

in fact conserved in the early stages of the reaction coordinate but becomes lost near the energy maximum as a consequence of the combined effects of very bad warping of orbitals and the strain imposed by the developing *trans* double bond. This merely restates the obvious fact that symmetry should be conserved only when it provides the lowest energy reaction path.¹ The observed *cis*-bicyclo[4.3.0]nonane system is the one expected from the symmetry-allowed ground-state bridging of the all-*cis*-cyclononatetraene intermediate. The symmetry conservation observed in the Ib \rightarrow III + VI conversion indicates that the oxygen atom plays an important role, probably involving mixing of its orbitals with those of the π system. MO calculations of II and II* are not yet complete, but it would appear that such orbital mixing will not change the orbital symmetry represented for the carbon atoms of II*.¹⁴

The photochemistry of Ia is most easily rationalized as proceeding through the excited all-*cis*-cyclononatetraene which then undergoes internal conversion before bridging in the ground state.

Acknowledgment. We are indebted to Badische Anilin- & Soda-Fabrik AG for a generous gift of cyclooctatetraene.

(14) Such is the case with furan and thiophene: D. S. Sappenfield and M. Kreevoy, *Tetrahedron Suppl.*, 19, 157 (1963).

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Resolution of an Alkyl Aryl Ketone with Asymmetry due to Restricted Rotation about the Carbonyl Group

Sir:

In connection with a program of studies on hindered alkyl mesityl ketones¹ we wish to report the first resolution of an alkyl aryl ketone, *t*-butyl 3-carboxy-2,4,6-trimethylphenyl ketone (**1**). **1** was synthesized by the sequence of reactions shown.²

Acid **1** was resolved with cinchonine (acetone solvent). A solution of the cinchonine salt (**5**) of the acid (60.7% first crop based on one diastereomer) in pyridine at 0° was poured into a concentrated hydrochloric acid-ice slush at -15°. The precipitated acid **1** was collected by filtration, washed with water, and dried; 46% yield (based on cinchonine salt). **1** (first crop) showed an initial⁴ specific rotation of $[\alpha]^{20.5D} +61^\circ$ (chloroform) which decreased to zero on standing. The half-life was calculated to be 6.2 min under these conditions. The cinchonine salt (**5**) showed mutarotation⁵

(1) A. G. Pinkus, W. C. Servoss, and K. K. Lum, *J. Org. Chem.*, **32**, 2649 (1967).

(2) Satisfactory elemental analyses were obtained for the new compounds **1** and **3**; the nmr and ir spectra are in accord with the structures shown. Compound **4** was previously prepared³ by a Friedel-Crafts reaction of mesitylene and the acid chloride. Further proof of structure included the decarboxylation of **1** to the known³ *t*-butyl mesityl ketone (**4**).

(3) D. V. Nightingale, R. L. Sublett, R. A. Carpenter, and H. D. Radford, *J. Org. Chem.*, **16**, 655 (1951).

(4) Obtained by extrapolation to zero time (of solution).

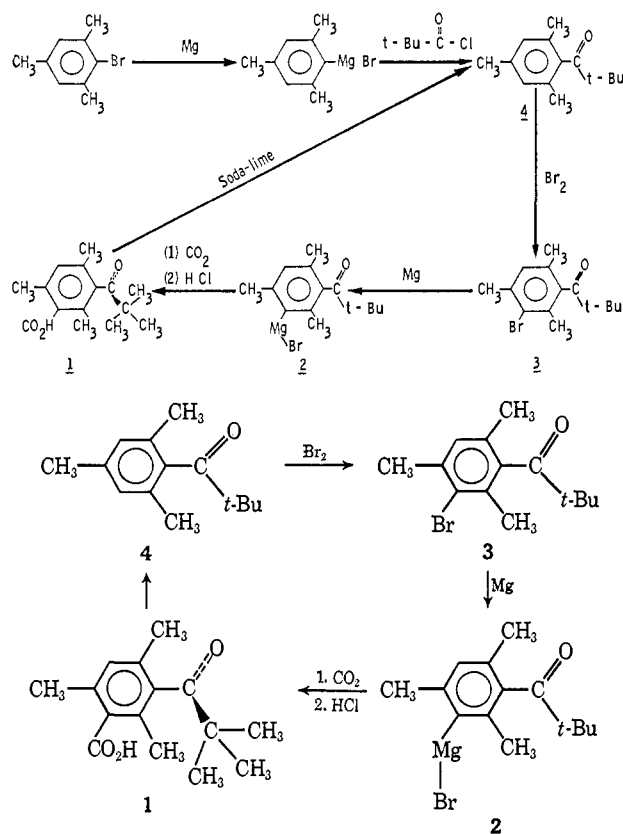
(5) The second crop of cinchonine salt (**5**) was used. A more detailed study will be reported in a more complete account of this work.

on being dissolved in chloroform, the specific rotation increasing from an initial⁴ value of +114° to a final constant value of +136° at 20.5°.

An interesting problem arises in considering possible explanations of the racemization. Scale models indicate that interference between the *t*-butyl group and the *o*-methyls prevents transformation into the enantiomer and either the aryl-carbonyl bond or the alkyl-carbonyl bond (of the model) must be broken in order to effect the conversion. This possibility does not appear likely for a racemization mechanism because of the high energy requirements involved in bond breaking. A more likely possibility would involve a low-energy bending of the *t*-butyl group away from the aryl group, thus increasing the C_{aryl}-CO-C_{*t*-Bu} angle. Studies to investigate this are under way, as well as the investigation of restricted rotation about related types of groupings.

Compound **2** is of interest in that this is the first molecule to our knowledge in which a keto carbonyl and a Grignard function exist simultaneously.

The first published attempts to resolve asymmetrically



substituted benzophenones were by Adams and his coworkers.⁶ More recently,⁷ Narayanan, Selvarajan, and Swaminathan⁸ claimed the first resolution⁹ of a compound of this type. They suggested that interconversion of the antipodal benzophenones occurred

(6) J. F. Hyde and R. Adams, *J. Am. Chem. Soc.*, **50**, 2499 (1928); M. E. Maclean and R. Adams, *ibid.*, **55**, 4683 (1933).

(7) The work reported in the present paper was complete when their paper⁸ was submitted: J. I. Riggs, Jr., Ph.D. dissertation, Baylor University, Aug 1966, and further unpublished work by A. G. Pinkus and S. M. Broughton.

(8) K. V. Narayanan, R. Selvarajan, and S. Swaminathan, *J. Chem. Soc., C*, 540 (1968).

(9) They observed $[\alpha]_D -2.2^\circ$ for a sample which was obtained after five quick crystallizations of the crude acid having $[\alpha]_D -1.79^\circ$. The racemization behavior of the compound was not reported.

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

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

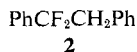
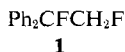
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On the Nature of the Lead Tetrafluoride Fluorinating Agent. Isolation of Lead(IV) Diacetate Difluoride¹

Sir:

Growing interest in lead tetrafluoride as an agent for adding fluorine to olefinic bonds² prompts us to report our observations on the nature of this substance. Dimroth and Bockemüller³ 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 reaction⁴ of liquid hydrogen fluoride with a solution of lead tetraacetate in chloroform at 0°. Among other things, they claimed³ 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 us⁵ 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.

We have now found that a chloroform solution of 1,1-diphenylethylene does not react with preformed lead tetrafluoride⁶ 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 yields⁵ (27–44%) realized with the reagent generated *in situ*. These experiments demon-

(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).

strate 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 $\text{Pb}(\text{OAc})_n\text{F}_{4-n}$ was probably the agent responsible for the fluorination.

We report herein the isolation of such a compound, namely lead(IV) diacetate difluoride, $\text{Pb}(\text{OAc})_2\text{F}_2$ (**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 product⁷ with a sharp but variable decomposition point in the range 190–210° (sealed capillary tube, bath preheated to 180°). *Anal.* Calcd for $\text{C}_4\text{H}_6\text{F}_2\text{O}_4\text{Pb}$: 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) carboxylate⁸ 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 spectrum¹⁰ 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.

(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. Monthey, *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**, 15263h (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.

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