s, 1 H); the signals due to a and b were partly superposed.

(8) Other simple aliphatic trialkylated enols have recently been generated and identified chemically as well as spectroscopically; see H. M. R. Hoffmann and E. A. Schmidt, *J. Amer. Chem. Soc.*, **94**, 1373, 7832 (1972); H. M. R. Hoffmann and E. A. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **12**, 239 (1973).

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Received October 16, 1973

A Crystalline Salt of the Sodium Anion (Na⁻)

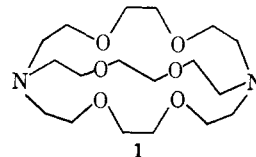
Sir:

We wish to report the synthesis of a new crystalline compound which contains the sodium anion, Na⁻. The mode of formation, stoichiometry, reactivity, crystal structure, and general appearance are consistent with this assignment. We believe that this compound, formed from sodium metal and the bicyclic polyoxa-

diamine, **1**, ("crypt"), represents the first example of a new class of compounds.

It has been presumed for some time that solutions of the alkali metals in amines and ethers contain species of stoichiometry M⁻. This assignment is based upon the variation of the optical absorption band with metal, solvent, and temperature,^{1,2} the oscillator strength,³ the reactions following photolysis of the solutions,⁴⁻⁷ and the kinetics of formation from M⁺ and e⁻_{solv.}^{8,9}

We have recently shown^{2,10-12} that cyclic polyethers which form "crown"¹³ and "cryptate"¹⁴ complexes with alkali cations greatly enhance the solubility of the alkali metals in amines and ethers. With **1** it is possible



to control the composition of the solution by adjusting the ratio of complexing agent to total dissolved metal. By using an excess of sodium metal (which is insoluble in ethylamine in the absence of the complexing agent), solutions as concentrated as 0.4 M in total sodium in ethylamine can be prepared. Most of the dissolved material has the stoichiometry, NaC⁺·Na⁻, in which NaC⁺ represents the cage complex formed by trapping a sodium cation inside of the "crypt." The complexation constant is large and the rate of release of Na⁺ from the crypt is relatively slow.¹⁵

When a concentrated solution of NaC⁺·Na⁻ in ethylamine is cooled to Dry Ice temperatures, a gold-colored crystalline solid precipitates. Single crystals, grown by slow cooling, have the form of thin hexagonal plates. The crystals and also the powder have a shiny metallic appearance which changes reversibly in color from gold at -190° to bronze at +40°. Just below the decomposition temperature of 83° the color is dark brown. Crystals which have been repeatedly washed with *n*-hexane or diethyl ether are stable *in vacuo* for days at room temperature and below.

The stoichiometry and integrity of the compound Na₂C₁₈H₃₆N₂O₆ were checked in several ways.

(1) Elemental analysis (Spang Microanalytical Lab-

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oratories, Ann Arbor, Mich.) on two separate samples gave the following observed *vs.* calculated percentages: Na, 10.90 *vs.* 11.05; C, 51.18 *vs.* 51.13; N, 6.64 *vs.* 6.70; H, 8.53 *vs.* 8.62.

(2) The volume and pressure of hydrogen produced by reaction with water¹⁶ yielded 0.94 and 0.95 ± 0.03 mol of H₂ per mole of compound for two samples.

(3) A sample which had been decomposed with water was titrated with HCl. It required 3.98 ± 0.05 equiv per mole. After neutralization of the NaOH produced, the titration curve was identical with that obtained by titration of NaC⁺·Cl⁻ in water.

(4) When the samples were dissolved in liquid ND₃ the proton nmr spectrum of the resulting deep blue solution was the same as that of a cryptate salt in this solvent except for a paramagnetic shift induced by the presence of the solvated electron. Decomposed samples when dissolved in CDCl₃ always gave only the cryptate proton nmr spectrum.

In spite of the shiny metallic appearance, the conductivity of extruded rods and of packed powders was so low that low-current methods were required. The powdered sample was compressed between two aluminum plates in an inert atmosphere box. Teflon spacers were used to prevent contamination by air and moisture. During measurement of the current with a Keithly electrometer, the samples were contained within a variable temperature Faraday cage. Ohm's law was obeyed, the current did not change with time, and reversal of the polarity reversed the current immediately. These results are consistent with electronic conduction. The reversible variation of the resistance with temperature, together with rough estimates of the contact area and thickness yield a specific resistance (ρ) which changes from $\sim 5 \times 10^{13}$ ohm cm at 0° to 7×10^9 ohm cm at 60°. The magnitude of the resistance, its change with temperature and the electronic nature of the conductivity are all characteristics of a semiconductor. However, a graph of $\log \rho$ *vs.* $1/T$ shows systematic curvature with a smaller slope at high temperatures. ESR studies of the washed powder show only a barely detectable signal at the highest gain.

Because **1** forms stable complexes with the alkali cations, we presumed that Na⁺ was trapped in the "crypt" and that the counterion was Na⁻. Another possibility was that the "outside" sodium consisted of Na⁺ and a partially delocalized electron pair.

Single-crystal X-ray diffraction studies show that the space group is *R*32 with three molecules per unit cell (hexagonal axes). Refinement of the structure (*R* = 0.085) gives the following information.

(1) One of the sodium species is trapped in the "crypt" with interatomic distances which are very close to those reported for the sodium cryptate iodide structure.¹⁷ This strongly indicates that the sodium cation is the trapped species.

(2) The other sodium species is outside of the "crypt" at a large distance from other atoms. For example, the amine nitrogen is at 5.55 Å and the closest oxygen is at 5.76 Å. The logical conclusion is that the outside sodium is negatively charged.

Since both the metal and the complexing agent can be

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varied, it is likely that other compounds of this type can be prepared.

Acknowledgments. This work was supported by the U. S. Atomic Energy Commission under Contract AT-11-1-958. We are grateful to Dr. P. S. Schroeder for many helpful discussions and to Drs. B. Rosenberg, R. Schwendeman, and G. I. Hatton for the use of equipment.

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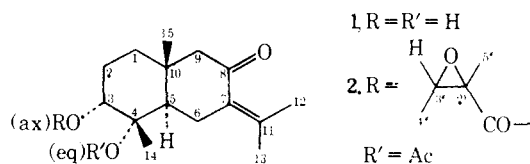
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Received October 17, 1973

Structure of a Sesquiterpene, Cuauhtemone, and Its Derivative. Application of Partially Relaxed Fourier Transform ¹³C Nuclear Magnetic Resonance

Sir:

The following studies were carried out mainly for the purpose of exploring the usage of partially relaxed Fourier transform (PRFT) ¹³C nmr techniques to structure determination. Cuauhtemone **1**, a plant growth inhibitor,¹ was obtained in 0.039% yield from the nonsaponifiable matter of the aerial part of *Pluchea odorata* (*Compositae*, the Mexican medicinal shrub "Cuauhtematl"), by silica gel chromatography: mp 140°; $[\alpha]_D$ 59.2°; C₁₅H₂₄O₃; mass spectrum M⁺ 252.1704 (base peak; calcd, 252.1725); uv (MeOH) 254 nm (ϵ 7700); CD (MeOH) 252 nm ($\Delta\epsilon$ -2.76), 322 ($\Delta\epsilon$ +1.25); ir (dilute solution in CHCl₃) 3640 (free OH), 3560 (intramolecularly bonded OH), 1675, and 1585 cm⁻¹. The diester **2** was obtained in a 0.012% yield by isopropyl ether extraction of the petroleum ether soluble material of the plant: mp 150°; $[\alpha]_D$ +145°; C₂₂H₃₂O₆ (correct elemental analysis and osmometric molecular weight); mass spectrum (no M⁺ observed) base peak 216.1493 (calcd for C₁₃H₂₀O, 216.1514); uv (MeOH) 255 nm (ϵ 7550); CD (MeOH) 248 nm ($\Delta\epsilon$ -1.70), 318 ($\Delta\epsilon$ +0.54); ir (CHCl₃) 1740 and 1650 cm⁻¹. Hydrolysis of **2** with sodium carbonate-methanol gave **1**. The uv and ir data suggested the presence of an *s*-cis tetrasubstituted enone moiety.



In spite of the relatively small number of protons, the pmr spectrum measured under various conditions was unique in that it only afforded very limited information, due to intensive coupling, overlap of signals, coincidence of magnetically nonequivalent protons (see **3**), and broadening upon addition of shift reagents. Accordingly the techniques of PFRT ¹³C nmr² were employed maximally (Figure 1).

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