through synchronous rotations of the two rings around the single bonds connecting them to the carbonyl group.

Acknowledgment. The authors express appreciation to the Robert A. Welch Foundation for a research grant in support of this work.

(10) Welch Foundation Postdoctoral Fellow, 1964–1966.

A. G. Pinkus, J. I. Riggs, Jr., S. M. Broughton[10]
Department of Chemistry, Baylor University
Waco, Texas 76703
Received June 14, 1968

On the Nature of the Lead Tetrafluoride Fluorinating Agent. Isolation of Lead(IV) Diacetate Difluoride[1]

Sir:

Growing interest in lead tetrafluoride as an agent for adding fluorine to olefinic bonds[2] prompts us to report our observations on the nature of this substance. Dimroth and Bockemüller[3] introduced lead tetrafluoride to organic chemistry. Owing to the difficulty of preparing and handling lead tetrafluoride in the dry state, these investigators prepared what they assumed to be this compound *in situ* by reaction[4] of liquid hydrogen fluoride with a solution of lead tetraacetate in chloroform at 0°. Among other things, they claimed[3] that their preparation of lead tetrafluoride saturated the double bond of 1,1-diphenylethylene to give the corresponding vicinal difluoride, 1,2-difluoro-1,1-diphenylethane (**1**). Recently, their reagent was shown by us[5] to react with 1,1-diarylethylenes to afford, in fact, rearranged geminal difluorides. For example, 1,1-diphenylethylene yielded 1,1-difluoro-1,2-diphenylethane (**2**). In the course of our study of the mechanism of this rearrangement some doubt arose whether the *in situ* produced fluorinating agent was actually lead tetrafluoride. Accordingly, an examination was undertaken of the action of preformed lead tetrafluoride on 1,1-diphenylethylene.

Ph_2CFCH_2F **1** $PhCF_2CH_2Ph$ **2**

We have now found that a chloroform solution of 1,1-diphenylethylene does not react with preformed lead tetrafluoride[6] under conditions that lead to the formation of **2** with the *in situ* generated reagent.[3,5] Addition of hydrogen fluoride or of boron trifluoride etherate to the mixture of olefin and preformed lead tetrafluoride was without effect. On the other hand, and of particular interest, when glacial acetic acid (1–4 mol) was added to this mixture, fluorination proceeded smoothly, and rearranged difluoride **2** was isolated in approximately the same yields[5] (27–44%) realized with the reagent generated *in situ*. These experiments demonstrate convincingly that the fluorinating agent produced by the lead tetraacetate–hydrogen fluoride system cannot be lead tetrafluoride. Furthermore, the results suggested that a compound of the type $Pb(OAc)_nF_{4-n}$ was probably the agent responsible for the fluorination.

We report herein the isolation of such a compound, namely lead(IV) diacetate difluoride, $Pb(OAc)_2F_2$ (**3**), from the lead tetraacetate–hydrogen fluoride system of Dimroth and Bockemüller.[3] Treatment at 0° under anhydrous conditions of a stirred solution of lead tetraacetate (24.7 g, 0.056 mol) in 50 ml of purified chloroform with 4.4 ml (0.22 mol) of liquid hydrogen fluoride causes **3** to separate as a white crystalline solid. The reaction is complete within 30 min and affords 18.2 g (90%) of product[7] with a sharp but variable decomposition point in the range 190–210° (sealed capillary tube, bath preheated to 180°). *Anal.* Calcd for $C_4H_6F_2O_4Pb$: C, 13.22; H, 1.65; F, 10.47; Pb, 57.08. Found: C, 12.63; H, 1.62; F, 9.64; Pb, 56.93.

The characterization of the product as lead(IV) diacetate difluoride rests on its elemental analysis and the following spectral and chemical properties. The infrared spectrum (Nujol and halocarbon oil mulls) displays peaks at 1382 and 1525 cm^{-1} characteristic of a lead(IV) carboxylate[8] in which the carbonyl oxygen atom is chelated to lead; another strong peak at 358 cm^{-1} is consistent with the presence of the Pb–O linkage.[9] The mass spectrum[10] of **3** (the peak heights of parent molecular ions, *m/e* 362, 363, and 364, are proportional to the natural abundance of lead isotopes) indicates that lead(IV) diacetate difluoride is monomeric in the gas phase. However, the fact that **3**, unlike lead tetraacetate, is insoluble in the common organic solvents suggests that the compound may not exist as the monomer in the solid state.[11]

Chemically, lead(IV) diacetate difluoride is a very reactive compound. It turns brown instantly on exposure to air and, in this respect, is more reactive than lead tetraacetate. Water converts **3** immediately to lead dioxide, hydrofluoric acid, and acetic acid. Glacial acetic acid transforms lead(IV) diacetate difluoride into lead tetraacetate in nearly quantitative yield. Particularly noteworthy is the observation that a suspension of **3** in chloroform at 0° converts 1,1-diphenylethylene to rearranged difluoride **2** in yields approximating those obtained with the fluorinating agent generated *in situ*.

Our investigation of the chemistry of lead(IV) diacetate difluoride is continuing with particular emphasis on a comparison of its behavior with that of lead tetraacetate toward various classes of compounds.

---

(1) This research has been supported by National Science Foundation Grant GP-4971.

(2) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 563.

(3) O. Dimroth and W. Bockemüller, *Ber.*, **64**, 516 (1931).

(4) The procedure of Dimroth and Bockemüller is essentially that described by O. Ruff, *Z. Anorg. Allgem. Chem.*, 98, 27 (1916).

(5) J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *J. Am. Chem. Soc.*, 85, 1609 (1963).

(6) Prepared by reaction of elemental fluorine with lead difluoride and kindly supplied by Dr. James B. Beal, Jr., of the Ozark-Mahoning Co., Tulsa, Okla. This compound, for which a satisfactory fluorine analysis was obtained, was a white crystalline substance. As far as could be determined this reagent appeared to possess the properties ascribed to lead tetrafluoride by H. von Wartenberg, *Z. Anorg. Allgem. Chem.*, **244**, 337 (1940).

(7) The work-up procedure is critical. The product is collected by suction on a polyethylene funnel and washed but once on the funnel with chloroform; all operations are conducted in an atmosphere of purified nitrogen. Compound 3 appears to be stable indefinitely in sealed polyethylene containers stored in a desiccator holding calcium chloride.

(8) No carbonyl bands above 1525 cm^{-1} are observed. See R. Partch and J. Monthony, *Tetrahedron Letters*, 4427 (1967); compare K. Heusler, H. Labhart, and H. Loeliger, *ibid.*, 2847 (1965).

(9) Y. Yukawa and M. Sakai, *Nippon Kagaku Zasshi*, 87, 84 (1966); *Chem. Abstr.*, **65**, 15263*h* (1966).

(10) Obtained through the kindness of Dr. Edward White.

(11) R. Criegee in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 280.

Joseph Bornstein, Leonidas Skarlos
Department of Chemistry, Boston College
Chestnut Hill, Massachusetts 02167
Received June 17, 1968