Ester **3** was reduced with lithium aluminum hydride to alcohol **8** whose nmr spectrum contained an AB pattern (2 H) centered at 3.5 ppm (J_{AB} = 12.0 cps), singlets (each 3 H) at 0.79 and 1.22 ppm, and a complex multiplet (5 H) extending from 0.5 to 1.9 ppm. Derivatives of **8** would be expected to solvolyze very rapidly to produce less strained isomers.[12] It is therefore not surprising that **8** is very rapidly destroyed upon exposure to traces of acid in aqueous dioxane and the isomer **9** is formed in nearly quantitative yield. The structure of **9** is defined by its spectral properties: mass spectral molecule ion at m/e 126 (m/e 168 for the acetate of **9**); infrared absorptions at 3340 (OH), 1655 (C=C), and 878 cm^{-1} (exocyclic C=C); nmr signals at 4.8 (2 H, characteristic pentuplet[13]), 3.68 (1 H, triplet), 2.0–2.7 (5 H, broad multiplet), and 0.92 ppm (6 H, singlet[14]).

One would expect the reactivity of the central bond[16] of bicyclo[2.1.0]pentanes to be altered depending on the nature of the bridgehead substituent. Our observation that treatment of **3** with *p*-TsOH in HOAc at 50° for 24 hr leads to no chemical change is in accord with the expected decrease in reactivity of this bond.

Several aspects of the solution and pyrolytic reactivity of substituted bicyclo[2.1.0]pentanes as well as the extension of the synthesis to other ring systems are presently under active investigation in our laboratories.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 423-G).

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[12] W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, 21, 2779 (1965).

[13] Varian Handbook of NMR Spectra, Spectrum 132 (methylenecyclopentane).

[14] The methyl groups in an authentic sample of 2,2-dimethylcyclopentanol which we prepared[15] also appeared as a singlet at 0.91 ppm.

[15] C. F. Wilcox, Jr., and M. E. Mesirov, *J. Am. Chem. Soc.*, 84, 2757 (1962).

[16] P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965); R. T. LaLonde and L. S. Forney, *J. Am. Chem. Soc.*, 85, 3767 (1963); R. T. LaLonde, *ibid.*, 87, 4217 (1965).

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The Thiolochromium(III) Ion

Sir:

Although HS$^-$ would seem to command interest as a ligand, if for no other reason than to compare it to its congener OH$^-$, little is known about its properties when coordinated to a metal ion. A possible reason for the limited attention it has received may be that, owing to the tendency of most metal ions to form insoluble sulfides, the preparation of complexes containing the thiolo group, HS, may be made difficult. By taking advantage of the property which Cr^{2+} has to capture groups on being oxidized, we have been able to prepare and characterize CrSH^{2+}. The CrSH^{2+} ion (almost certainly thiolopentaaquochromium(III)) is formed by a variety of sulfur-containing oxidizing agents acting on Cr^{2+}. With PbS, Ag$_2$S, or S$_2$O$_3$$^{2-}$ the yield is low. Of the oxidizing agents tried, the highest yield was obtained using polysulfide as oxidant.

The polysulfide solution was prepared by dissolving 0.04 mole of Na$_2$S and 0.04 g-atom of sulfur in water and diluting to 1 l. A 25-ml portion of this solution was slowly introduced, under nitrogen, into 40 ml of an acid solution of Cr(II) containing 3 mmoles of Cr(ClO$_4$)$_2$ and 3 mmoles of HClO$_4$. The color change, from blue to green, is instantaneous. The solution was stirred vigorously by means of a magnetic stirrer. Nitrogen was bubbled through the solution during the addition of the polysulfide to expel the H$_2$S which is formed in the reaction. Finally O$_2$ was introduced to oxidize the excess of Cr(II). When this procedure was followed, no elementary sulfur was precipitated. The resulting green solution was passed through a Dowex 50X2 cation-exchange column. Sodium perchlorate was used as eluent. A 0.5 *M* solution eluted a sharp brownish green band which was followed by a colorless band of Zn^{2+} (introduced into the chromous solution during its preparation from chromic perchlorate by means of a Zn amalgam). A gray band of hexaaquochromium(III) was eluted by a 1 *M* solution, and a sharp green band, containing polynuclear chromium species of a charge greater than 3, remained on the column. Yields of CrSH^{2+} from 10 to 20% were obtained by this method.

The composition of the complex contained in the sharp brownish green band was verified by oxidation with excess bromine followed by fuming with nitric acid and precipitation as BaSO$_4$. Chromium was determined[1] spectrophotometrically as chromate at 372 mμ. The ratio of Cr to S found was 1.02. The oxidation number of the sulfur ligand was determined by oxidation with a standard iodine solution. Elementary sulfur is formed as in the iodometric determination of free H$_2$S. Two equivalents (actually 2.06) of iodine was consumed for each mole of complex.

The absorption spectrum of the new ion has three maxima in the visible–near-ultraviolet region, 574 mμ (ϵ 27), 434 (43), and 259 ($\sim$7000), and is not affected by increasing the acidity from pH 2 to 0. The ion-exchange behavior of the complex ion is typical for a +2 ion, indicating that the anion HS$^-$ and not the H$_2$S molecule is coordinated to the metal ion. The strongly acidic nature of coordinated H$_2$S (which is completely dissociated even in 1 *M* acid) is to be expected by comparison to its congener H$_2$O. The first dissociation constant of water is increased by coordination to chromium(III) from 2×10^{-16} to 10^{-4} in the hexaaquo ion.[2] Hence it is not surprising that H$_2$S with a dissociation constant of 10^{-7} [3] will behave as a strong acid when replacing a water molecule in the hexaaquo ion.

CrSH^{2+} has a remarkable stability at room temperature. When kept under nitrogen, the half-life for the aquation reaction at pH 2 and 25° is 55 hr. The rate does not change much when (H$^+$) is increased to 1 *M*. In the presence of air the ligand is slowly oxidized to

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[1] G. W. Haupt, *J. Res. Natl. Bur. Std.*, 48, 414 (1952).

[2] J. E. Earley and R. D. Cannon in "Transition Metal Chemistry," R. L. Carlin, Ed., Vol. 1, Marcel-Dekker Inc., New York, N. Y., 1965.

[3] L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 216.

elementary sulfur. When O_2 was passed through the solution of pH 2 no $CrSH^{2+}$ was left after 24 hr, and the main product was the hexaaquo ion with a small quantity of a +1 ion, possibly $CrSO_4^+$. In 1 M H^+ the oxidation is slower and an appreciable amount of unchanged complex was recovered after 24 hr. On shorter exposure to the atmosphere a highly charged cationic green species could be detected on the ion-exchange column.

The products of the reaction of $CrSH^{2+}$ with iodine and bromine (in excess) were separated by ion-exchange chromatography. It was shown that the halopentaaquochromium(III) ions, $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_5Br^{2+}$, respectively, were obtained in high yield[4] along with some hexaaquo ion. If, however, only 1 equiv of iodine was allowed to react with $CrSH^{2+}$, a more highly charged species was obtained, which could well be the μ-disulfido-bischromium(III) ion $[CrSSCr]^{4+}$. The same intermediate was obtained when 1 equiv of Fe^{3+} was used to oxidize the complex.

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[4] A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 3108 (1963).

[5] On sabbatical leave from the Hebrew University, Jerusalem, Israel.

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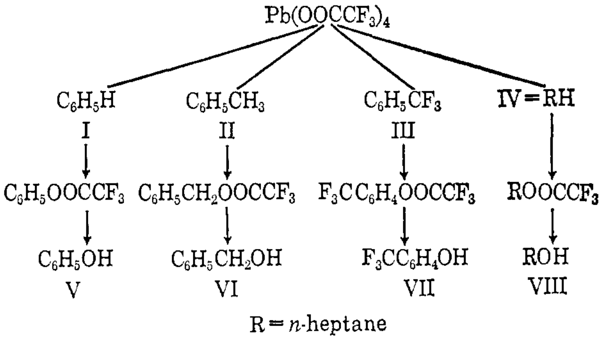
Comparative Lead(IV) Chemistry. Reactions of Lead Tetra(trifluoroacetate). I

Sir:

There is great current interest in the use of lead(IV) derivatives to functionalize organic substances, and the tetrachloride, tetraacetate, and tetrabenzoate have all proved useful in a wide variety of synthesis.[1] Reported in this communication are reactions of lead(IV) which are unprecedented and potentially of great use.

During the course of a program[2] designed to delineate certain mechanisms of lead tetraacetate (LTA) reactions it became desirable to prepare lead tetra(trifluoroacetate) (LTTFA).[3] This reagent, a white crystalline solid easily decomposed by moisture, reacts with solvents normally inert to LTA oxidation. Thus, nonactivated hydrocarbons such as benzene and heptane are converted to their trifluoroacetoxy substitution products (and subsequently to the corresponding alcohols by mild hydrolysis). Scheme I shows the reactions studied to date.

Scheme I



The reactions were carried out as follows. To purified I, II, III, or IV, stirred at room temperature, was added dried, powdered LTTFA.[4] Within 5 min the solid oxidant turned black and became gummy. Stirring was continued for 30 min, whereupon the solid partially dissolved and the liquid became discolored. The liquid phase was treated with an equal volume of aqueous NaOH with stirring, and, after neutralization, was made basic again with $NaHCO_3$. The phases were separated and the aqueous phase was extracted with ether. The organic solutions were combined, dried over $MgSO_4$, and evaporated to give V, VI, VII, or VIII in 45 ± 10% yield.[5] The isomer ratios within products VII and VIII are under current investigation.[6]

Alternatively, I, II, III, or IV was added to a mixture of CF_3COOH, $(CF_3CO)_2O$, and Pb_3O_4 and stirred at room temperature until the orange color dissipated (replaced by brown). Work-up as above yielded the same products in similar yield.[7] Modification of the procedures to exclude atmospheric oxygen, light, and peroxides did not alter the outcome of the reactions.

Proof of the trifluoroacetate ester intermediates comes from their isolation and characterization by gas chromatography[8] and infrared spectroscopy. This was accomplished by washing the treated solutions with a minimum of $NaHCO_3$ solution, to avoid complete hydrolysis of the labile esters, and vacuum distilling the desired ester from the crude product mixture.

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[1] (a) R. Criegee in "Oxidations in Organic Chemistry," Part A, K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965; (b) J. Kochi, *J. Org. Chem.*, 30, 3268 (1965); (c) R. Moriarty, *Tetrahedron Letters*, 4363, 4369 (1966); (d) H. Yale, *J. Med. Chem.*, **9**, 478 (1966); (e) C. Campbell, *Chem. Commun.*, 192 (1965); (f) M. Lj. Mihailovic, *Tetrahedron*, 23, 721 (1967).

[2] R. Partch, *J. Org. Chem.*, **30**, 2498 (1965); *Tetrahedron Letters*, 3071 (1964).

[3] Prepared by mixing 7.5 g of Pb_3O_4 in 15 g of $(CF_3CO)_2O$ and 26 g of CF_3COOH and stirring at room temperature until colorless. *Cf. Chem. Abstr.*, **56**, 1603 (1962).

[4] The total product from ref 3, above, was placed under vacuum and the excess liquid evaporated until a white solid remained. Assuming the preparation of LTTFA from Pb_3O_4 follows the same stoichiometry as the preparation of LTA, it can be assumed that the dried powder contains 1.1 × 10^{-2} mole of LTTFA.

[5] Based on 1.1 × 10^{-2} mole of LTTFA.

[6] Several publications give ample data for orientation of substitution into aliphatic and aromatic molecules. Among these, relative to lead(IV) chemistry, are: D. Harvey, *J. Chem. Soc.*, 4860 (1964); D. Hey, *ibid.*, 2747 (1954); 3963 (1955). In addition, J. Shelton, *J. Am. Chem. Soc.*, **88**, 5222 (1966), has listed data for substituent effects on free-radical attack on aromatic systems.

[7] Acetoxylation of *activated* aromatic molecules by LTA is well documented and has been shown to be acid catalyzed. Evidence to date strongly suggests an ionic electrophilic reaction path for such reactions. When CF_3COOH is present in the reacting medium, analogy with the above suggests a possible ionic path in the reaction of LTTFA with *unactivated* benzene. However, the trifluoroacetoxylation of heptane as well as the very mild conditions required for LTTFA decomposition in benzene suggest a free-radical mechanism is prevalent in both cases. See ref 6 and references cited therein.

[8] An Aerograph A-90-p2 instrument, using a 2 m × 10 mm column packed with SE-30 on Fluoropak, was used for all chromatographic determinations. Helium was the carrier gas and the column temperatures varied between 100 and 200°.