Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.55; H, 8.60.

Registry No.—**6**, 18634-49-6; **7**, 18634-50-9; **8**, 18634-51-0; **9**, 18634-52-1; **11**, 18634-53-2; **13**, 18634-54-3; **14**, 18634-55-4; **15**, 18634-56-5; **16**, 18634-57-6.

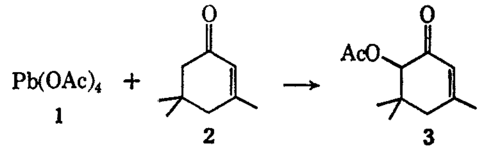
Reaction of Lead Tetraacetate with Isophorone[1]

Jerry W. Ellis

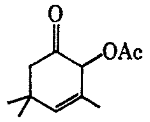
Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920

Received September 1, 1968

The reaction of lead tetraacetate (**1**) with isophorone (**2**) was studied and an improved procedure for the preparation of 6-acetoxyisophorone (**3**) is reported. As indicated,[2] when acetic acid was used as a solvent, acetate **3** could be isolated in only 38% yield. Using benzene as a solvent in the presence of CaH_2 or BF_3,[3] only slightly better yields were observed. Benzene and $CaCO_3$ [4] gave yields of 74% but the best yields were obtained using benzene alone where the product was isolated by crystallization in 78% yield. The yields could be increased by distillation of the mother liquors.[2] As with saturated ketones,[5] the reaction was faster in acetic acid, or in the presence of acids[3] or bases.



1 **2** **3**



4

It is of interest that acetate **3** was the only product observed. Gas chromatograms of the crude reaction mixtures and mother liquors remaining after crystallization of the product showed only starting material, acetate **3**, and with the crude reaction mixtures, usually 1% or less other materials. These minor components could be other products, or oxidation products of the trace impurities (<1%) in the starting material. In the case of the uncatalyzed reaction in benzene, approximately 99% of the organic starting material was accounted for either as acetate **3** or unreacted starting material. Other products might have been expected since rearrangements are known to occur,[6,7] and, since isophorone is known to enolize approximately equally in both directions[8,9] and the enol form is apparently the species that is attacked,[10] products such as **4** might also have been expected. However, **4** could have rearranged to **3** under the conditions of the reaction since a similar rearrangement is known.[11] The structural assignment of **3** was confirmed by its ir and nmr spectra.

Experimental Section

Melting points were taken on a Thomas–Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrometer; nmr spectra were recorded on a Varian HA-60 spectrometer using $DCCl_3$ as a solvent and tetramethylsilane as an internal standard. Gas chromatograms were obtained with a Perkin-Elmer 154L instrument using a thermal conductivity detector and a column of 0.25 in. × 5 ft 5% neophentylglycol sebacate on nonacid washed Chromosorb W with the He flow rate at 60 ml/min. Peak areas were determined by the height times width at half-height method and the peak areas due to **3** were multiplied by 1.2 to correct for detector response differences. Microanalyses were performed by M-H-W Laboratories of Garden City, Mich. The lead tetraacetate was dried over KOH under reduced pressure. Tests for completion were made with KI–starch indicator paper.

Reaction of Isophorone with $Pb(OAc)_4$ in Benzene.—A mixture of 150 ml of benzene, 10.0 g (0.0725 mol) of **2**, and 35.0 g (0.0787 mol) of $Pb(OAc)_4$ was refluxed with stirring for 90 hr. The mixture was cooled, washed once with water, saturated NaCl, saturated $NaHCO_3$, and saturated NaCl; the organic layer was dried ($MgSO_4$) and filtered; and solvent was removed at 45° under reduced pressure giving 14.0 g of light yellow solid. Vpc analysis at 200° of the crude product dissolved in ether showed 3% starting material, 1% minor component, and 96% acetate **3**. The ether solution was concentrated by evaporation to give 8.99 g of **3**, mp 76–78°, (lit.[2] mp 77–77.5°). A second crop of 2.08 g brought the total to 11.07 g (78%). A vpc analysis at 198° showed the 2.69 g of material in the mother liquor to be 69% **3**, 28% **2**, and approximately 1% each of three minor components. Vpc analysis at 240° of the crude reaction mixture and the mother liquors remaining after crystallization of **3** showed no additional products to be present.

The product **3** exhibited the following properties: bp 136–137° (9 mm) [lit.[2] 141–145° (12 mm)]; ir (KBr) 1740 (ester C═O), 1675 (C═O), 1635 (C═C), 1238 cm^{-1} (C—O—C); nmr δ 5.92 (m, 1, with line spacings of 1.1 Hz, olefinic proton), 5.22 (s, 1, CHOAc), 2.20 (s, 3), 1.97 (s, 3), 1.1 (s, 3), 0.98 (s, 3).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.21; H, 8.53.

Registry No.—**1**, 546-67-8; **2**, 78-59-1; **3**, 19019-49-9.

---

[1] Support from the Council of Faculty Research, Eastern Illinois University is gratefully acknowledged.

(2) A. W. Fort, *J. Org. Chem.*, **26**, 332 (1961).

(3) H. B. Henbest, D. N. Jones and G. P. Slater, *J. Chem. Soc.*, 4472 (1961).

(4) M. P. Hartshorn and A. F. A. Wallis, *ibid.*, 5254 (1964).

(5) G. W. K. Cavill and D. H. Solomon, *ibid.*, 4426 (1955).

(6) L. H. Zalkow and J. W. Ellis, *J. Org. Chem.*, **29**, 2626 (1964).

(7) J. A. Marshall and L. Bundy, *Chem. Commun.*, 500 (1966).

(8) H. Nozaki, T. Yamaguti, S. Ueda, and K. Kondo, *Tetrahedron*, **24**, 1445 (1968).

(9) C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

(10) R. Criegee in "Oxidations in Organic Chemistry," part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 277.

(11) J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, **89**, 3457 (1967).

Ring Expansion of Tetramethyl-1,3-cyclobutanedione with Difluoramine[1]

C. M. Orlando, Jr.,[2] and M. H. Gianni

Government Research Laboratory, Esso Research and Engineering Laboratory, Linden, New Jersey

Received August 5, 1968

Recent advances in the chemistry of difluoramine have demonstrated its utility in the synthesis of a

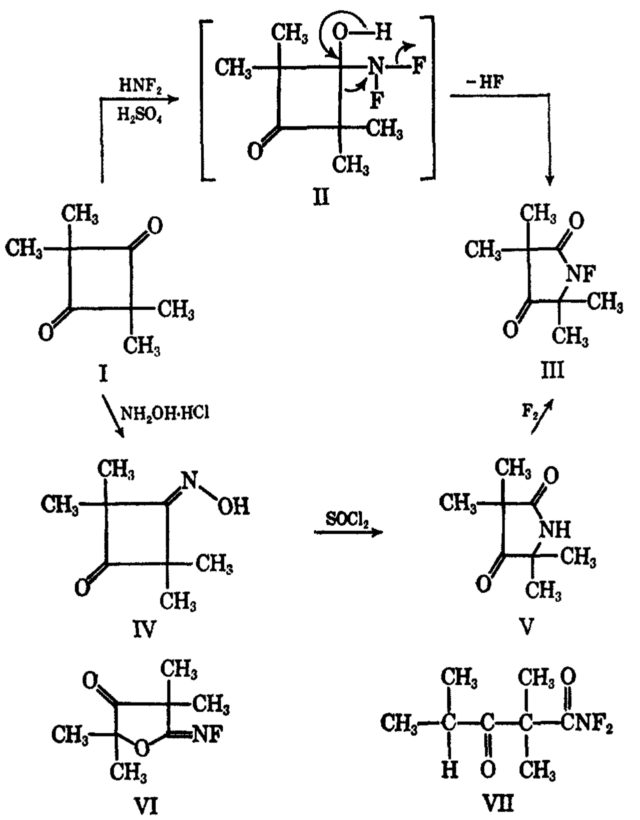
---

(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Ordinance under Contract No. DA 30-069-ORD-2487.

(2) To whom inquiries should be addressed at General Electric Research and Development Center, Schenectady, N. Y.

number of organic nitrogen–fluorine compounds.[3] The formation of α-difluoraminocarbinols in the reactions of difluoramine with aliphatic aldehydes and ketones has recently been disclosed.[3e] In this report, we describe the reaction of difluoramine and tetramethyl-1,3-cyclobutanedione to give the N-fluoropyrrolidinedione (III) (Scheme I).

SCHEME I



The sulfuric acid (98%) catalyzed reaction of I with excess difluoramine resulted in a 65% yield of a crystalline solid. The infrared spectrum of this compound displayed two distinct carbonyl bands at 5.65 and 5.80 μ. The former absorption was indicative of the presence of a five-membered-ring ketone. However, one could not distinguish between the presence of an N-fluoramide or a cyclic N-fluorimine structure based upon the latter absorption.[4] The ^{19}F nmr spectrum of the product displayed one signal at ϕ +97 which conclusively established the presence of the N-fluoramide group.[6] Based upon these data, the product was assigned the N-fluoropyrrolidinedione structure III and not the alternative isomer VI. Further confirmation of the assignment was obtained by the independent synthesis of III. The Beckmann rearrangement of the oxime IV gave the pyrrolidinedione V and the latter upon fluorination afforded a compound identical in all respects with the product obtained from the difluoramine reaction.

The mechanism of this ring expansion reaction can be considered analogous to the Beckmann rearrangement. A reasonable mechanistic path for this transformation would involve the acid-catalyzed addition of difluoramine to I giving the α-difluoraminocarbinol intermediate II. Subsequent loss of hydrogen fluoride from this intermediate and bond migration would result in the formation of the observed product. A less likely path for the formation of III would involve cyclization of a ring-opened N,N-difluoramide intermediate VII.

Experimental Section

Caution: Difluoramine is explosive and should be handled with care; see ref 10 for precautions.

All melting points were determined in sealed capillary tubes with a partial-immersion thermometer. Infrared spectra were determined on a Perkin-Elmer Model 137B Infracord. The nmr spectra were taken in tetramethylsilane–Freon 11 solution (used as references) using both an A-60 and HR-60 spectrometers. Tetramethyl-1,3-cyclobutanedione was obtained from Eastman Chemical Products Inc., Kingsport, Tenn.

Reaction of Tetramethyl-1,3-cyclobutanedione with Difluoramine.—Sulfuric acid (3.0 ml, 98%) in a 15-ml glass pressure reactor[11] was degassed several times using a liquid-nitrogen cooling bath. Tetramethyl-1,3-cyclobutanedione (1.2 g, 0.0085 mol) was added to the reactor containing the frozen sulfuric acid and this mixture was charged with difluoramine[12] (0.731 g, 0.013 mol). The temperature rose gradually over a 14-hr period from −128° to 0°. The bath was removed and the mixture was stirred for 3 hr at room temperature. The unreacted difluoramine was removed from the reactor and the reaction mixture was diluted with 8 ml of water. This solution was extracted with 20 ml of ether and the extract was washed with a solution of 5% aqueous sodium carbonate and then with water. The ether extract was dried over magnesium sulfate and evaporated. A white crystalline solid was obtained, 0.963 g (65%), mp 56.5–58°.

Anal. Calcd for $C_8H_{12}FNO_2$: C, 55.50; N, 8.09; F, 10.98; mol wt, 173. Found: C, 55.62; N, 7.92; F, 12.1; mol wt, 186.

The proton nmr spectrum of this compound showed two peaks of equal intensity at τ 8.55 and 8.70 (two different types of CCH_3). The fluorine nmr spectrum showed one sharp signal at ϕ +97 (-CONF). The infrared spectrum in chloroform solution showed absorption at 5.65 (five-membered-ring ketone), 5.80 (-CONF carbonyl), and 10.9 μ (NF).

2,2,4,4-Tetramethyl-1,3-cyclobutanedione monoxime was prepared according to the method of Miller.[13] A white crystalline solid was obtained in 56.5% yield, mp 140–143° (lit.[13] mp 144–144.5°).

3,3,5,5-Tetramethyl-2,4-pyrrolidinedione was prepared according to the method of Miller.[13] A white crystalline solid was obtained in 51% yield, mp 225–227° (recrystallized from methanol) (lit.[13] mp 220–222°).

N-Fluoro-3,3,5,5-tetramethyl-2,4-pyrrolidinedione.—3,3,5,5-Tetramethyl-2,4-pyrrolidinedione (0.98 g, 0.0063 mol) was suspended in 15 ml of acetonitrile and a stream of helium containing 10% fluorine by volume was bubbled through the solu-

---

[3] (a) J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967); (b) C. L. Bumgardner and J. P. Freeman, *Tetrahedron Lett.*, **45**, 5547 (1966); (c) K. Baum, *J. Org. Chem.*, **32**, 3648 (1967); (d) W. H. Graham and J. P. Freeman, *J. Amer. Chem. Soc.*, **89**, 716 (1967); (e) J. P. Freeman, W. H. Graham, and C. O. Parker, *ibid.*, **90**, 121 (1968); (f) D. D. Rosenfeld, J. R. Lovett, and E. Schmall, *J. Org. Chem.*, **33**, 2521 (1968).

[4] Although a δ-N-fluorolactam has been reported to have an infrared carbonyl frequency at 5.75 μ,[5] very little has been described concerning the C=NF frequency in cyclic systems.

[5] T. E. Stevens and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 182 (1967).

[6] The ^{19}F nmr signal for an N-fluoramide has been reported to be at ϕ +88.9.[7] The ^{19}F resonance signal of most N-fluorimines are reported to have negative ϕ values.[8] While some N-fluorimines display positive ϕ values, the signal region is generally below ϕ +48.[9] These reported ϕ values are all relative to Freon 11 (CCl_3F) as reference.

[7] R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **32**, 416 (1967).

[8] (a) R. C. Petry and J. P. Freeman, *ibid.*, **32**, 4034 (1967); (b) G. N. Sausen and A. L. Logothetis, *ibid.*, **32**, 2261 (1967); (c) C. M. Sharts, *ibid.* **33**, 1008 (1968).

[9] (a) A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966); (b) T. O. Stevens, *ibid.*, **33**, 2660 (1968).

[10] J. P. Freeman, A. Kennedy, and C. B. Colburn, *J. Amer. Chem. Soc.*, **82**, 5304 (1960).

[11] This reactor was fitted with a Fisher-Porter Teflon valve and was purchased from Scientific Glass Apparatus Co., Bloomfield, N. J.

[12] A Freon 21–liquid nitrogen cooling bath (−128°) was used in all operations involving transfer of gaseous difluoramine.

[13] L. L. Miller, Ph.D. Thesis, Cornell University, 1937.

tion for 8.5 min. The rate of gas flow was 11.55 l./hr. The suspended solid gradually dissolved in the solvent as the fluorination proceeded and after 5 min the material was completely dissolved. After the fluorination was completed, the system was flushed with helium for 20 min to remove the residual fluorine. A wet solid residue remained after the solvent was evaporated. This material was vacuum sublimed at room temperature and 0.005 mm. A flaky white solid was obtained, 0.142 g (26.4%),[14] mp 56–57.5° (mixture melting point with product from difluoramine reaction was 57.5–58°).

Anal. Calcd for $C_8H_{12}FNO_2$: C, 55.50; N, 8.09; F, 10.98; mol wt, 173. Found: C, 55.22; N, 7.94; F, 11.4; mol wt, 198.

The infrared spectrum and the proton and fluorine nmr spectra were identical with the respective spectra of the product obtained in the difluoramine reaction.

Registry No.—I, 933-52-8; difluoramine, 10405-27-3; III, 18993-54-9.

Acknowledgment.—The authors wish to thank Dr. A. A. Zimmerman for his helpful discussions regarding this work, Mr. P. Q. Ng for his laboratory assistance, and J. Lowsky, W. Petersen, and R. Hoagland for microanalyses.

---

[14] Optimum conditions for the fluorination were not determined and the percentage yield was based upon the recovery of 0.5 g of starting material. Over fluorination in this reaction resulted only in the formation of base-soluble products.

The Reaction of Acyl Halides with Organotin Hydrides. The Effect of Halide and Hydride Structure on Product Distribution[1]

Edward J. Walsh, Jr., Richard L. Stoneberg, Monica Yorke,

Department of Chemistry, Allegheny College, Meadville, Pennsylvania 16335

and Henry G. Kuivila

Department of Chemistry, State University of New York, at Albany, Albany, New York

Received October 3, 1968

In our previous studies of the scope and mechanism of this reaction we have concentrated on the reduction of acid chlorides with tri-*n*-butyltin hydride.[2,3] When the reductions were carried out neat most of these chlorides gave mainly ester with varying amounts of aldehyde. The aldehyde, however, was often the main product when the reaction was carried out in solution. We indicated that the two acid bromides observed displayed behavior quite different from that of the acid chlorides[2] since the yield of aldehyde in the neat reactions was considerably higher suggesting that a different mechanism may be operative when bromides are used.

$$3RCOX + 3R'_3SnH \rightarrow RCHO + RCO_2CH_2R + 3R'_3SnX$$

Kupchik and Kiesel[4,5] have demonstrated that reductions of certain acid chlorides, neat or in solution, gave predominantly ester when they employed triphenyltin hydride indicating that the structure of the hydride may also be of importance in product distribution.

We have examined the reactions of other acid chlorides, bromides and two fluorides with trimethyl and tri-*n*-butyltin hydride and have found that the product distribution is sensitive to the type of halide and hydride employed. In Table I we report the reduction of acid chlorides with trimethyltin hydride; the reduction of acid bromides and an aromatic and aliphatic acid fluoride with both hydrides. The acid bromides are reduced by tri-*n*-butylin hydride to give predominantly aldehyde whereas trimethyltin hydride reductions gave mainly ester products. The reduction of acid fluorides affords only ester in both cases studied.

The acid fluorides were comparatively unreactive with either trimethyl or tri-*n*-butyltin hydride. When they hydride and benzoyl fluoride were mixed, neat at ambient temperature, no discernible reaction occurred even after 5 days. In a 0.6 *M* solution of refluxing benzene the reaction can be completed in 5 days while under the same conditions with an added 2 mol % of AIBN the reaction is finished within 31 hr. Both reactions gave only benzylbenzoate and tri-*n*-butyltin fluoride as the products.

The reasons for the differences in product distribution with respect to type of organotin hydride and acid halide used are obscure at this point but we feel it probably is due to changes in the ester-forming process which can be complicated.[3]

Experimental Section

All infrared spectra were determined on a Perkin-Elmer Model 337 double-beam spectrophotometer. Gas chromatographic analysis was carried out on a dual column F & M Scientific Co., Model 720 gas chromatograph.

Materials.—The acid bromides and chlorides were obtained commercially in high purity. The acid fluorides[6] and tin hydrides[2] were prepared by previously described methods.

Reduction of Acid Bromides.—Owing to the vigor of this reaction, the hydride was added to an equimolar amount of bromide in an ice bath. As the reaction subsided the system was flushed with nitrogen and stoppered. These reactions were complete within 20 hr as evidenced by the disappearance of the Sn–H band at 1810 cm^{-1} in the infrared region. The reaction mixtures were then examined by gas chromatography and the products were identified by comparison of their retention times with those of authentic samples.

Determination of Aldehyde with 2,4-Dinitrophenylhydrazine.—The procedure used was essentially that developed by Iddles.[7] An aliquot was taken from the reaction mixture, dissolved in 25 ml of ethanol and added to a 300-ml saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* HCl. The precipitate was then collected on a tared filtering funnel, dried at

---

[1] This research was supported, in part, by an Undergraduate Research Participation Grant from the National Science Foundation.

[2] H. G. Kuivila and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **88**, 571 (1966).

[3] E. J. Walsh, Jr., and H. G. Kuivila, *ibid.*, **88**, 576 (1966).

[4] E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 3690 (1964).

[5] E. J. Kupchik and R. J. Kiesel, *ibid.*, **31**, 456 (1966).

[6] G. Olah, S. Kuhn, and S. Beke, *Ber.*, **89**, 862 (1956); C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

[7] as described in "Organic Reagents for Organic Analysis," 4th ed, Hopkins and Williams, Ltd., London, 1944, pp 52–55.