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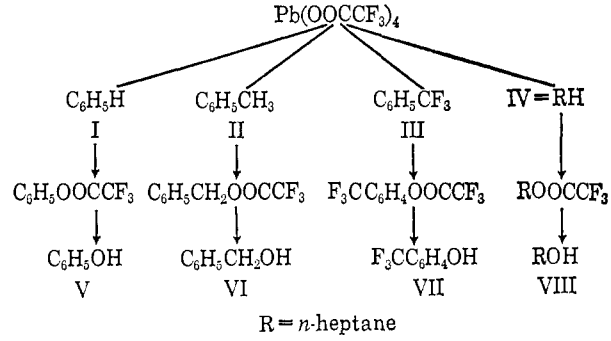
Comparative Lead(IV) Chemistry. Reactions of Lead Tetra(trifluoroacetate). I

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.

(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°.

A preliminary search was made for possible by-products in the reaction of LTTFA with benzene. Gas chromatography demonstrated that both biphenyl and benzotrifluoride were absent. This suggests that even though the reactions are conspicuously "free radical" in nature they do not follow a route involving "free" trifluoroacetoxy radicals.[9]

In an attempt to determine the relative specificity of reaction with aromatic and aliphatic molecules, LTTFA was prepared in the presence of both benzene and *n*-heptane. Chromatographic and spectroscopic product identification demonstrated a higher yield of phenyl than of heptyl ester. This was anticipated since there are considerable data on the ease of free-radical aromatic substitution relative to aliphatic substitution in competition.[10]

Comparative acyloxylations of *activated* aromatic substrates are known. Indeed, polycyclic and heterocyclic aromatics are both acetoxylated and methylated by lead tetraacetate, with the free-radical methylation taking place at higher temperatures only. *Nonactivated* aromatics, *e.g.*, benzene, and saturated hydrocarbons remain unaffected by LTA.[11] There is general agreement that aromatic acyloxylation with lead(IV) carboxylates (other than LTTFA) follows an ionic reaction sequence. The fact that LTTFA reacts readily with heptane and benzene, to yield heptyl trifluoroacetates and phenyl trifluoroacetate, respectively, suggests that this oxidant has unique power.

Solvents found stable to LTTFA, even above 50°, are CF_3COOH and hexafluorobenzene.[12] The utility of the above reactions and the reaction of LTTFA with alcohols and amines (in C_6F_6 and CF_3COOH) are under investigation.

(9) Compare: D. Davies, *J. Chem. Soc.*, 2351 (1963); D. Harvey, *ibid.*, 4860 (1964); M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5981 (1954).
(10) Table I in J. Shelton, *ibid.*, **88**, 5222 (1966).
(11) D. Harvey, *J. Chem. Soc.*, 4860 (1964); D. Hey, *ibid.*, 3963 (1955).
(12) There is no reaction of the fluorine atoms on polyfluoroaromatic compounds, under reflux conditions, with neutral $KMnO_4$, CrO_3 (HOAc, pyridine, or H_2SO_4), $Cu(OAc)_2$, MnO_2, and HNO_3 (private communication from Professor R. Filler, Illinois Institute of Technology). A recent report, however, does describe oxidation by peracid; *cf. Chem. Abstr.*, **66**, 4361 (1967).

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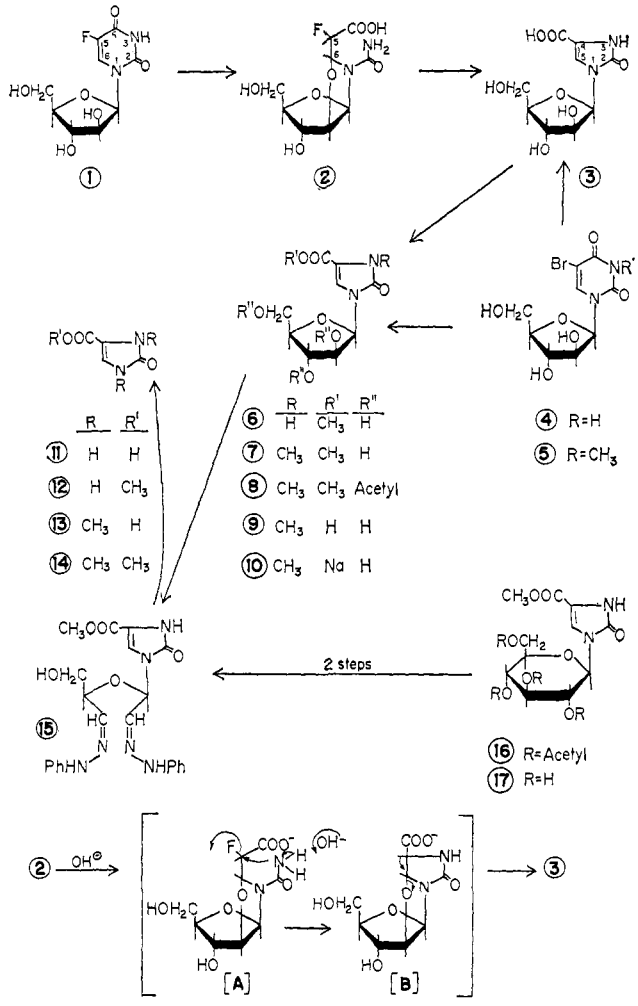
Nucleosides. XLII. A Nucleoside Rearrangement. Formation of 2-Oxo-4-imidazoline-4-carboxylic Acid Nucleosides[1]

Sir:

A recent report[2] from this laboratory demonstrated that the chemotherapeutically active[3] compounds, 1-β-D-arabinofuranosyl-5-fluorouracil (**1**, FUA) and its 5-fluorocytosine analog, are transformed in warm 0.1 *N* sodium hydroxide solution to the "6,2′-anhydro," open-chain ureide **2**. The properties of **2** have been investigated further and we now wish to report our preliminary findings on a new rearrangement of 5-halogenated arabinosyl nucleosides (see Chart I).

Chart I



The formation of **2** from FUA is accompanied by loss of ultraviolet absorption.[2] When **2** was heated in 1.0 *N* NaOH solution at 60° for 20 hr a new product was formed, as shown by the appearance of an absorption band at 267 mμ. The crystalline product **3**, mp (after drying) 230–233° dec (54% yield from water), was fluorine free and analyzed for $C_9H_{12}N_2O_7$.[4] The same product (**3**) was also obtained after 3 hr under similar reaction conditions in 61% yield *directly* from the known[5] 1-β-D-arabinofuranosyl-5-bromouracil (**4**). Evidence presented below shows that **3** is 1-(β-D-arabinofuranosyl)-2-oxo-4-imidazoline-4-carboxylic acid and that the over-all formation of **3** from **1** or **4** involved a ring contraction hitherto unreported in the nucleoside area.

(1) This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748).
(2) J. J. Fox, N. C. Miller, and R. J. Cushley, *Tetrahedron Letters*, 4927 (1966).
(3) J. J. Fox, N. Miller, and I. Wempen, *J. Med. Chem.*, **9**, 101 (1966), and leading references therein.
(4) Satisfactory elemental analyses were obtained for all crystalline compounds with melting points reported herein.
(5) J. H. Hunter, U. S. Patent 3,155,646 (1964). The authors are indebted to Dr. Masao Kunori, formerly of this laboratory, for a sample of **4**.