

[CONTRIBUTION FROM THE ETHYL CORPORATION]

Sodium α -Sodio acetate, its Preparation and Proof of Structure

BY D. O. DEPREE AND R. D. CLOSSON

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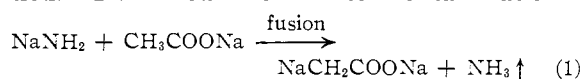
A new organosodium compound, sodium α -sodio acetate, may be prepared by the reaction of sodium amide with sodium acetate in an open system at 200°. Reactions with *n*-octyl bromide to give sodium *n*-decanoate, with benzyl chloride to yield sodium phenylpropionate, with carbon dioxide to yield disodium malonate, and with deuterium oxide to yield sodium α -deuteroacetate provide proof of structure. Quantitative analysis for sodium α -sodioacetate is carried out by hydrolysis with deuterium oxide and subsequent determination of the amount of sodium α -deuteroacetate formed.

Morton and his associates¹ have demonstrated that substituted dibasic acids $RCH(COOH)_2$ may be prepared by carboxylation of the product resulting from the reaction of the sodium salt of a monobasic acid with a metallating agent of the type $R'Na$.

They found that aliphatic acids gave lower yields than phenylacetic acid, and the reaction appeared to become more difficult as R was made smaller. These reactions can be explained on the basis of a postulated α -sodio intermediate, but Morton and his associates did not isolate the intermediate.

This work suggested that one might prepare the corresponding intermediate, sodium α -sodioacetate, from sodium acetate. This, the structurally simplest intermediate, has never been reported. This compound was of particular interest because its unique α -sodium makes it a promising starting point for synthesis of many compounds from low-cost sodium acetate.

A new approach, synthesis through the metallation of sodium acetate by sodamide in an open, nitrogen-flushed system was selected for exploration. This would eliminate contamination of

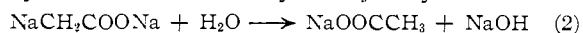


the product by unreacted organosodium metallating agent. It was anticipated that the sodamide, which melts at 210°, could act both as a metallating agent and as a solvent for the sodium acetate providing the sodium α -sodioacetate was stable at this temperature. This was found to be the case.

When equimolar quantities of sodium amide and anhydrous sodium acetate are heated to approximately 200°, the evolution of ammonia is immediate and rapid.

The product of the reaction is a light gray solid, insoluble in hydrocarbons and ethers. It is unreactive toward dry air at room temperature and is thermally stable at temperatures up to 280°, where it decomposes with the evolution of gas and formation of a carbon-rich residue. The product does not melt at temperatures below its decomposition point.

When the reaction product is added to water, heat is evolved and sodium acetate and sodium hydroxide are formed by the hydrolysis



If deuterium oxide is used, sodium α -deuteroacetate is obtained, and if this deuteroanalysis is con-

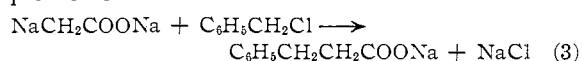
ducted at 0° in an ether suspension to limit deuterium exchange, the ratio of sodium α -sodioacetate to sodium acetate in the product may be determined. The small amount of deuterium exchange (less than 10%) occurring at 0° on deuteroanalysis of sodium α -sodio acetate must be due to either the heat liberated by the reaction or the high alkalinity of the system. If deuteroanalysis of sodium α -sodioacetate is conducted without cooling in the absence of a solvent, the amount of sodium di- and trideuteroacetate produced is greater than the amount of the monodeutero product.

Analysis of a series of reaction products gave sodium α -sodioacetate compositions ranging from 63 to 80% purity.

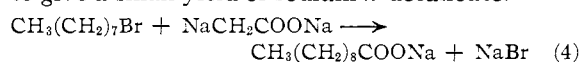
It was found that the purity of the product is dependent both on the intimacy to which the reagents are preblended and to the length of time that the reaction product is allowed to remain in contact with ammonia at reaction temperature. Better preblending of the reagents gives higher yields of sodium α -sodioacetate. Prolonged contact of the product with ammonia tends to promote side reactions and lower the yield. Attempts to find a solvent for the α -sodio compound to permit purification have been unsuccessful. For this reason the reaction product was employed without further purification in all investigations of its reactions.

Chemical Properties.—A study of the reactions of the α -sodio compound with various reagents provided further proof of its identity and demonstrated the utility of the new compound.

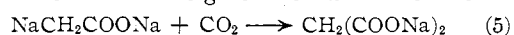
Reaction of sodium α -sodioacetate with labile organic halides provides a means of synthesizing longer chain acids. For example, reaction of the compound with benzyl chloride gives phenyl propionic acid.



On the other hand, reaction of sodium α -sodioacetate with certain non-labile aliphatic chlorides results in dehydrohalogenation. This is not surprising in light of the anticipated high basicity of the sodio compound. An exception to this is octyl bromide, which reacts with sodium α -sodioacetate to give a small yield of sodium *n*-decanoate.



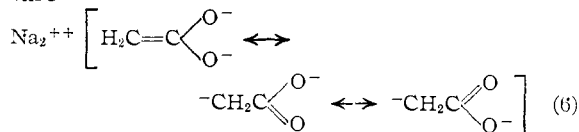
The new sodium compound may be carboxylated with carbon dioxide to give disodium malonate.



All of the reactions described require relatively

(1) A. A. Morton, F. Fallwell, Jr., and L. Palmer, *THIS JOURNAL*, **60**, 1426 (1938).

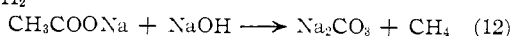
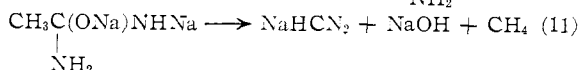
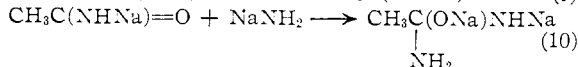
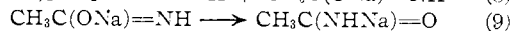
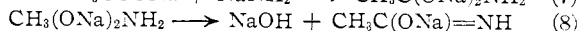
high temperatures for initiation, and result in substitution on the α -carbon atom. The remarkable thermal stability of the compound (decomposition at 280°) and the inertness of the compound toward oxygen and other reagents at room temperature suggests internal stabilization, and we suggest that the doubly charged anion of sodium α -sodioacetate is a resonance hybrid of the structure



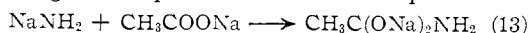
Sodium acetate appears to be the only member of the family that gives an α -sodio derivative possessing this high thermal stability. Sodium α -sodiopropionate as well as the α -sodio derivatives of the sodium salts of *n*-butyric and isobutyric acids were prepared under identical conditions. Ammonia was liberated immediately and decomposition also occurred in very short order. These other sodio compounds are thus thermally unstable at 200° ; this instability is typical of those acids having a hydrogen on a saturated β -carbon atom.

Previous investigators of the reaction of sodium amide with anhydrous sodium acetate used other reaction conditions and obtained different results.

Freidlin and Lebedeva showed that when sodium amide and anhydrous sodium acetate are intimately mixed and then heated in a sealed tube to temperatures between 200° and 300° , sodium cyanamide is produced.² The reaction sequence which they postulated for this process is



It is likely that the first step is the same in both instances and that the open system used in the current work permits escape of ammonia so that the following two steps would describe the process



The reaction to form sodium α -sodioacetate is much more rapid than that producing sodium cyanamide.

Experimental

Materials.—Sodium amide was obtained from Farchan Research Laboratories. Anhydrous sodium acetate was obtained from J. T. Baker Chemical Co. and Fisher Scientific; water content was 1.75% or less.

Deuterium oxide (99.5+ % O) was obtained from Stewart Oxygen Co.

The nitrogen was oil-pumped prepurified nitrogen having a maximum oxygen content of 0.0012% and a maximum water vapor content of 0.0012%.

Apparatus.—The preparation of sodium α -sodioacetate may be conducted either in glass or in steel. Arrangements

for stirring and for maintaining an atmosphere of nitrogen must be provided.

Preparation of Sodium α -Sodioacetate.—Equimolar quantities of sodium amide and anhydrous sodium acetate were preblended under nitrogen, and added slowly under nitrogen to the reaction vessel, which was held at approximately 200° . Ammonia was liberated immediately and rapidly. When addition was completed, heating and stirring were continued for a short time and then the reaction vessel was cooled to room temperature. Yields of sodium α -sodioacetate for two preparations were 63.7 and 80.1%.

Reaction with Benzyl Chloride.—Sodium α -sodioacetate (36.8 g., 82%, 0.3 mole), suspended in 200 ml. of refluxing xylene, was treated dropwise with 34.6 g. of benzyl chloride diluted with xylene. Heating under reflux was continued two hours, and then the suspension was cooled and filtered. The solids were washed with *n*-hexane, dried, dissolved in water and acidified with hydrochloric acid. A yellow oil separated, and was extracted with ether (three extractions). The ether extract was fractionated and a fraction boiling over 270° collected. A portion of this product was recrystallized from petroleum ether three times to give phenylpropionic acid as waxy crystals melting at 47.5° , lit.³ 48.6° . The amide melted at 104 – 105° , lit.⁴ 105° .

Reaction with *n*-Octyl Bromide.—Sodamide (3.9 g., 0.1 mole) and 8.2 g. of anhydrous sodium acetate (0.1 mole) were allowed to react as described above. The reaction product was suspended in a solution of 19.3 g. of *n*-octyl bromide (0.1 mole) in 50 ml. of *n*-nonane. The stirred suspension was refluxed for six hours and cooled, and the solids were separated by filtration, dissolved in water and the water solution was acidified. A yellow oil separated from solution. This was taken up in ether and dried over calcium chloride. Evaporation of the ether extract gave 3.5 g. of a yellow waxy product melting at approximately room temperature (m.p. capric acid 31.5°).³

The acid was identified by conversion to the anilide (m.p. 62° , lit.⁵ 61°) and to the amide (m.p. 98° , lit.^{6,7} 98°).

Reaction with Carbon Dioxide.—The reaction product from 78 g. of sodamide and 164 g. of anhydrous sodium acetate was added slowly to a carbon dioxide swept vessel heated to 213° . After 10 minutes, carbon dioxide was being taken up as rapidly as it could be fed. Five minutes later the addition of sodium α -sodioacetate was complete, and the vessel was cooled and the product removed. Analysis of the product by cerate oxidimetry⁸ indicated a disodium malonate content of 30.8%.

Analysis for Sodium α -Sodioacetate.—Analyses for sodium α -sodioacetate content were made on certain of the reaction products from sodium amide and sodium acetate.

The ratio of sodium α -sodio acetate to unreacted sodium acetate was determined in the following manner:

A sample of the reaction product of sodamide and sodium acetate weighing approximately 1 g. was slurried in approximately 2–3 ml. of anhydrous diethylene glycol dimethyl ether and the slurry was cooled to 0° . Under an atmosphere of nitrogen, 3 ml. of deuterium oxide was added slowly. The excess deuterium oxide and the glycol ether were removed by vacuum in a drying pistol. When all the liquids had been removed, the pistol was heated under vacuum at 140° for 16 hours to decompose any residual hydrate. The anhydrous product was allowed to react at 100° with an excess of dimethyl sulfate, and the methyl acetates formed were condensed and examined with a mass spectrometer.

The amount of deuterium exchange was limited by this treatment to less than 10%, as shown by the ratio of the height of the 75 peak to the total heights of the 76 and 77 peaks. From the ratio of the 74 peak to the corrected 75 peak; assuming equal sensitivity for methyl acetate and deuteromethyl acetate and correcting for normal isomer distribution, the mole ratio of sodium α -sodioacetate to sodium acetate in the sample was determined. Deuterolysis of

(3) F. Weger, *Ann.*, **221**, 77 (1883).

(4) A. W. Hofmann, *Ber.*, **18**, 2740 (1885).

(5) P. W. Robertson, *J. Chem. Soc.*, **93**, 1037 (1908).

(6) A. W. Hofmann, *Ber.*, **15**, 984 (1882).

(7) T. H. Rowney, *Ann.*, **79**, 243 (1951).

(8) G. F. Smith, "Cerate Oxidimetry," published by G. Frederick Smith Chemical Co., 807 McKinley Ave., Columbus, Ohio, 1942, p. 114.

(2) L. H. K. Freidlin and A. I. Lebedeva, *J. Gen. Chem. (U.S.S.R.)*, **9**, 996 (1939).

sodium acetate by the same method gave a molar ratio of deuterated to non-deuterated acetate ion of $1/27$, corresponding well with the $1/28$ naturally occurring.

The total acetate ion present in the same reaction product as that used for hydrolysis with deuterium oxide was determined as follows:

A weighed sample (approx. 10 g.) of the reaction product was hydrolyzed and dissolved in 500 ml. of water. A 10-ml. aliquot was taken and added slowly to phosphoric acid heated to 140° , and the acetic acid formed was collected by steam distillation. Titration with sodium hydroxide gave the acetate ion content of the original sample.

The sodium α -sodioacetate content of the fusion product of sodium amide and sodium acetate was calculated from the total acetate ion content and the ratio of sodium α -sodioacetate to unreacted sodium acetate.

Thermal Stability.—The thermal stability of the α -sodio compound was determined by placing a small sample of the material in a 20-ml. test-tube through which a slow current of nitrogen was passed. The tube was placed in an oil-bath and the temperature gradually raised. Gas flow rates to and from the tube were observed, as well as the appearance of the material in the tube.

The material appeared stable until a temperature of 280° was reached. Decomposition became quite rapid at 295° .

Acknowledgment.—The authors are indebted to Dr. H. C. Brown of Purdue University for the suggestion of deuterium oxide as an analytical reagent for sodium α -sodioacetate.

BATON ROUGE 1, LA.

[CONTRIBUTION NO. 121 FROM THE CENTRAL RESEARCH DEPARTMENT OF THE MINNESOTA MINING AND MANUFACTURING Co.]

High Temperature, Vapor Phase Reactions of Some Fluorocarbon Derivatives with Oxidizing Agents

BY W. A. SEVERSON AND T. J. BRICE

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Vapor phase, high temperature (450 – 650°) reactions of perfluoroalkanesulfonyl fluorides or fluorocarbon derivatives having the structures R_fCF_2X ($X = H, Cl, Br, I$) with oxidizing agents, principally NO_2 , were carried out. NO_2 gave, in several cases, good yields of perfluoroalkane-carboxylic acid fluorides; the products usually were isolated as the acids because of hydrolysis and separation problems. R_fCF_2H compounds require a sensitizing agent in addition to NO_2 before the reaction to form the acid fluoride proceeds; chlorine and bromine were successfully used as sensitizing agents.

High temperature, vapor phase oxidation reactions of three classes of fluorocarbon derivatives were studied; these classes are (1) perfluoroalkanesulfonyl fluorides, (2) fluorocarbon derivatives containing $-CF_2H$ groups and (3) fluorocarbon halides. The principal reaction studied was that with NO_2 , although other oxidizing agents were used with sulfonyl fluorides. The reaction of the $-CF_2H$ derivatives required chlorine or bromine as a sensitizing agent before reaction with NO_2 would proceed.

The perfluoroalkanesulfonyl fluorides used were prepared in good yield by electrochemical fluorination of hydrocarbon sulfonyl halides in liquid hydrogen fluoride as described by Brice and Trott.¹

Perfluoroalkyl or chloroperfluoroalkyl compounds containing, as a potentially reactive group, a terminal $-CF_2H$ group, are well known to be rather inert chemically and have not been extensively studied. They can be converted to the corresponding $-CF_3$, $-CF_2Cl$ or $-CF_2Br$ derivatives by high temperature thermal halogenation or by ultraviolet light catalyzed halogenation. Thus C_3F_7H can be converted to C_3F_7Br or C_3F_7Cl .² No other well-controlled chemical reactions have been reported.

These $-CF_2H$ -containing compounds can be obtained by several methods, as, for example, by electrochemical fluorination of organic compounds in anhydrous hydrogen fluoride³ or by the pyrolysis of CF_2HCl .⁴ The electrochemical process

yields compounds such as $F(CF_2)_nCF_2H$, while the CF_2HCl pyrolysis yields $Cl(CF_2)_nCF_2H$. An alternate convenient method for preparing the compounds $F(CF_2)_nCF_2H$ is the pyrolysis in ethylene glycol of the salt $F(CF_2)_nCF_2CO_2Na$.⁵ This method was used in the present work.

Fluorocarbon halides having the structure $F(CF_2)_nCF_2X$, where $X = Br$ or I , were prepared by the reactions of silver salts of carboxylic acids with the proper halogen.

General Procedure.—The general procedure was to pass the fluorocarbon derivative and the oxidizing agent in the vapor phase through an unpacked tube. The tubes were made of resistant metals such as nickel, nickel alloys, stainless steel or platinum; nickel tubes usually were used. The products were collected in a series of cold traps, then separated and identified.

Reactions of Perfluoroalkanesulfonyl Fluorides with NO or NO_2 .⁶—The reactions with NO_2 and NO were not first oxidation experiments performed, but proved to be the most interesting and are described more fully. The reaction threshold lies at about 450° with about a constant product distribution obtainable up to about 650° . After a series of preliminary experiments had established that a major product from $C_8F_{17}SO_2F$ and NO_2 was $C_7F_{15}COF$ plus a little $C_6F_{13}COF$, the effects of certain variables on the yields of acid fluorides were studied in more detail. The variables studied were NO_2 : $C_8F_{16}SO_2F$ mole ratio, temperature, contact time and reactor material.

At the optimum tube temperature of 550° and a contact time of 15 to 20 seconds, it was found that

(1) T. J. Brice and P. W. Trott, U. S. Patent 2,732,398, January 24, 1956; Abstracts of 126th A.C.S. Meeting, Sept., 1954, p. 42M; see also T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(2) T. J. Brice, W. H. Pearson and J. H. Simons, *THIS JOURNAL*, **68**, 968 (1946).

(3) J. H. Simons, *et al.*, *Trans. Electrochem. Soc.*, **95**, 47 (1949).

(4) J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 359 (1947).

(5) I. Auerbach, F. H. Verhoek and A. L. Henne, *THIS JOURNAL*, **72**, 299 (1950).

(6) See W. A. Severson and T. J. Brice, U. S. Patent 2,765,326, October 2, 1956.