Summary

After several years' standing a sirupy preparation of turanose crystallized spontaneously and by nucleation with these crystals it has been possible to obtain rapid crystallization of large quantities of turanose. Directions for the preparation of the sugar in good yield from melezitose are given and some of its properties are recorded. Turanose shows a large and rapid mutarotation. A discussion of the structures of turanose and melezitose, in so far as present evidence permits, is presented.

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SALTS OF NITRILES. IV. SODIUM ALPHA-PHENYLBUTYRONITRILE[1,2]

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Previous reports[3] have described the preparation of the sodium and potassium salts of certain nitriles, and presented evidence for the nitride–carbide tautomerism of the anions of the salts, *e. g.*,

$$[C_6H_5C(R){=}C{=}N^-]Me^+ \rightleftarrows [C_6H_5C^-(R)CN]Me^+ \qquad (1)$$

Rising and Braun[3] made a quantitative study of the course of the reaction of phenylacetonitrile with sodium, and of the chemical behavior of the salt sodium phenylacetonitrile, $[C_6H_5CHCN]Na$. The present authors have studied quantitatively the analogous reaction of α-phenylbutyronitrile with sodium. They have found that the course of the reaction may be summarized in the equation

$$2C_6H_5C(C_2H_5)HCN + 2Na \longrightarrow [C_6H_5C(C_2H_5){=}C{=}N]Na + NaCN + C_6H_5C_3H_7 \quad (2)$$

The hydrogen formed in the reaction of sodium with the nitrile reduces part of the salt to toluene and sodium cyanide

$$2C_6H_5C(C_2H_5)HCN + 2Na \longrightarrow 2[C_6H_5C(C_2H_5){=}C{=}N]Na + 2H \qquad (3)$$

$$[C_6H_5C(C_2H_5){=}C{=}N]Na + 2H \longrightarrow C_6H_5C_3H_7 + NaCN \qquad (4)$$

This reaction corresponds to that observed by Rising and Braun with sodium phenylacetonitrile, which is reduced by hydrogen to toluene and sodium cyanide. There are described also herein the conditions used for the preparation of the salts sodium and potassium α-phenylbutyronitrile. A study of the behavior of sodium α-phenylbutyronitrile has

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[1] The work here reported forms part of the dissertation of E. W. Lowe, to be presented in partial fulfilment of requirements for the doctorate degree at the University of Chicago.

[2] Original manuscript received August 31, 1929.

[3] Rising and Zee, THIS JOURNAL, (a) **49**, 541 (1927) and (b) **50**, 1699 (1928); Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929); Rising and Braun, *ibid.*, **52**, 1069 (1930).

brought to light a number of important facts. (1) The solid salt is extremely unstable and is obtainable only in an inert atmosphere, such as nitrogen. When exposed to air it bursts into flame. (2) The salt is somewhat unstable even in ether solution and decomposes very slowly, with the formation of sodium cyanide. This is believed to be a reaction of the nitride tautomer

$$[C_6H_5C(C_2H_5){=}C{=}N^-]Na^+ \longrightarrow NaN{=}C + C_6H_5C(C_2H_5) \qquad (5)$$

The instability of the salt makes the preparation of the pure compound extremely difficult to accomplish. This is unquestionably the chief cause of the earlier difficulties experienced in duplicating the work of Dr. Zee.[4] (3) Finally, it has been shown that ethylation of sodium α-phenylbutyronitrile produces α-phenyl-α-ethylbutyronitrile, $C_6H_5C(C_2H_5)_2CN$, in fairly good yield. This is probably a reaction of the carbide salt, since the product is a C-alkyl derivative

$$[C_6H_5C^-(C_2H_5)CN]Na^+ + C_2H_5I \longrightarrow C_6H_5C(C_2H_5)_2CN + NaI \qquad (6)$$

Silver and mercury salts of the nitrile are expected to yield N-alkylated derivatives, in part at least, and are being studied.

Experimental Part

1. Preparation of Sodium α-Phenylbutyronitrile in Ether Solution.—The apparatus used for the preparation of the salt was similar to that devised by Braun (Diagram, Ref. 3) for the reaction of phenylacetonitrile with sodium. Air and moisture were at all times rigorously excluded from this apparatus, an atmosphere of nitrogen being used for the reaction and for all operations in which sodium α-phenylbutyronitrile in solution or in solid form was handled. α-Phenylbutyronitrile of boiling point 110.5–111° at 11 mm., and n^{20}_D 1.5094[5] (pure α-phenylbutyronitrile n^{20}_D 1.5092) was used, prepared by the method of Bodroux and Taboury.[6] For the preparation of sodium α-phenylbutyronitrile, sodium dust (10 g., a 26% excess) was prepared in dry xylene as usual. After removal of the xylene, the sodium was covered with 250 cc. of dry ether, the ether was brought to boiling and the nitrile (50 g.) was dropped slowly into the reaction flask during the course of five hours; the reaction mixture was then refluxed for one and one-half hours more. As the reaction progressed sodium cyanide was precipitated and the ether solution became bright yellow. The reaction which occurred is expressed in Equation 2. After separation of the ether solution from the sodium cyanide by filtration, the filrate F was made up to 400 cc. with ether and 50 cc. of it was used for the isolation of sodium α-phenylbutyronitrile for analysis. The rest of the filtrate containing the salt in ether solution was reserved for treatment with ethyl iodide to convert the salt into α-phenyl-α-ethylbutyronitrile.

2. Isolation of Sodium α-Phenylbutyronitrile, $[(C_6H_5)C(C_2H_5){=}C{=}N^-]Na^+$ and $[(C_6H_5)C^-(C_2H_5)CN]Na^+$.—A 50-cc. portion of filtrate F was allowed to flow into 2 liters of low-boiling ligroin, whereupon sodium α-phenylbutyronitrile was precipitated as a finely divided, pale yellow solid.—The salt was separated from the ether–ligroin mixture and analyzed, air being rigorously excluded in all operations.

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[4] See footnote, THIS JOURNAL, **50,** 1699 (1928).

[5] Measurements of indices of refraction were made with an Abbé refractometer.

[6] Bodroux and Taboury, *Bull. soc. chim.*, [7] **4,** 666 (1910).

Anal. Subs., 0.2405, 0.2956: Na_2SO_4, 0.1235, 0.1510. Calcd. for $C_{10}H_{10}NNa$: Na, 13.70. Found: Na, 16.64, 16.55.

The high sodium content suggested that some decomposition of the salt into sodium cyanide had occurred during its preparation, a suspicion which was later confirmed, as will presently be shown. When the preparation of the salt was carried out more rapidly, this difficulty was largely overcome. It was found best also to concentrate the original ether solution of the salt to a volume of 175–200 cc. during its filtration from sodium cyanide. After filtration about half of this volume was allowed to flow into 5 liters of low-boiling ligroin. The ligroin and ether were then drawn off as rapidly as possible (with the loss of a considerable part of the salt, which was carried away with the solution). Analysis of the salt showed it to be pure.

Anal. Subs., 0.6143, 0.3267: Na_2SO_4, 0.2581, 0.1380. Calcd. for $C_{10}H_{10}NNa$: Na, 13.70. Found: Na, 13.60, 13.68.

Solid sodium α-phenylbutyronitrile was found to be exceedingly unstable; when exposed to air it smokes and bursts into flame. In ether solution the salt decomposes slowly with the formation of sodium cyanide.

3. **Ethylation of Sodium α-Phenylbutyronitrile.**—The remainder of filtrate F (350 cc.) containing sodium α-phenylbutyronitrile was treated with ethyl iodide (25 g.) during the course of several hours. The procedure followed was that used by Braun for the analogous reaction of sodium phenylacetonitrile with ethyl iodide. Equation 6 expresses the reaction which occurred. At the end of the reaction sodium iodide and traces of sodium cyanide (see Section 4) were removed from the reaction mixture by extraction with water. The ether solution remaining was then dried and the ether removed by evaporation. The residue of oil was fractionated at 13 mm.

FRACTION 1.—B. p. 57.5–65°, 14 g., propylbenzene, formed in the reaction of α-phenylbutyronitrile with sodium (Equation 2).

Anal. Subs., 0.2924, 0.3098: CO_2, 0.9648, 1.0190; H_2O, 0.2640, 0.2771. Calcd. for C_9H_{12}: C, 89.92; H, 10.08. Found: C, 89.78, 89.96; H, 10.10, 10.04.

FRACTION 2.—B. p. 65–110°, 1–2 g., a mixture.

FRACTION 3.—B. p. 110–115°, 3.5 g., unchanged α-phenylbutyronitrile.

FRACTION 4.—B. p. 115–118°, 15 g., α-phenyl-α-ethylbutyronitrile.

Anal. Subs., 0.3130, 0.4832: N, 23.00 cc. (20°, 749 mm.), 35.04 cc. (20°, 749 mm.) (over 50% KOH). Subs., 0.3783, 0.3366: CO_2, 1.1503, 1.0240; H_2O, 0.2953, 0.2647. Calcd. for $C_{12}H_{15}N$: N, 8.09; C, 83.17; H, 8.73. Found: N, 8.28, 8.17; C, 82.93, 82.97; H, 8.76, 8.80.

FRACTION 5.—B. p. 118–195°, 1–2 g., not identified.

FRACTION 6.—Decomposes above 195°; a gummy solid.

4. **Determination of Sodium Cyanide.**—Sodium cyanide is formed (a) as one of the products of the reaction of α-phenylbutyronitrile with sodium (Equation 2), and (b) by the slow decomposition of sodium α-phenylbutyronitrile itself in ether solution. The cyanide (a) formed *by* and *during* the action of sodium on the nitrile was collected on the filter of the reaction apparatus.[7] The amount formed was determined by the Liebig method,[8] and found to be 8.1 g. A further formation of sodium cyanide (b) in filtrate F was observed. This solution, originally clear, slowly deposited a small quantity of a colorless salt which was suspected to be sodium cyanide. The amount of cyanide thus formed was determined in a number of instances. (1) Filtrate F obtained from 50 g. of nitrile and 10 g. of sodium was allowed to stand for forty hours. A

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[7] See Diagram, Rising and Braun, Ref. 3.

[8] Liebig, *Ann.*, **77**, 102 (1851).

white precipitate of sodium cyanide was deposited, in amount 0.744 g., determined by the Liebig method. (2) Filtrate F obtained from 20 g. of nitrile and 5.9 g. of sodium was allowed to stand for five days. A precipitate was formed as in (1). Ethylation of the nitrile salt in the solution was then carried out, and the amount of cyanide formed during the five days and the time of ethylation was determined by analysis for cyanide of the aqueous extract of the ethylation reaction mixture; total cyanide, 0.0986 g. (3) Ethylation of filtrate F obtained from 50 g. of nitrile and 10 g. of sodium was carried out as usual. Total cyanide, determined as in (2), was found to be 0.176 g. Clearly, sodium α-phenylbutyronitrile has a tendency to decompose slowly in its ether solution. The conditions which cause, or favor, this change are not as yet understood, nor has any product of the decomposition, aside from sodium cyanide, been isolated. The decomposition may be a reaction of the nitride salt (Equation 5).

5. Quantitative Summary of the Course of the Reaction of α-Phenylbutyronitrile with Sodium.—There follows a list of products formed in the reaction of 50 g. of nitrile with 10 g. of sodium, together with the yields obtained, calculated on the basis of Equations 2 and 6 (correction is made for the recovered α-phenylbutyronitrile).

(a) Recovered α-phenylbutyronitrile: 4 g., or 8%.

(b) Propylbenzene: 16 g., or 84.2% of the calculated amount.

(c) Sodium cyanide: 8.1 g., or 95.6% of the calculated amount. This quantity includes that formed in the reaction expressed in Equation 2, and, in addition, any traces of cyanide formed by the slow decomposition of α-phenylbutyronitrile up to the time of filtration.

(d) Sodium α-phenylbutyronitrile: since the yield of this product cannot be determined directly owing to the instability of the salt in solid form, the yield of its ethylation product may be taken as a fairly accurate measure of the amount of salt formed; yield of α-phenyl-α-ethylbutyronitrile, 17.1 g., or 62.4% of the calculated amount.

6. Potassium α-Phenylbutyronitrile, $[(C_6H_5)C(C_2H_5){=}C{=}N^-]K^+$ and $[(C_6H_5)C^-(C_2H_5)CN]K^+$.—The potassium salt was prepared by a procedure resembling that used for the preparation of sodium α-phenylbutyronitrile. The potassium salt obtained contained 20.80 and 20.67% of potassium (calculated potassium is 21.34%). The salt is a pale yellow, unstable substance which decomposes rapidly on exposure to air.

Summary

1. The reaction of α-phenylbutyronitrile with sodium has been studied quantitatively and the course of the reaction established.

2. Sodium α-phenylbutyronitrile and the analogous potassium salt have been prepared and isolated by a method similar to that developed by Rising and Braun for obtaining sodium α-phenylbutyronitrile.

3. Sodium α-phenylbutyronitrile decomposes slowly in ether solution into sodium cyanide.

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