SODIUM SALTS OF AROMATIC NITRILES. I[1]

BY MARY M. RISING AND TSOH-WU ZEE[2]

While investigating methods of drug synthesis the authors have discovered a series of sodium salts of aromatic nitriles, intermediates in the production of certain medicinals.   As so often happens in research, the incidental discovery has proved to be of more consequence than are the findings from all the rest of the investigation; these nitrile derivatives are of peculiar importance from the theoretical aspect, and of considerable value as preparative agents.

An earlier paper[3] describes the preparation of α-sodium-α-phenylbutyronitrile, a member of the new series, and discusses the properties of the salt. This work was made the point of departure for a systematic investigation of other salts of the same type and the present paper describes the synthesis and behavior of sodiumphenylacetonitrile, which, like α-sodium-α-phenylbutyronitrile, apparently exists in tautomeric nitride and carbide forms, of structures $(C_6H_5)HC{=}C{=}NNa$ and $(C_6H_5)(CN)HCNa$, respectively.   The earlier discussion of α-sodium-α-phenylbutyronitrile is amplified and the importance of both salts from the point of view of organic theory is emphasized.

Metal derivatives of nitriles have been studied by a number of chemists. Victor Meyer[4] recognized the salt-forming property of phenylacetonitrile and similar nitriles and believed their salts to be carbides.   Thus he would assign to sodium phenylacetonitrile the structure $(C_6H_5)(CN)HCNa$.

Ernst von Meyer[5] and his students[6] made an extended study of sodium

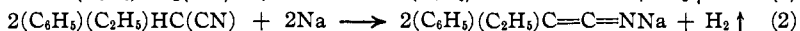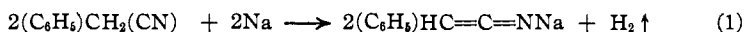[3] Rising and Zee, THIS JOURNAL, 49, 541 (1927).

[4] Victor Meyer, Ber., 21, 1291 (1888).

[5] E. von Meyer, J. prakt. Chem., 22, 262 (1880); 38, 336 (1895); 52, 81 (1895).

[6] Holtzwart, ibid., 38, 343 (1889); 39, 230 (1889); Wache, ibid., 39, 245 (1889).

derivatives of aliphatic nitriles and of phenylacetonitrile. This work will be discussed later in connection and comparison with our own.

Nef and some of his students, notably Hesse, have contributed largely to our knowledge of the behavior and structures of the salts of nitriles and related compounds. Nef was particularly interested in the constitution of the salts, and considered that the metal atom is held by nitrogen, just as in salts of hydrocyanic acid, the latter being the parent substance of nitriles.[7] Hesse[8] studied the sodium salt of cyanoacetonitrile. He found that the compound evolves hydrocyanic acid upon treatment with strong acid and concluded that the metal in the salt is attached to nitrogen; his structure for the salt is that of a nitride, $(CN)HC\!\!=\!\!C\!\!=\!\!NNa$.

The behavior of sodiumcyano-acetonitrile bears a striking resemblance to that of the salts of aromatic nitriles prepared by us. Phenylacetonitrile and α-phenylbutyronitrile are salt forming by virtue of the hydrogen atom carried by the carbon atom adjacent to the nitrile group. By their separate treatment with sodium globules in dry ether at room temperature there are produced in excellent yields the solid salts sodiumphenylacetonitrile and α-sodium-α-phenylbutyronitrile. Equations for these reactions follow.

$$2(C_6H_5)CH_2(CN) \ + \ 2Na \ \longrightarrow \ 2(C_6H_5)HC\!\!=\!\!C\!\!=\!\!NNa \ + \ H_2 \uparrow \qquad (1)$$
$$2(C_6H_5)(C_2H_5)HC(CN) \ + \ 2Na \ \longrightarrow \ 2(C_6H_5)(C_2H_5)C\!\!=\!\!C\!\!=\!\!NNa \ + \ H_2 \uparrow \quad (2)$$

The salts show two well defined and significant sets of properties which throw light upon their constitution: (1) they are decomposed by water and all acids; (2) they react by substitution.

Behavior of Sodium Salts with Acids. Sodiumphenylacetonitrile.— Treatment of this salt with cold sulfuric acid caused an evolution of hydrocyanic acid and the formation of an oil of boiling point 204–205° which proved to be benzyl alcohol. The hydrocyanic acid formed in the reaction was identified by qualitative test and determined quantitatively. The benzyl alcohol was identified in two ways: (1) by oxidation to benzaldehyde and conversion of the aldehyde into benzaldehydephenylhydrazone; (2) by conversion into 3-nitrophthalic α-monobenzyl ester.[9]

α-**Sodium-α-phenylbutyronitrile.—**When this salt was treated with cold sulfuric acid evolution of hydrocyanic acid occurred and a yellow solid of melting point 89–90° was formed which proved to be symmetrical diethylstilbene, $(C_6H_5)(C_2H_5)C\!\!=\!\!C(C_2H_5)(C_6H_5)$. The hydrocyanic acid was identified by qualitative test and measured quantitatively. The solid product of melting point 89–90° was shown to be diethylstilbene (1) by analysis and (2) by conversion into the dibromide $[(C_6H_5)(C_2H_5)CBr]_2$.

The reactions of the salts with acid are believed to occur in successive stages

[7] Nef, *Ann.*, **287**, 265 (1895).

[8] Hesse, Doctor's *Dissertation*, University of Chicago, **1896**.

[9] Nicolet and Sacks, THIS JOURNAL, **47**, 2348 (1925).

$$(C_6H_5)HC=C=NNa + H_2SO_4 \longrightarrow (C_6H_5)HC=C=NH + NaHSO_4 \quad (3)$$
$$(C_6H_5)HC=C=NH \longrightarrow HN=C= \uparrow + (C_6H_5)HC= \quad (4)$$
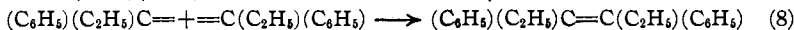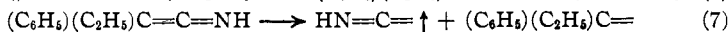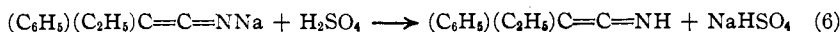$$(C_6H_5)HC= + HOH \longrightarrow (C_6H_5)H_2COH \quad (5)$$

and

$$(C_6H_5)(C_2H_5)C=C=NNa + H_2SO_4 \longrightarrow (C_6H_5)(C_2H_5)C=C=NH + NaHSO_4 \quad (6)$$
$$(C_6H_5)(C_2H_5)C=C=NH \longrightarrow HN=C= \uparrow + (C_6H_5)(C_2H_5)C= \quad (7)$$
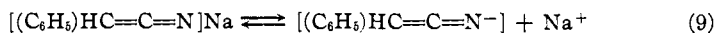$$(C_6H_5)(C_2H_5)C=+=C(C_2H_5)(C_6H_5) \longrightarrow (C_6H_5)(C_2H_5)C=C(C_2H_5)(C_6H_5) \quad (8)$$
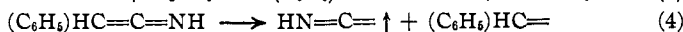
Certain features of these reactions are worthy of emphasis. (1) The sodium salts are assigned the structures of nitrides; the presence of the group $—C=C=NNa$ accounts for the formation of hydrocyanic acid. (2) The weak and unstable acids $(C_6H_5)HC=C=NH$ and $(C_6H_5)(C_2H_5)-C=C=NH$ are thought to decompose spontaneously into hydrocyanic acid and the unstable fragments $(C_6H_5)HC=$ and $(C_6H_5)(C_2H_5)C=$, respectively. (3) The absorption of water by the bivalent carbon atom of the fragment $(C_6H_5)HC=$ explains the formation of benzyl alcohol from sodium phenylacetonitrile; two of the similarly unsaturated fragments $(C_6H_5(C_2H_5)C=$ from α-sodium-α-phenylbutyronitrile may unite to form diethylstilbene.

The decomposition of α-sodium-α-phenylbutyronitrile with acid was found to furnish the amount of hydrocyanic acid demanded by our theory, but only 69% of the expected amount of diethylstilbene (equations 6–8). The similar decomposition of sodiumphenylacetonitrile produced only 49% of the amount of hydrocyanic acid and 52% of the benzyl alcohol demanded by equations 3–5. Two questions at once arise. Why should not both the salts be decomposed quantitatively into hydrocyanic acid? No data at present available afford an answer to this query. Further, why should not the treatment of sodiumphenylacetonitrile with acid produce the olefin, symmetrical diphenylethylene, $(C_6H_5)HC=CH(C_6H_5)$, in addition to benzyl alcohol, and why should not α-phenylpropyl alcohol, $(C_6H_5)(C_2H_5)HCOH$, be formed from α-sodium-α-phenylbutyronitrile and acid, in addition to diethylstilbene? The failure to isolate diphenylethylene and α-phenylpropyl alcohol does not preclude entirely the possibility of their formation, which would account for the low yields of benzyl alcohol and diethylstilbene obtained. Further efforts will be made to determine the fate of that part of the salts so far unaccounted for in their reaction with acid.

Substitution Reactions of Sodium Salts.—An entirely different type of reaction is shown by α-sodium-α-phenylbutyronitrile when the salt is treated with an alkyl iodide or chloroformic ester: here substitution occurs, the alkyl or carbalkoxy group becoming attached to the carbon atom carrying the phenyl group in the nitrile. For instance, with chloroformic methyl ester in dry ether the salt reacts to form α-phenyl-α-cyanobutyric methyl ester, $(C_6H_5)(C_2H_5)C(CN)(CO_2CH_3)$. The identity of the cyano

ester was definitely established by its conversion into phenylethylmalonic dimethyl ester, $(C_6H_5)(C_2H_5)C(CO_2CH_3)_2$, in a series of reactions described in a previous report.[10]   The fact that the substituting group attaches itself to a carbon atom rather than to nitrogen is evidence in favor of a carbide structure for the salt taking part in substitution reactions, (C_6H_5)-$(C_2H_5)(CN)CNa$.   In a similar way, the alkylation of sodiumphenylacetonitrile leads to the production of α-phenylbutyronitrile, and the structure of the salt so reacting is considered to be that of a carbide, $(C_6H_5)(CN)$-$HCNa$.

The "double behavior" of our sodium salts has convinced us that each exists in two forms, a nitride, which produces hydrocyanic acid when treated with acid, and a carbide, which is reactive in substitutions; and that the nitride and carbide are tautomers.   The situation is probably more accurately expressed in an assumption of tautomerism of the negative ions of the salts.   For example, the nitride and carbide forms of sodium-phenylacetonitrile are ionized
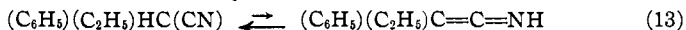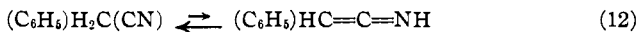
$$[(C_6H_5)HC\!\!=\!\!C\!\!=\!\!N]Na \rightleftharpoons [(C_6H_5)HC\!\!=\!\!C\!\!=\!\!N^-] + Na^+ \qquad (9)$$

and

$$[(C_6H_5)(CN)HC]Na \rightleftharpoons [(C_6H_5)(CN)HC^-] + Na^+ \qquad (10)$$
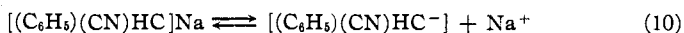
The nitride and carbide ions are mutually convertible

$$[(C_6H_5)HC\!\!=\!\!C\!\!=\!\!N^-] \rightleftharpoons [(C_6H_5)(CN)HC^-] \qquad (11)$$
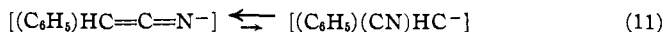
An analogous tautomeric relationship of the nitride and carbide ions of α-sodium-α-phenylbutyronitrile is probable.   The use of a substituting agent would force the tautomerization expressed in Equation 11 to the right; this change could be reversed by treatment of the carbide salt with acid.

An obvious corollary to the tautomeric relationship of the nitride and carbide salts is the existence of tautomeric forms of phenylacetonitrile and α-phenylbutyronitrile

$$(C_6H_5)H_2C(CN) \rightleftharpoons (C_6H_5)HC\!\!=\!\!C\!\!=\!\!NH \qquad (12)$$
$$(C_6H_5)(C_2H_5)HC(CN) \rightleftharpoons (C_6H_5)(C_2H_5)C\!\!=\!\!C\!\!=\!\!NH \qquad (13)$$

The two forms of each nitrile may be designated as "nitrile" and "imide;" the relationship of nitrile and imide to the carbide and nitride salts, respectively, should be apparent.   The accomplishment of the separation of the tautomeric forms of the nitriles would constitute valuable evidence for the theory of tautomerism.   The attempt to perform this separation in the case of α-phenylbutyronitrile is already under way and interesting results have been obtained which will be reported when the investigation has been completed.

The assumption of tautomerism offers a simple explanation of the behavior of the salts discussed and of the nitriles themselves.   Apparently

[10] Ref. 3, p. 544.

their treatment with sodium produces nitrides, the metal reacting with the trace of "imide" nitrile present. When the nitrides are treated with acid no tautomerization occurs since it is the nitride form which reacts to form hydrocyanic acid. When, however, the nitride salts are in suspension in dry ether in the presence of a substituting agent such as chloroformic ester, the salts, being measurably soluble in ether, are dissociated slightly and an opportunity for tautomerization of the nitride into the carbide ion would be afforded. As the latter is used up in the substitution reaction, tautomerization proceeds until all of the nitride ion is converted into carbide.

The work so far described thus inaugurates an intensive study of nitride-carbide tautomerism of certain nitriles and their salts. There are a number of points of similarity between this type of tautomerism and the enol-keto variety of acetoacetic ester.

The sodium salts discussed are theoretically interesting from quite another point of view, which will be most clearly understood from a consideration of the work of E. von Meyer.[5] He studied the reaction of aliphatic nitriles and of phenylacetonitrile with sodium in dry ether at the boiling point of ether. Von Meyer summarizes the reaction of the latter nitrile with sodium as follows

$$3C_6H_5CH_2CN + 2Na \longrightarrow NaCN + C_6H_5CH_3 + C_{16}H_{13}N_2Na \qquad (14)$$

The salt $C_{16}H_{13}N_2Na$ yielded on treatment with acid an oil of composition $C_{16}H_{14}N_2$. Von Meyer proved its structure to be $C_6H_5CH_2C(\!=\!NH)\text{-}CH(C_6H_5)(CN)$.

It is desired to emphasize two features of von Meyer's work in relation to our own. The first of these is the more important and concerns the essential nature of the reactions under consideration. In his attempt to devise a mechanism for the reaction of nitriles with sodium, von Meyer assumed the formation of intermediate compounds; for example, the salt sodiumacetonitrile, CH_2NaCN, from acetonitrile and sodium. He did not, however, isolate any such intermediate. This salt was considered to react with acetonitrile to form a sodium salt of dimolecular acetonitrile, $C_4H_5N_2Na$. Reasoning similarly for phenylacetonitrile, the salt $C_6H_5\text{-}CHNaCN$ was assumed to be formed, though not isolated. This substance is none other than the sodiumphenylacetonitrile which we have obtained in pure form. The reaction of sodiumacetonitrile with acetonitrile, or of sodiumphenylacetonitrile with phenylacetonitrile, to form salts of dimolecular nitriles resembles very closely an aldol condensation, the condensation products being $CH_3C(\!=\!NNa)CH_2CN$, and $C_6H_5CH_2C(\!=\!NNa)\text{-}CH(C_6H_5)(CN)$, respectively. The formation of such intermediate compounds as CH_2NaCN and $C_6H_5CHNaCN$ is demanded by the modern theory of aldol condensations, but their isolation occurs very rarely, doubtless on account of their extreme instability. It would appear that we have succeeded in isolating two such intermediate products. Confirmatory evi-

dence of our hypothesis will be sought in an attempt to produce sodium dimolecular phenylacetonitrile, $C_6H_5CH_2C(=NNa)CH(C_6H_5)(CN)$, by condensation of sodiumphenylacetonitrile with phenylacetonitrile.

The second point of contact between von Meyer's work and our own concerns the variation in products obtained by him and by us. In our work there was no indication of the formation of a sodium salt of a dimolecular nitrile, nor of sodium cyanide, nor of a paraffin, from the nitriles and sodium under the conditions used. That our products were pure monomolecular sodium salts and that there was no indication of the formation of sodium salts of dimolecular nitriles, or of sodium cyanide, has been proved conclusively from the analytical data, a typical set of which follows.

TABLE I

PERCENTAGE COMPOSITION OF SODIUMPHENYLACETONITRILE AND RELATED COMPOUNDS

	Composition of sodiumphenyl-acetonitrile, NaC_8H_6N		Composition calcd. for reaction product containing 1 part sodium cyanide to 1 part dimolecular sodium salt(Eq. 14), %	Composition of dimolecular sodium salt, $NaC_{16}H_{13}N_2$, %
	Calcd., %	Found. %		
Na	16.53	16.23	15.07	8.97
N	10.07	10.32	13.77	10.93
C	69.03	69.28	66.85	74.96
H	4.34	4.58	4.29	5.11

These figures show that our salt is pure sodium phenylacetonitrile. The analytical data for α-sodium-α-phenylbutyronitrile are to be found in the Experimental Part of this paper and constitute ample evidence of its purity.

A vital question presents itself as to the cause of the differences in results obtained by von Meyer and by ourselves. It has seemed to us to be important to make a thorough study of this phase of the problem and experimental work in progress at the present time should enable us to formulate a definite answer to the question, which will appear in a later report.

The work so far described is but the beginning of a series of more extensive investigations. Among the most important and interesting of these are the following: (1) the effort to separate the tautomeric forms of α-phenylbutyronitrile will be continued. (2) Silver salts of the nitriles will be prepared if possible, and alkylated. They should yield N-alkyl derivatives of the type $(C_6H_5)HC=C=NR$. (3) The attempt will be made to obtain the sodium salt of a dimolecular nitrile by condensation of sodiumphenylacetonitrile with phenylacetonitrile. (4) We shall try to improve the low yields obtained in the alkylation of the two sodium salts discussed. (5) Further knowledge of the behavior of salts of nitriles will be sought in a study of analogous salts.

Experimental Part

1. **Sodiumphenylacetonitrile,** $(C_6H_5)HC=C=NNa$ or $(C_6H_5)(CN)HCNa$.—The procedure followed for the preparation of sodiumphenylacetonitrile was the same as

that used to obtain its homolog, α-sodium-α-phenylbutyronitrile.[11]   The product of the reaction, a yellow amorphous solid, was shown by analysis to be pure sodiumphenylacetonitrile.

Anal. Subs., 0.4420, 0.0822: Na_2SO_4, 0.2216, 0.0414. Calcd. for NaC_8H_6N: Na, 16.53. Found: 16.23, 16.30. Subs., 0.1852, 0.2732: N_2, 17.05 cc. (20°, 743.5 mm.), 25.38 cc. (22°, 745.8 mm.) (over 50% KOH). Calcd. for NaC_8H_6N: N, 10.07. Found: 10.32, 10.34. Subs., 0.2385, 0.1959; CO_2, 0.6059, 0.4984; H_2O, 0.0983, 0.0806. Calcd. for NaC_8H_6N: C, 69.03; H, 4.34. Found: C, 69.28, 69.38; H, 4.58, 4.57.

Yields of the salt were good, between 80 and 90%. Equations expressing this reaction and others to be discussed subsequently are to be found in the theoretical discussion.

Behavior with Acid.   (1) Determination of **Hydrocyanic Acid.**—Sodiumphenylacetonitrile is decomposed by acids with liberation of a gas and formation of a yellow oil. The gas was shown by qualitative test to be hydrocyanic acid and was determined quantitatively. For this purpose sodiumphenylacetonitrile (10 g.) was placed in a flask fitted with a two-holed stopper which carried a dropping funnel and an outlet tube, the latter leading into dilute sodium hydroxide (50 cc.) contained in a side arm flask. Fifty per cent. sulfuric acid[12] was dropped slowly upon the salt from the dropping funnel, whereupon there occurred a brisk evolution of hydrocyanic acid which lasted some moments.   The gas was brought into the alkali by means of suction, air entering the system through the dropping funnel.   After this operation was finished the alkali was neutralized with dilute sulfuric acid and the cyanide present in it was determined by titration with silver nitrate, potassium iodide being used as indicator.[13]

Anal. Subs., 10.2000, 5.1738: 36.10, 18.25 cc. of N $AgNO_3$, factor 0.9960. Calcd. for NaC_8H_6N: CN, 18.70.   Found: 9.16, 9.13.

Thus about 49% of the amount of hydrocyanic acid demanded by Equation 4 was produced.

(2) Separation and Identification of **Benzyl Alcohol.**—The sulfuric acid solution remaining from the decomposition of sodiumphenylacetonitrile just discussed was extracted twice with ether to remove the oil produced by treatment of the salt with acid. The ether extracts were washed twice with sodium carbonate and dried over anhydrous sodium sulfate.   Fractionation of the oil remaining after the removal of the ether yielded 4 g. of distillate of boiling point 204–205°; pure benzyl alcohol boils at this temperature. A tarry residue remained in the distilling flask. The distillate showed the reactions of benzyl alcohol.   (a) It was oxidized by treatment with chromic anhydride to benzaldehyde, which was converted into benzaldehydephenylhydrazone, when treated with phenylhydrazine, according to the method described by Mulliken.[14] The product of the reaction melted at 155–156°; this is the melting point of the hydrazone obtained by treatment of benzyl alcohol of known purity, first with chromic anhydride and then with phenylhydrazine.   (b) It reacts with 3-nitrophthalic anhydride
to   form   an   α-monobenzyl   ester, $C_6H_3(NO_2)(COOH)(CO_2CH_2C_6H_5)$. Our ester

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[11] Ref. 3, p. 543.

[12] Fifty per cent. sulfuric acid was chosen since acid of greater strength charred the salt, while acid weaker than fifty per cent. formed a yellow jelly-like substance. Hydrocyanic acid was invariably evolved, regardless of the strength of the acid used.

[13] Houben-Weyl, "Die Methoden der Organischen Chemie," G. Thieme, Leipzig, **1921**, Vol. I, p. 238.

[14] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1904**, Vol. I, p. 168.

showed the melting point of pure 3-nitrophthalic-α-monobenzyl ester, 175°. The melting point of a mixture of our ester and 3-nitrophthalic-α-monobenzyl ester of known purity was 175°. By the decomposition of 10 g. of sodiumphenylacetonitrile, 4 g. of benzyl alcohol was obtained, or 52% of the amount required by Equation 5.

Substitution Reactions.—Sodiumphenylacetonitrile was alkylated by treatment of a suspension of the salt in dry ether with an excess of ethyl iodide. The reaction was allowed to continue for several days at room temperature, and the reaction mixture was finally heated under reflux for an hour. The largest yield of the reaction product, α-phenylbutyronitrile, so far obtained is 10%. The unused sodium salt remained suspended in the ether mixed with white sodium iodide formed in the reaction. The effort will be made to increase the yield by modifications of the method described.

2. α-Sodium-α-phenylbutyronitrile, $(C_6H_5)(C_2H_5)C$=C=NNa or $(C_6H_5)(C_2H_5)$-$(CN)CNa$.—α-Sodium-α-phenylbutyronitrile was prepared by a method described in detail in the earlier report of the authors.[3] Analyses of the salt proved its purity.

Anal. Subs., 0.2577, 0.1336: Na_2SO_4, 0.1098, 0.0567. Calcd. for $NaC_{10}H_{10}N$: Na, 13.76. Found: 13.80, 13.75.

Behavior with Acid. (1) Determination of Hydrocyanic Acid.—Treatment of α-sodium-α-phenylbutyronitrile with cold sulfuric acid produced hydrocyanic acid, exactly as in the case of sodiumphenylacetonitrile. The amount formed was determined quantitatively by the method used for sodiumphenylacetonitrile.

Anal. Subs., 0.8441, 0.8577: 50.45, 51.15 cc. of 0.1 N $AgNO_3$, factor 0.9928. Calcd. for $NaC_{10}H_{10}N$: CN, 15.56. Found: 15.43, 15.39.

Thus the decomposition produced almost exactly the amount of hydrocyanic acid required by Equation 7.

(2) Identification of Diethylstilbene.—The other product of decomposition of α-sodium-α-phenylbutyronitrile with acid was a dark yellow solid of melting point 89–90°, readily separated from the sulfuric acid solution by filtration, which proved to be symmetrical diethylstilbene, $(C_6H_5)(C_2H_5)C$=$C(C_2H_5)(C_6H_5)$. The analytical data for this substance follow.

Anal. Subs., 0.1078, 0.2300: CO_2, 0.3608, 0.7698; H_2O, 0.0854, 0.1805. Calcd. for diethylstilbene, $C_{18}H_{20}$: C, 91.46; H, 8.53. Found: C, 91.28, 91.28; H, 8.80, 8.72.

The quantity of diethylstilbene formed from α-sodium-α-phenylbutyronitrile on treatment with acid was determined. From 0.8441 g. and 0.8577 g. of the salt 0.4140 g. and 0.4160 g. of diethylstilbene were obtained, respectively, or 68.6% of the amount demanded by Equation 8. It is probable that the yield will be nearer to that required by theory when larger quantities of salt are used for the decomposition. The identification of the compound was completed by its transformation into a dibromide by treatment with a solution of bromine in carbon tetrachloride. Bromine was slowly absorbed and the dark yellow color of diethylstilbene changed to a pale yellow. The dibromide melted with decomposition at 122–123°. Analysis for bromine by the Carius method gave the following results.

Anal. Subs., 0.8115, 0.6113: AgBr, 0.7762, 0.5866. Calcd. for $C_{18}H_{20}Br_2$: Br, 40.36. Found: Br, 40.70, 40.83.

Substitution Reactions.—The reaction of α-sodium-α-phenylbutyronitrile with chloroform ester in dry ether has been studied. The sodium atom of the salt is replaced by the group —CO_2CH_3, the product of the reaction being α-phenyl-α-cyanobutyric methyl ester, $(C_6H_5)(C_2H_5)C(CN)(CO_2CH_3)$. The cyano ester was isolated, its imino ester prepared and converted by hydrolysis into phenylethylmalonic dimethyl ester. These reactions are described in full detail in the earlier paper of Rising and Zee.[3]

Summary

1.   A new field of investigation of nitride-carbide tautomerism is outlined.

2.   The sodium salt of phenylacetonitrile and that of α-phenylbutyronitrile have been prepared.   Their behavior with acid suggests the nitride structures $[(C_6H_5)HC{=}C{=}N^-]Na^+$ and $[(C_6H_5)(C_2H_5)C{=}C{=}N^-]Na^+$ for the two salts.

3.   The behavior of the salts in substitution reactions suggests for them carbide structures $[(C_6H_5)(CN)HC^-]Na^+$ and $[(C_6H_5)(C_2H_5)(CN)C^-]Na^+$.

4.   The "double behavior" of the salts indicates a tautomeric relationship between the nitride and carbide forms.

5.   The salts are considered to be unstable intermediate products in the aldol-like condensation reactions described by E. von Meyer.

CHICAGO, ILLINOIS

THE USE OF THE CARIUS METHOD FOR THE DETERMINATION OF SULFUR IN THE LESS VOLATILE PETROLEUM OILS[1]

BY JOHN M. DEVINE[2] AND F. W. LANE[3]

Largely because of the tedious and difficult technique involved, the Carius method has been shunned in the determination of sulfur in petroleum, although it is the method recognized as standard by most organic analysts.   It is inapplicable to low sulfur oils, as the relatively small sample that must be used gives an amount of barium sulfate that is not readily handled.   When the greatest accuracy is required in the determination of sulfur in petroleum oils containing 0.5% or more of this element, the Carius method must presumably be used.

To insure complete decomposition of petroleum oils, the procedure usually applied to organic compounds needs some revision with regard to weight of sample, quantity of fuming nitric acid and method of heating. Such changes are also necessary because the percentage of sulfur, even in high sulfur petroleums, is much less than is usually found in the average organic substance.   Mabery and Smith[4] noted that certain conditions must be observed if the method is to give accurate results with sulfur containing petroleum oils.   Unfortunately they failed to state these conditions fully or to present data from which the accuracy of their statements could be judged.

It is believed, therefore, that the experimental conditions worked out

[4] Mabery and Smith. *Am. Chem. J.*, **16**, 84 (1894).