

acetate. The required amount of hydrogen (1 mole, 90 cc.) was absorbed in six hours. Evaporation of ethyl acetate gave a semi-solid (0.680 g.) which on crystallization from benzene gave 3-(2-naphthylamino)-propanol as white needles, m.p. 77°.

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.6; H, 7.5; N, 7.0. Found: C, 78.0; H, 8.0; N, 6.8.

Acknowledgments.—The authors wish to thank Dr. T. S. Gore for the microanalysis and the Kay-Fries Chemicals, Inc., West Haverstraw, N. Y., for the valuable gift of diethyl ethoxymethylene-malonate and other chemicals.

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[CONTRIBUTION FROM THE ETHYL CORPORATION]

Sodium β -Sodiomethacrylate, A New Sodium Organic with Possible Cyclic Structure

BY D. O. DEPREE

RECEIVED JUNE 8, 1959

A new organosodium compound, sodium β -sodiomethacrylate, may be prepared by the reaction of sodium amide with sodium methacrylate in an open system at about 200°. Proof of its β -sodio substitution has been afforded by its ready reaction with carbon dioxide to give disodium itaconate and reaction with dimethyl sulfate to give sodium ethacrylate. A cyclic structure for the compound is proposed as an explanation of its high thermal stability. The infrared spectrum of the compound is consistent with such a structure. A mechanism of formation is proposed.

The synthesis of sodium α -sodioacetate by the reaction of sodium amide with sodium acetate was described in a previous publication.¹ The remarkably high thermal stability (decomposition at 280°), as well as the inertness of this compound to air oxidation, was explained on the basis of the formation of a resonance hybrid involving distribution of the negative charge between the α -carbon and the carbonyl groups. This work suggested that lower thermal stability and higher reactivity could be expected if one were to metalate an organic acid salt in which there could be no resonance stabilization involving the carbonyl group.

To test this hypothesis, sodium methacrylate was metalated with sodium amide by the same technique at 200°. It was anticipated that the β - $CH_2C(CH_3)CO_2Na + NaNH_2 \rightarrow$



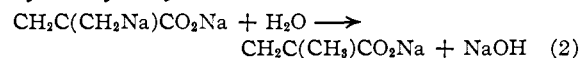
sodio derivative would decompose below its synthesis temperature, because the compound would be expected to have the lower stability of an allylic sodium compound with no resonance contribution available from the carboxyl portion of the molecule. Unexpectedly, the compound had a high thermal stability and formed readily.

Preparation.—Equimolar quantities of sodium amide and anhydrous sodium methacrylate were carefully blended and then added gradually to a heated vessel (180–220°). The evolution of ammonia was immediate and steady. The mixture was heated until evolution of ammonia ceased.

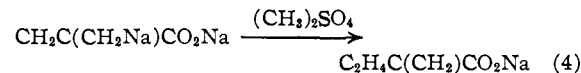
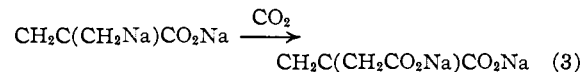
The product of this reaction is a tan solid, insoluble in hydrocarbons. The material reacts slowly with dry air at room temperature and shows only slight thermal instability at temperatures up to 290°, where it darkens without evolution of gas. Decomposition occurs very slowly at 250° on prolonged heating. The product softens but does not melt at temperatures below its decomposition temperature. It does not sublime at temperatures up to 200° under vacuum.

Chemical Properties.—When the reaction product is added to water, heat is evolved and sodium

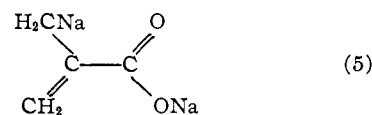
methacrylate and sodium hydroxide are formed by the hydrolysis



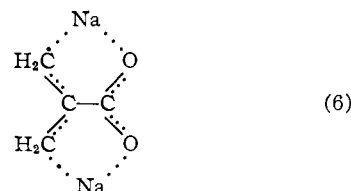
A study of the reactions of the β -sodio compound with carbon dioxide and with dimethyl sulfate provides proof of its identity. Carboxylation with carbon dioxide at room temperature yields disodium itaconate, and methylation with dimethyl sulfate yields sodium ethacrylate.



Probable Structure.—A study of the reactions carried out with sodium β -sodiomethacrylate leads to the conclusion that substitution consistently occurs in the β -position. This indicates the structure



However, the high thermal stability suggests greater stabilization than that afforded by the allylic portion of the molecule. Accordingly, the following cyclic structure is proposed for the compound



This structure is a hybrid in which both the allylic structure and the carbonyl portion of the molecule can contribute to its stabilization. Furthermore, a high degree of symmetry is provided which also contributes to the stability. These considerations would also explain the ease of formation of the com-

(1) D. O. DePree and R. D. Closson, *THIS JOURNAL*, **80**, 2311 (1958).

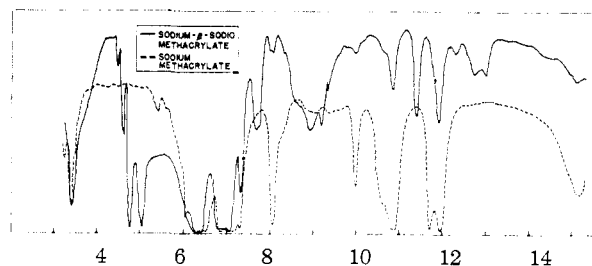
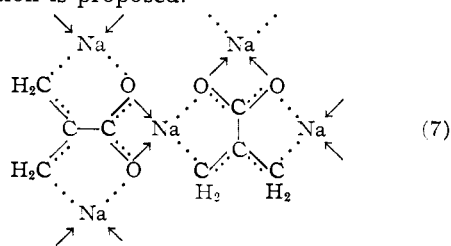


Fig. 1.

pound. This structure pictures the compound as a condensed ring double chelate in which a carbon atom forms one claw in each ring.

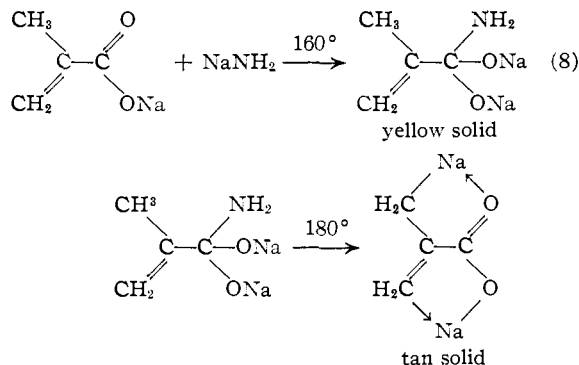
The proposed structure is consistent with the infrared spectrum of the compound, which is compared in Fig. 1 with the spectrum of the parent compound, sodium methacrylate. Because this is not a pure compound but rather a product mixture, the new bands cannot be used for structural interpretation; only changes in bands present in the sodium methacrylate spectrum are justifiable bases for interpretation. It can be noted, however, that both the C=C stretching band at 6.06 μ and the =CH band at 3.23 μ have disappeared in the spectrum of the sodio compound. The RR'C=CH₂ band at 10.83 μ is heavily attenuated. These changes indicate that there are no localized C=C groups in the new compound. This indication, considered along with the shift in the C—O stretch bands for the carboxylate ions in the 6 and 7 μ regions, suggests that the compound is conjugated as shown in the cyclic structure proposed.

The cyclic structure might suggest that the material would readily sublime. Attempts to sublime the material under vacuum at temperatures up to 200° were unsuccessful. It may be, however, that the compound exists in molecular association so that the sodium atoms may be coordinated with neighboring molecules to provide a coordination number of four. The following type of interaction is proposed.



Postulated Mechanism.—A one-to-one addition compound of sodium amide and sodium methacrylate is first formed. This is then thermally decomposed to form the β -sodio compound. A similar mechanism was postulated in the synthesis of sodium α -sodioacetate.¹ The reaction may be conducted stepwise to yield a bright yellow, stable intermediate which upon heating to 180° evolves ammonia with the formation of the β -sodio compound.

Here the addition is described as involving addition of sodium amide across the carbonyl group. However, the possibility of 1,4-addition (or a combination of 1,2- and 1,4-addition) cannot be ruled out. This intermediate is being further investi-



gated. The intermediate compound reacts mildly with water to liberate ammonia and does not react with carbon dioxide at room temperature.

Experimental

Sodium β -Sodiummethacrylate. (A) **Preparation.**—Equimolar quantities of sodium amide and anhydrous sodium methacrylate were pre-blended under nitrogen and added slowly under nitrogen to the reaction vessel, which was held at a temperature between 180 and 220°. Ammonia was liberated immediately and steadily. When addition was completed, heating and stirring were continued for a short time and then the reaction vessel was cooled to room temperature.

(B) **Reaction with Carbon Dioxide.**—Sodium β -sodiummethacrylate (30 g.), prepared as described above, was placed in a vessel swept with carbon dioxide. The product immediately became warm and increased in volume, turning a light tan in color. Carbon dioxide was fed to the flask until there was no further evidence of reaction. The weight of the product was 38.9 g.

The product was hydrolyzed with 200 ml. of water and then acidified with hydrochloric acid. A great deal of carbon dioxide was evolved. The solution was evaporated under vacuum to dryness and the dried product extracted with 300 ml. of anhydrous ethanol. The extract was evaporated to dryness to yield 20.5 g. of crude acid, corresponding to a 67% yield of itaconic acid. A portion of the crude product was recrystallized from ethanol. The recrystallized product decomposed with melting at 160–180° (decomposition temperature for itaconic acid, 161°).²

Carboxylation was also carried out in refluxing diethylene glycol dimethyl ether and the product was worked up in the same manner.

The product was identified as itaconic acid by conversion to the diamide (m.p. 190°, lit.³ 192°), the anhydride (m.p. 64–68°, lit.⁴ 68°) and by rearrangement by boiling in dilute acid solution to citraconic acid (m.p. 91°, lit.⁵ 91°).

(C) **Reaction with Dimethyl Sulfate.**—Sodium β -sodiummethacrylate (26 g.) suspended in 100 ml. of xylene and heated to 100° was treated dropwise with 25 ml. of dimethyl sulfate. A vigorous reaction set in, causing the xylene to reflux. The reaction mixture was heated one hour and cooled, and the solids were filtered off, washed with petroleum ether, and dried. The dried solids were dissolved in 200 ml. of water and the water solution was acidified with dilute sulfuric acid. The oily solution formed was extracted with two 100-ml. portions of diethyl ether. The ether extract was evaporated under vacuum to give 5–10 ml. of a dark oil. The oil dissolved in ether was treated with 10 g. of phosphorus trichloride. The solution was separated by decantation and treated with 10 g. of aniline. The ether solution was filtered off and evaporated to yield a viscous oil which crystallized on long standing. The crystalline ethacrylanilide was carefully dried of oil and recrystallized twice from ethanol (m.p. 83°, lit.⁶ 82°).

(2) R. Fittig and C. F. Langworthy, *Ann.*, **304**, 145 (1899).

(3) O. Strecker, *Ber.*, **15**, 1640 (1882).

(4) R. L. Shriner, S. G. Ford and L. J. Roll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 369.

(5) Fittig and Langworthy, ref. 2, p. 147.

(6) E. E. Blaise and A. Luttringer, *Bull. soc. chim. France*, **33**, No. 3, 765 (1880).

(D) **Thermal Stability.**—The thermal stability of sodium β -sodiummethacrylate was determined by placing a small sample of the material in a 20-ml. test-tube through which a slow stream 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 280–290° was reached. Decomposition occurred on prolonged heating at temperatures above 250°.

Preparation of Sodium Methacrylate–Sodium Amide Addition Compound.—Sodium methacrylate and sodium amide (0.1 mole each) were carefully ground together with a mortar and pestle and then placed in a nitrogen-swept test-tube in an oil-bath. The temperature was gradually raised, and at 165° the material turned a bright yellow but no am-

monia was evolved. This appearance remained as the temperature was raised to 170°. A sample was removed and treated at room temperature with carbon dioxide. No reaction occurred. The mixture was then heated to 180° where ammonia evolution began and the material began to turn orange-tan in color. The temperature was gradually raised to 200°. The mixture was then cooled to room temperature and treated with carbon dioxide. A vigorous exothermic reaction occurred with a decolorization of the product and a large absorption of gas.

Acknowledgment.—The author is indebted to Dr. R. P. Curry for the interpretation of the infrared spectrum of the compound.

BATON ROUGE 1, LA.

[CONTRIBUTION NO. 560 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

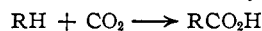
Carboxylations Effected by Ionizing Radiation

BY B. C. MCKUSICK, W. E. MOCHEL AND F. W. STACEY

RECEIVED JUNE 24, 1959

Irradiation of a mixture of a hydrocarbon and carbon dioxide with high-energy electrons gives carboxylic acids. For instance, toluene is converted to phenylacetic acid. The radiation energy is used inefficiently ($G = 0.01$ – 0.1). Formic acid can be used in place of carbon dioxide to obtain carboxylic acids. Irradiation of a mixture of a hydrocarbon and hydrogen cyanide leads to nitriles.

Direct carboxylation of hydrocarbons by carbon dioxide is considered a thermodynamically un-



favorable reaction, particularly under non-alkaline conditions. Thus Rabinowitch¹ estimates that ΔF for such carboxylation of methane is 11.8 kcal./mole, of benzene 4.6 kcal./mole.² Until recent work by Turton,³ attempts to accomplish the reaction were unsuccessful, even by the method of generating alkyl radicals in the presence of carbon dioxide. Turton³ exposed a gaseous mixture of benzene and C^{14}O_2 to β -particles from K^{85} and showed that $\text{C}_6\text{H}_5\text{C}^{14}\text{O}_2\text{H}$ was formed.

Ionizing radiation has been used recently to effect carboxylation of compounds other than hydrocarbons. Turton³ obtained a mixture of the three pyridinecarboxylic acids by applying his method to pyridine. Dose and Ettore⁴ showed that amino acids are formed when aqueous amine solutions saturated with carbon dioxide are irradiated with X-rays. In this way they converted ethylamine to a 7:3 mixture of β - and α -alanine. They also obtained pyruvic acid by irradiating an aqueous solution of sodium bicarbonate and acetaldehyde with X-rays.

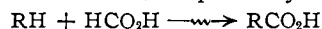
We have succeeded in carboxylating several hydrocarbons by mixing them with solid carbon

dioxide and irradiating the mixture with 2-Mev. electrons. Thus, cyclohexane was converted to cyclohexanecarboxylic acid, cyclohexene to a mixture of cyclohexenecarboxylic acids, and toluene to phenylacetic acid. Under the same conditions, we obtained lactic acid from ethanol and, like Dose and Ettore,⁴ α -alanine from ethylamine. Irradiation of a gaseous mixture of methane and carbon dioxide gave acetic acid.

Aliphatic C–H bonds are more readily carboxylated under these conditions than are aromatic C–H bonds. No methylbenzoic acids were detected in the toluene experiment and no benzoic acid was detected in an experiment with benzene under the conditions of our cyclohexane experiment. In view of Turton's elegant work,³ some benzoic acid must have been formed in our experiment, but in too small amount to be easily found by our less sensitive methods.

Yields and efficiencies were low. Thus, exposure of a mixture of 750 g. of solid carbon dioxide and 500 ml. of cyclohexane to 2.6×10^8 joules of electronic energy (equivalent to all the energy in our 500-watt beam of 2-Mev. electrons during nine minutes) gave only 229 mg. (0.04% yield) of cyclohexanecarboxylic acid. The efficiency of energy utilization in terms of G , the molecules of product formed per 100 electron-volts of energy absorbed, was only 0.07.

Carboxylation can also be effected with formic acid in place of carbon dioxide. Irradiation of formic acid solutions of cyclohexane or benzene with 2-Mev. electrons gave cyclohexanecarboxylic acid and benzoic acid, respectively. Again effi-



ciency was low ($G = 0.01$ – 0.02). Since formic acid carboxylates benzene under the influence of ionizing radiation much more readily than does carbon

(1) E. L. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 184.

(2) This does not mean, of course, that the formation of a new C–C bond by carboxylation is invariably an unfavorable reaction. Formation of acids by carboxylation of Grignard reagents or sodium phenolates are familiar reactions. T. T. Tchen, F. A. Loewus and B. Vennesland, *J. Biol. Chem.*, **213**, 547 (1955), find that ΔF for the enzyme-catalyzed carboxylation of phosphoenol pyruvate is -7.2 kcal./mole.

(3) C. N. Turton, A/Conf. 15/P/284, Second United Nations Internatl. Conf. on the Peaceful Uses of Atomic Energy (March 4, 1958).

(4) K. Dose and K. Ettore, *Z. Naturforsch.*, **13B**, 784 (1958).