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Textbook Errors, 31

The Pyrolytic Decomposition of Carboxylate Salts to Ketones

A number of organic chemistry textbooks¹ state that acetone is obtained when dry barium or calcium salts of acetic acid are heated. These texts usually extrapolate this statement to include the pyrolytic decomposition of all calcium or barium carboxylates to carbonyl compounds.

However, critical examination of the chemical literature discloses that such statements are not warranted with respect to the salts, although excellent yields of ketones can be obtained by the vapor phase decarboxylation of the carboxylic acids themselves over a variety

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, Calif.

¹ Since the purpose of this column is to prevent the spread and continuation of errors and not to evaluate individual texts, the source of errors discussed will not be cited. To be presented, the error must occur in at least two independent standard books.

of catalysts (1). The topic has four aspects: pyrolytic decomposition of carboxylate salts to simple ketones, of mixed carboxylate salts to mixed ketones, of dicarboxylate salts to cyclic ketones, and of mixed carboxylate and formate salts to aldehydes.

Most of the chemical literature on this topic is very old; the earliest statements repeatedly confirm the observation that dry distillation of calcium acetate does indeed yield acetone; technical manuals in use up to 1914 describe the preparation of acetone from "grey acetate of lime" (the calcium salt of pyroligneous acid).

With the exception of the transformation of calcium phenylacetate into dibenzyl ketone in 83% yield (2), there is virtually no literature devoted to a scrupulous study of composition and yield of reaction products obtained from the dry distillation of calcium or barium carboxylates. The mere observation that hosts of investigators have attempted (with considerable success in some instances) to prepare ketones from other than barium and calcium carboxylate salts provokes a

suspicion of dissatisfaction on the part of many investigators with the products obtained by pyrolysis of barium and calcium carboxylates.

Fittig (3) reported that the dry distillation of calcium acetate gave a neutral product, with a boiling range of 60–130°, from which he isolated acetone, methyl ethyl ketone, C₅H₁₀O, and C₆H₁₀O; no yields were reported.

Limpricht (4) stated that calcium *n*-butyrate gave a liquid product with a boiling range of 144–222°. From this were isolated eight compounds, aldehydes as well as ketones. Two ketones, C₈H₁₆O and C₁₀H₂₀O, were isolated and analyzed, but not characterized.

Friedel (5) also studied the products obtained from the pyrolysis of calcium *n*-butyrate; he isolated from the reaction mixture *n*-butyraldehyde, methyl *n*-propyl ketone, ethyl *n*-propyl ketone, and di-*n*-propyl ketone; however, he did not report the presence of C₈H₁₆O or C₁₀H₂₀O ketones.

Barbaglia and Gucci (6) distilled 2 kg of dry calcium isobutyrate; 580 g of ketone mixture boiling at 55–165° was obtained. Diethyl ketone, methyl isopropyl ketone, ethyl isopropyl ketone, diisopropyl ketone, isobutyraldehyde, and even pinacolone were obtained from the reaction mixture!

Nef (7) attempted to rationalize these results by postulating loss and gain of methylene radicals from the organic moieties present in the salts.

Two references (8, 9) are cited for the preparation of mixed ketones from the pyrolytic decomposition of mixed salts of barium acetate with higher molecular weight barium carboxylates; 60% yields were claimed by Morgan and Holmes (9). However, no mixed ketones other than methyl ketones are reported to have been prepared by this method.

Frequently this reaction is also cited as a method for the preparation of cyclic ketones from salts of dicarboxylic acids. Yet Kon (10) pyrolyzed calcium β,β-dimethylglutarate to give a distillate with a boiling range of 100–280°! From this distillate were isolated 30% acetone, 5% mesityl oxide, 33% isophorone, and unstated amounts of unsaturated hydrocarbons.

Zelinsky (11) distilled calcium sebacate to yield a "cyclononanone" with the following properties: bp 95–97° (17–18 mm), $d_4^{22.5}$ 0.8665, $\eta_D^{22.5}$ 1.4412, semicarbazone mp about 105°, oxidized to an acid of mp 99°. Several years later the incomparable work of

Ruzicka and Brugger (12) cited the unequivocal synthesis of cyclononanone (in low yields, however, by distillation of thorium sebacate) with markedly different properties: bp 93–95° (12 mm), d_4^{17} 0.9587, η_D^{17} 1.4730, semicarbazone mp 178–179°, oxidized to azelaic acid of mp 106°. In addition, Ruzicka and Brugger reported that other cyclic ketones and methyl *n*-octyl ketone were isolated from their reaction mixture.

Several organic chemistry texts and laboratory manuals report the preparation of cyclopentanone in good yield by distilling adipic acid from small amounts of calcium or barium oxide. But private communications, corroborated by laboratory observation by the authors, indicate that mere slow distillation of pure adipic acid gives excellent yields of cyclopentanone! Large chemical manufacturers are plagued by this undesired intramolecular decarboxylative cyclization of adipic acid.

The statement that aldehydes are obtained by pyrolytic decomposition of mixed salts of calcium formate and higher calcium carboxylates seems to be based upon one report over a century old, that of Piria (13). No quantitative results were cited by this investigator.

For the most part none of these references support the sweeping generalizations made in many texts of organic chemistry concerning the utility of the pyrolytic decompositions of calcium or barium carboxylates into simple ketones, mixed ketones, cyclic ketones, or aldehydes.

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