

*Anal.* Subs., 0.2012:  $\text{Na}_2\text{SO}_4$ , 0.0943. Subs., 0.1987:  $\text{CO}_2$ , 0.3126;  $\text{H}_2\text{O}$ , 0.1277. Calcd. for  $\text{C}_6\text{H}_{11}\text{O}_2\text{Na}$ : Na, 14.93; C, 46.75; H, 7.14. Found: Na, 15.05; C, 46.81; H, 7.14.

### Summary

Convenient procedures for the preparation of the sodium salts of the  $\omega$ -hydroxy derivatives of butyric, valeric and caproic acids have been described.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## SALTS OF AROMATIC NITRILES. II. POTASSIUM PHENYLACETONITRILE

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RECEIVED AUGUST 3, 1928

PUBLISHED JANUARY 8, 1929

There appeared recently a paper<sup>1</sup> by one of the present authors and Dr. Tsoh-Wu Zee in which were discussed the method of preparation and the behavior of sodium phenylacetonitrile,  $[(\text{C}_6\text{H}_5)\text{HC}=\text{C}=\text{N}]\text{Na}$  and  $[(\text{C}_6\text{H}_5)(\text{CN})\text{HC}]\text{Na}$ , and of sodium  $\alpha$ -phenylbutyronitrile,<sup>2</sup>  $[(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{C}=\text{C}=\text{N}]\text{Na}$  and  $[(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)(\text{CN})\text{C}]\text{Na}$ . The paper was accompanied by a statement to the effect that the purity and identity of these salts, which were obtained a number of times by Rising and Zee, were established conclusively from the analytical data and the reactions of the compounds, but that since the departure of Dr. Zee for China it had proved so far impossible to repeat his work and obtain the salts again in pure form.

In view of the experimental difficulties encountered in obtaining the sodium salts by the workers who followed Zee, a study of the potassium salts of phenylacetonitrile and  $\alpha$ -phenylbutyronitrile was undertaken, and the present paper describes the preparation of potassium phenylacetonitrile,  $[(\text{C}_6\text{H}_5)\text{HC}=\text{C}=\text{N}]\text{K}$ , and  $[(\text{C}_6\text{H}_5)(\text{CN})\text{HC}]\text{K}$ , and its conversion into  $\alpha$ -phenylbutyronitrile in fairly good yield by treatment with ethyl iodide. The method used by Zee to obtain the sodium salts has been modified slightly and a method of purification of the potassium salt has been developed which will undoubtedly prove useful for other salts of this variety.

A few weeks after the publication of our last report on the sodium salts, the attention of one of the present authors was called by F. W. Upson and T. J. Thompson to a paper of theirs<sup>3</sup> which appeared in 1922 upon

<sup>1</sup> Rising and Zee, *THIS JOURNAL*, **50**, 1699 (1928).

<sup>2</sup> This salt was described in an earlier paper by Rising and Zee, *ibid.*, **49**, 541 (1927).

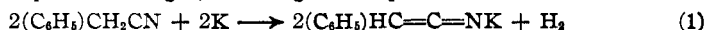
<sup>3</sup> Upson and Thompson, *ibid.*, **44**, 181 (1922).

"The Preparation and Properties of Several Phenyl Alkyl Succinic Acids," at the end of which these authors describe, incidentally to the main theme of their work, the interesting behavior of a substance, not obtained by them in pure form, produced by the reaction of sodium amide upon phenylacetonitrile in ether. The properties of this substance led Upson and Thompson to conclude that it was sodium phenylacetonitrile, of nitride structure,  $(C_6H_5)HC=C=NNa$ . It is a source of great satisfaction to us to find that the conclusions of these workers regarding the structure of the salt are thus in agreement with our own. The results of their work and of ours present striking confirmation of the theory first proposed by Nef and Hesse<sup>4</sup> with regard to the structure of salts of organic nitriles. Upson and Thompson also suggest that an imide form of phenylacetonitrile,  $(C_6H_5)HC=C=NH$ , is an intermediate compound in certain condensation reactions, undergoing "rearrangement" to the nitrile form,  $(C_6H_5)H_2C(CN)$ , in the course of these reactions. An analogous rearrangement of the imide form of the dinitrile of malonic acid,  $(CN)HC=C=NH$ , to the nitrile form,  $(CN)H_2C(CN)$ , was previously proposed by Nef and Hesse. We regret that we failed to give credit in our previous papers to Upson and Thompson for their work in this field. Their paper had escaped our notice due to the two facts that no reference to their observations was included in the title of their paper, and that the indexes of *Chemical Abstracts* and other literature contained no reference to this part of their work.

Rising and Zee obtained sodium phenylacetonitrile in pure form;<sup>1</sup> they found interesting evidence for the Nef theory of bivalent carbon in the nature of the decomposition products of the salt with acid, and explained the behavior of this salt and of its homolog, sodium  $\alpha$ -phenylbutyronitrile, in the reactions studied, upon the assumption of nitride-carbide tautomerism, obviously an extension of the Nef theory with regard to the tautomerism of hydrocyanic acid, the parent substance of nitriles; they also made suggestions regarding the role of sodium phenylacetonitrile in the aldol-like condensations described by von Meyer<sup>5</sup> and others.<sup>6</sup> Work along these lines is being continued by Rising, the results to be reported in due time.

### Experimental Part

**Potassium Phenylacetonitrile**  $(C_6H_5)HC=C=NK$  and  $(C_6H_5)(CN)HCK$ .—This salt was prepared by the treatment of potassium powder with phenylacetonitrile in dry ether in an atmosphere of nitrogen, according to the equation



The salt can be obtained in pure condition only when the most rigorous precautions are

<sup>4</sup> Hesse, Doctor's "Dissertation," University of Chicago, 1896.

<sup>5</sup> E. von Meyer, *J. prakt. Chem.*, **22**, 262 (1880); **38**, 336 (1895); **52**, 81 (1895).

<sup>6</sup> Holtzwardt, *ibid.*, **38**, 343 (1889); **39**, 230 (1889); Wache, *ibid.*, **39**, 245 (1889).

taken to exclude moisture and carbon dioxide; hence it has seemed best to describe the procedure used in some detail.

**Apparatus.**—The reaction vessel was a 200-cc. flask carrying a reflux condenser; in the top of the condenser was placed a stopper carrying a tube of calcium chloride, an inlet tube for nitrogen reaching to the bottom of the reaction flask and a dropping funnel closed by means of a tube of calcium chloride. It is of the utmost importance that this apparatus be thoroughly dried. For this purpose a stream of dry nitrogen was drawn through it for forty-eight hours, the apparatus being heated during this time.

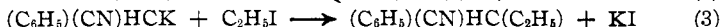
**Reagents.**—The nitrogen used for drying all apparatus was purified by being drawn first through two vessels of alkaline pyrogallol, then over calcium chloride, next through concentrated sulfuric acid and finally over phosphorus pentoxide. The ether which served as the reaction medium was washed with water, placed once over calcium chloride and then twice over bright sodium. After the ether was distilled from the sodium the last traces of water were removed by treatment with sodium-lead alloy. Kahlbaum's phenylacetonitrile, of boiling point 230–231° (uncorr.), and of known purity, was used. Potassium powder was prepared as follows: small squares of freshly cut potassium, weighed under dry xylene, were placed in the reaction flask already described, which contained 30 cc. of xylene (thiophene-free, and dried over sodium-lead alloy). The flask, loosely stoppered, was warmed until the potassium melted; the flask was then tightly closed, and shaken vigorously with a vertical movement until the molten metal was converted into an exceedingly fine powder. The xylene was decanted, the metal was washed very thoroughly with dry ether and finally covered with a layer of dry ether.

**Preparation of Potassium Phenylacetonitrile.**—Potassium dust (4.2 g.), covered with 30 cc. of ether, was placed under the reflux condenser described. The reaction apparatus was then swept out with nitrogen. Phenylacetonitrile (14 g.), used in 11% excess of the calculated amount to force all of the potassium to react and dissolved in ether to make 60 cc., was allowed to drop slowly into the reaction flask from the dropping funnel. As the reaction began, hydrogen was evolved, a bulky yellow precipitate formed and the ether boiled. When no more hydrogen was evolved, the reaction mixture was warmed for half an hour. The product of the reaction was sticky and could not be readily removed from the flask; the ether was therefore decanted from it, and the residue was washed rapidly several times with ether. The flask and contents were then placed in a vacuum desiccator over phosphorus pentoxide and the last of the ether was drawn off by suction. As the ether was removed the salt swelled and became brittle. The crude product sometimes contained unused potassium metal. Usually, however, the potassium content was somewhat low, due probably to the fact that the excess of nitrile used was not completely removed from the sticky mass. The yield of the salt obtained was 10 g., or 60% of the theoretical. Some loss of product occurred because it could not be removed completely from the reaction flask; the yield was also somewhat lowered due to the fact that some of the potassium dust was lost in the process of washing it with ether.

**Purification of Potassium Phenylacetonitrile.**—The crude salt was purified as follows: 10 g. of it was treated with 150 cc. of dry benzene in a dry flask in an atmosphere of nitrogen, whereupon much of the crude product dissolved. The benzene solution of the salt was separated from the residue by filtration, a stream of nitrogen being meanwhile allowed to play over the surface of the solution. Following filtration, the benzene solution was treated with dry, low-boiling ligroin to reprecipitate the salt, which was separated by filtration through silk, being kept in an atmosphere of nitrogen during the filtration. The salt was washed several times with ligroin and quickly put into a desiccator over phosphorus pentoxide. The salt, now pure, was kept in an atmosphere of nitrogen until analyzed.

*Anal.* Subs. 0.1025, 0.1298:  $K_2SO_4$ , 0.0571, 0.0721. Subs., 0.3444, 0.2476:  $N_2$ , 27.70, 20.20 cc. (22°, 746.5 mm.) (over 50% KOH). Subs., 0.3073, 0.3594:  $CO_2$ , 0.6963, 0.8141;  $H_2O$ , 0.1080, 0.1255. Calcd. for  $KC_8H_8N$ : K, 25.19; N, 9.03; C, 61.86; H, 3.89. Found: K, 24.97, 24.92; N, 8.95, 9.06; C, 61.79, 61.77; H, 3.90, 3.88.

**Behavior of Potassium Phenylacetoneitrile.**—The crude salt is a dark yellow, crystalline substance, becoming a lighter yellow after recrystallization. It is exceedingly sensitive to traces of water and acids, which decompose the salt with the formation of hydrocyanic acid. It reacts with ethyl iodide to form  $\alpha$ -phenylbutyronitrile, as follows



For the preparation of  $\alpha$ -phenylbutyronitrile by this method the salt was prepared in the usual way, the quantities of reagents being those previously specified, and was treated, without being separated from the reaction mixture, with ethyl iodide (18 g.), a 7% excess. The procedure and course of the reaction resemble that described in a previous paper<sup>1</sup> for the preparation of  $\alpha$ -phenylbutyronitrile from sodium phenylacetoneitrile. In the present case, however, the yield of nitrile was much better, being 10 g., or 64.4% of the theoretical yield calculated from the amount of potassium used.

### Summary

1. The preparation of potassium phenylacetoneitrile is reported.
2. The identity of the salt was established by analysis and by its reactions.
3. Its decomposition by acid into hydrocyanic acid indicates a nitride structure for the salt  $[(C_6H_5)HC=C=N]K$ .
4. Its conversion into  $\alpha$ -phenylbutyronitrile by treatment with ethyl iodide indicates that the salt also exists in a carbide form (tautomeric with the nitride),  $[(C_6H_5)(CN)HC]K$ .

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## CONCENTRATION OF HYDRAZINE HYDRATE SOLUTIONS

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RECEIVED AUGUST 3, 1928

PUBLISHED JANUARY 8, 1929

Usually, aqueous solutions of hydrazine contain less than 30% of available hydrazine (40–45% hydrazine hydrate), since this concentration may be realized by refluxing<sup>1</sup> a mixture of water (75 parts), hydrazine sulfate (200 parts) and sodium hydroxide (160 parts), and then distilling. For many purposes such a solution of hydrazine hydrate is satisfactory. When more concentrated solutions are desired, the expedient is usually adopted of starting similarly but with less water, or with a minimum volume of water and considerable alcohol.<sup>2</sup> Such devices are far from satisfactory owing to poor yields.

<sup>1</sup> "Organic Chemical Reagents," 3, 40 (1921), University of Illinois Bulletin, Vol. 19, No. 6, Oct. 9, 1921.

<sup>2</sup> Vanino, "Handbuch der Präparativen Chemie," F. Enke, Stuttgart, 1913, Vol. I, p. 114.