vent-separated ion pairs and, to some extent, free ions.[13]

If one accepts the ion-pair Sn2 mechanism for the reactions of **3** with weakly basic nucleophiles in protic solvents, one would expect that solvolyses of **3** would also occur *via* ion pairs. This view is supported by the observation that changing the solvent for the reaction of bromide **3b** with LiN_3 from MeOH to 60% MeOH changed the kinetic order from second order to mixed order. For the reaction in 60% MeOH a plot of the pseudo-first-order rate constant k_{obsd} *vs.* [N_3^-] was linear, as expected for a reaction where the azide and solvolysis products are derived from a common precursor.[6] From the kinetic analysis, $k_N/k_S = 2180$, which compared well with the value of 2150 derived from a product analysis. In MeOH, $k_N/k_S \cong 6000$ for **3b** and *ca.* 120 for mesylate **3c**. The view that the common precursors for the azide and solvolysis products are ion pairs was given strong support by the observation of a large β-deuterium isotope effect[14] and a large k^{OMs}/k^{Br} leaving group effect[9] for solvolyses in 60% MeOH (probes 9 and 10, respectively).

The success of the tertiary allylic system **3** in evoking ion-pair Sn2 mechanisms, relative to *tert*-alkyl systems, probably depends on: (a) the electron-withdrawing effect of the $C_7H_7SO_2$ group, which is sufficient to inhibit ion-pair dissociation, but not ion-pair formation, (b) the delocalizing effect of the vinyl group, which decreases the positive charge on the protons of the methyl groups in **3**, and thus decreases the tendency toward elimination, and (c) the smaller steric effect resulting from replacement of an alkyl group by a vinyl group, which facilitates nucleophilic attack on the cation and may inhibit elimination.[15]

Acknowledgment. We are grateful to Professor V. J. Shiner, Jr., for a number of helpful discussions.

(13) The Winstein ionization scheme is assumed. See V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971), for a recent elaboration of this scheme.

(14) This value is close to that observed for near Lim solvolyses (*e.g.*, for *tert*-BuCl in water the value is 1.37 per CD_3). See E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964, for a discussion.

(15) As a corollary it should be noted that the elimination reactions which accompany these ion-pair Sn2 reactions no doubt occur by ion-pair E2 mechanisms. In our opinion, ion-pair E2 mechanisms, rather than concerted E2 mechanisms, are responsible for the second-order components which commonly appear in the rate expressions when high concentrations of lyate ion are introduced into solvolysis reactions of tertiary halide (or like) substrates.

(16) National Institutes of Health Predoctoral Fellow, 1958–1971.

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A Novel Antiferromagnetic Oxo-Bridged Manganese Complex

Sir:

An insight into antiferromagnetic interactions is provided by our study of the novel complex di-μ-oxo-tetrakis(2,2'-bipyridine)dimanganese(III,IV) perchlorate trihydrate. This unusual complex contains two manganese atoms in different oxidation states bridged by two oxygen atoms; one of the manganese atoms is subject to "Jahn–Teller distortions." Thus, a unique labeling of one manganese atom gives results that pro-
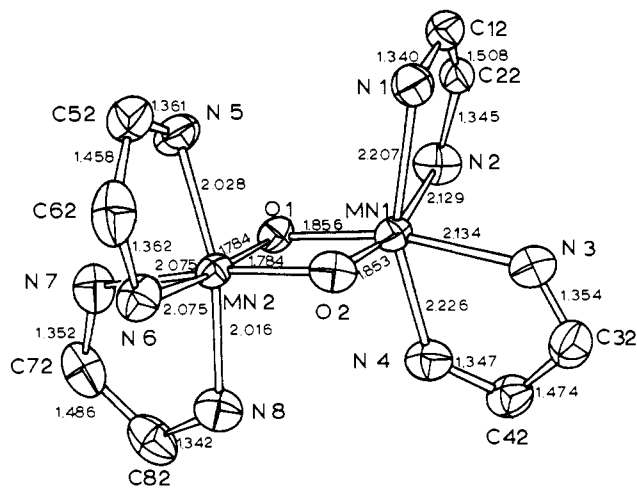

Figure 1.

vide a means for interpreting other physical properties.

The complex resulted from an attempt to grow crystals of the previously prepared tris(2,2'-bipyridine)manganese(III) perchlorate[1] and appears to be identical with the product obtained from oxidation of tris(2,2'-bipyridine)manganese(II).[2] The greenish black crystals are monoclinic (space group $P2_1/c$, $a = 13.877$ (2), $b = 13.936$ (2), $c = 24.310$ (3) Å; and $\beta = 103.56$ (1)°). The density calculated for four molecules (mol wt 1119.1) per unit cell is 1.626 g/cm^3, in agreement with 1.62 g/cm^3 obtained by flotation. A total of 8058 unique reflections with $2\theta \leq 50°$ was measured on a Syntex $P\bar{1}$ diffractometer using monochromatized Mo Kα radiation and a 2θ-θ scan technique. The 4948 reflections with $I > 1.2\sigma(I)$ were used in the subsequent analysis. The structure was solved by the heavy atom method and refined by full-matrix and block diagonal least-squares techniques to an R, the usual residual, of 0.080.

The chelate portion of the cation is shown in Figure 1 together with pertinent bond distances. The two manganese atoms are unmistakably different, the smaller distances about Mn(2) indicating that this atom is Mn(IV), a d^3 ion. The lengthening of the Mn(2)–N(6) and Mn(2)–N(7) distances relative to Mn(2)–N(5) and Mn(2)–N(8) is related to N(6) and N(7) being trans to the oxo bridge. Assuming that the Mn–N bonds trans to the oxo bridge are lengthened by 0.053 Å, the difference between axial and equatorial distances about Mn(1) is 0.138 Å. This lengthening is in excellent agreement with the value of 0.141 Å found in the only distorted high-spin manganese(III) complex reported in the literature.[3] These observations on the distances support the hypothesis that Mn(2) is the d^3 ion and Mn(1) is a high-spin d^4 ion.

The magnetic moment was determined by the Gouy method to be 1.79 ± 0.03 BM per manganese atom at room temperature, decreasing to 1.33 BM per manganese at liquid nitrogen temperature. From the $\chi(T)$ data we infer that the electrons on the manganese atoms of each dimeric unit are aligned in an antiparallel

(1) J. C. Summers, Ph.D. Thesis, University of Florida, Gainesville, Fla., 1968.

(2) R. S. Nyholm and A. Turco, *Chem. Ind. (London)*, 74 (1960).

(3) (a) M. Bartlett and G. J. Palenik, *Chem. Commun.*, 416 (1970); (b) M. Bartlett, Ph.D. Thesis, University of Waterloo, Waterloo, Canada, 1970.

fashion *via* a superexchange mechanism. Direct metal–metal interaction is believed to be magnetically unimportant because of the relatively large Mn(2)–Mn(1) distance of 2.716 Å.

The acetonitrile and diffuse reflectance spectra of the dimer, which are similar, bear a striking resemblance to the spectra of tris(2,2′-bipyridine)manganese(III) and tris(o-phenanthroline)manganese(III).[1] The spectral features of the Mn(IV) ion are expected to be superimposed upon those of the Mn(III) ion; however, the Mn(IV) transitions are of sufficiently high energy and low probability to be obscured by the strong charge-transfer absorptions lying at energies greater than 20 kK, and, thus, the spectrum of the dimer is essentially that of the Mn(III) ion.

On the basis of the structural, spectroscopic, and magnetic data, we conclude that it is appropriate to describe this dinuclear complex as being composed of superexchange coupled Mn(III) and Mn(IV) atoms and that the superexchange cannot involve extensive delocalization of the one e_g electron. The $\chi(T)$ data were fit by a nonlinear least-squares technique to a simple isotropic Heisenberg spin Hamiltonian

$$\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$$

for a 2–3/2 spin system. The energy levels $\epsilon_{1/2} = 0$, $\epsilon_{3/2} = -3J$, $\epsilon_{5/2} = -8J$, and $\epsilon_{7/2} = -15J$ were used together with $g = 2.003$ and assuming TIP $= 60 \times 10^{-5}$ cgs unit. The best fit was for $J/k = -147°$.

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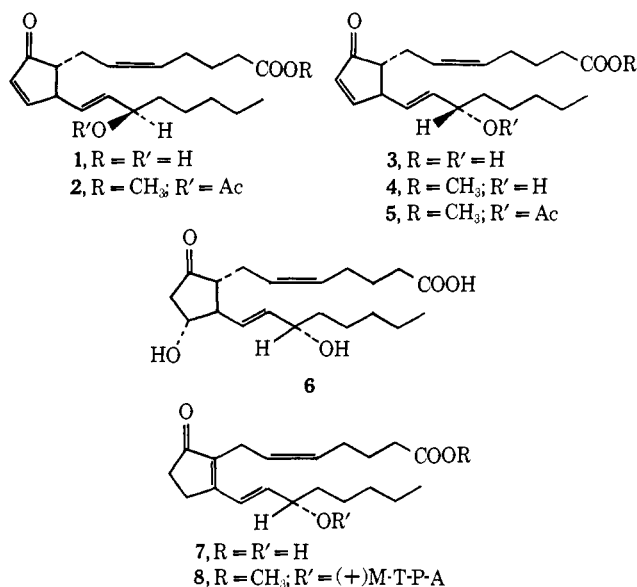## Occurrence of Esters of (15S)-Prostaglandin A2 and E2 in Coral

Sir:

All known natural mammalian prostaglandins have the S configuration at the C_{15} asymmetric center.[1] A recent report by Weinheimer and Spraggins[2] described the isolation from a soft coral, the gorgonian *Plexaura homomalla* occurring in coastal waters off Florida, of a prostaglandin, (15R)-PGA2 (1) and its acetate, methyl ester (2), having the "nonmammalian" configuration at C_{15}. We have now found that some forms of *P. homomalla* contain, instead of the (R)-prostaglandins, esterified derivatives of (15S)-PGA2 (3) and (15S)-PGE2 (6) identical with the prostaglandins de-derived from mammalian sources. Also, in some single specimens of this gorgonian, both (15R)- and (15S)-prostaglandins may occur.

Specimens of *P. homomalla* that are immediately frozen in liquid nitrogen or Dry Ice upon collection

(1) D. A. Nugteren, D. A. VanDorp, S. Bergström, M. Hamberg, and B. Samuelsson, *Nature (London)*, 212, 38 (1966).
(2) A. J. Weinheimer and R. L. Spraggins, *Tetrahedron Lett.*, 5183 (1969).

1, R = R′ = H
2, R = CH₃; R′ = Ac

3, R = R′ = H
4, R = CH₃; R′ = H
5, R = CH₃; R′ = Ac

6

7, R = R′ = H
8, R = CH₃; R′ = (+)M·T·P·A

and then extracted with organic solvents give essentially only the prostaglandin 15-acetate, methyl esters. However, coral samples that are allowed to stand in water or methanol at ambient temperatures for some time after collection undergo hydrolysis or methanolysis, giving mixtures containing PGA2 and its methyl ester upon extraction. The (15R) and (15S) forms of these two prostaglandins differ slightly in silica gel tlc polarity, using the AIX system,[3] the (15R) isomers being less polar, so that preliminary identification in coral extracts can be made. During the processing of a recent collection of *P. homomalla*, a single specimen was analyzed and surprisingly found to contain prostaglandins of the (15S) configuration. Since then, numerous specimens from various locations in the Caribbean area have been found to contain (15S)-PGA2 and its methyl ester. From many of these, no (15R)-prostaglandins could be detected but spots having the tlc mobility and color reactions of (15S)-PGE2 and its methyl ester were observed. Furthermore, from some individual specimens, spots corresponding to both (15R)- and (15S)-PGA2 and their methyl esters were seen.[4,5]

Additional confirmation of configuration at C_{15} in coral-derived (15S)-PGA2 was obtained by conversion to (15S)-PGE2 and (15S)-PGF2α[6] and by base-catalyzed rearrangement to (15S)-PGB2 (7). The latter exhibited a positive Cotton effect in the optical rotatory dispersion curve identical with that obtained from mammalian-derived (15S)-PGB2 and the mirror image of that obtained from coral (15R)-PGB2.[7]

The method of Dale, Dull, and Mosher[8] was also

(3) M. Hamberg and B. Samuelsson, *J. Biol. Chem.*, 241, 257 (1966).
(4) After the completion of this work we learned from Professor Bengt Samuelsson (Royal Veterinary College, Stockholm) that a careful analysis of *P. homomalla* from Florida waters disclosed the presence of a small amount of the (15S) isomer of the PGA compounds together with the predominant (15R) isomer; R. Light and B. Samuelsson, *Eur. J. Biochem.*, in press.
(5) A single dried specimen was also obtained and found to contain (15R)- and (15S)-PGB₂ as determined by the nmr spectrum of its (+)-α-methoxy-α-trifluoromethylphenyl acetates (see below).
(6) G. L. Bundy, W. P. Schneider, F. H. Lincoln, and J. E. Pike, *J. Amer. Chem. Soc.*, 94, 2123 (1972).
(7) Private communication from Dr. W. C. Kreuger of The Upjohn Co.
(8) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, 34, 2543 (1969).