Silver salt is an insoluble white powder, darkening slightly upon exposure to light. It gave 34.40 per cent. Ag; calculated, 34.24 per cent.

We have attempted to saponify the cyanogen group of this compound and thus obtain the tricarboxylic acid but it has resisted all attempts. Neither potassium hydroxide nor hydrochloric acid in a sealed tube gave the desired result. We expect to investigate the character of this nitrogen atom and the salts of the acid more fully, as well as the exact constitution of the anhydride from which it was formed.

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THE SYNTHESIS OF CERTAIN AROMATIC SUCCINIC ACIDS.

BY S. AVERY AND FRED W. UPSON.

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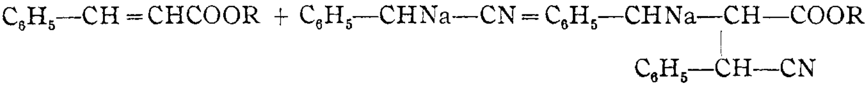
In the preceding article by one of us and McDole it is pointed out that in the synthesis of α,β-diphenylglutaric acid apparently two stereoisomers were obtained. It was conceived, however, that one of these might be the isomeric succinic acid formed according to the reaction:



$$C_6H_5\text{—}CH{=}CHCOOR + C_6H_5\text{—}CHNa\text{—}CN = \begin{array}{r} C_6H_5\text{—}CHNa\text{—}CH\text{—}COOR \\ | \quad\;\; \\ C_6H_5\text{—}CH\text{—}CN \end{array}$$

This ester on saponification would yield the unknown benzyl-phenylsuccinic acid.

For the purpose of comparing this acid with the product described in the preceding article it was decided to effect its synthesis in such a way as to leave no doubt in regard to its constitution.

Accordingly 25 grams of sodium benzylmalonic ester were condensed with 21 grams of bromphenylacetic ester. The heavy brown oily product thus obtained was heated in a bomb with hydrochloric acid but no crystalline product was obtained, although a large amount of carbon dioxide was liberated. The oil was then boiled with potassium hydroxide solution, in which it partially dissolved. On separating from the undissolved portion and acidifying, crystals mixed with an oil came down. This mixture was extracted several times with hot water, which on cooling deposited crystals in a fairly pure state. These were filtered off and washed free from oily and resinous matter with a mixture of chloroform and petroleum ether. After recrystallization from a mixture of ether and chloroform, pure white, very fine, needle-like crystals melting sharply at 176° were obtained. The acid is difficultly soluble in hot, almost insoluble in cold water; soluble in ether and alcohol; insoluble in chloroform and petroleum ether and difficultly soluble in benzene.

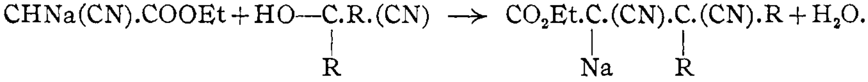
Titration.—0.0615 gram acid required 4.25 cc. N/10 sodium hydroxide; calculated for 2 acid hydrogens in $C_{17}H_{16}O_4$, 4.32 cc.

The silver salt is a white amorphous precipitate. It gave 43.13 per cent. Ag; calculated, 43.30 per cent.

The yield of the acid was very unsatisfactory and a considerable amount was lost in repeated recrystallizations to obtain an absolutely pure product from which to determine the melting point. As the analytical data above given indicated that the desired substance had been obtained, it seemed unnecessary to pursue the subject further, especially as in the meantime the nature of the apparently low melting glutaric acid had been determined.

While the work in this and the preceding article was in progress Higson and Thorpe[1] published an article describing the synthesis of alkyl succinic acids by the condensation of ethyl sodiumcyanoacetate with aldehyde cyanohydrines.

Quoting from their article: "The condensation between ethyl sodiocyanoacetate and either a ketone or an aldehyde-cyanohydrine proceeds in nearly all the cases investigated very smoothly at the ordinary temperature * * * * The reaction may be represented by the following general equation:

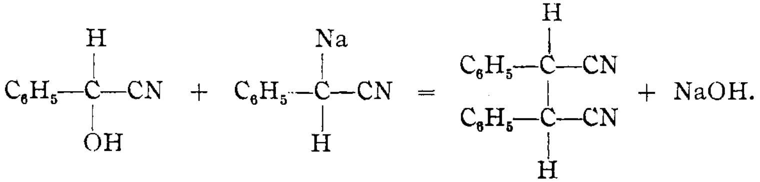


$$CHNa(CN).COOEt + HO{-}\underset{R}{C}.R.(CN) \rightarrow CO_2Et.\underset{Na}{C}.(CN).\underset{R}{C}.(CN).R + H_2O.$$

* * * * The alkyl derivatives of succinic acid can then be prepared from these ethyl salts by hydrolysis with hydrochloric acid according to the equation:

$$CO_2Et.CH(CN).CR_2.(CN) \rightarrow CO_2H.CH_2.CR_2.CO_2H''.$$

It seemed, therefore, of interest to see if benzyl cyanide could be made to condense in a like manner with aldehyde cyanohydrines in the synthesis of similar products. Accordingly, the first condensation attempted was between benzaldehyde cyanohydrine and sodiumbenzylcyanide which should give the nitrile of diphenylsuccinic acid. Thirty grams of benzaldehyde were treated with a saturated solution of acid sodium sulphite, and then with 29 grams of potassium cyanide, yielding 47.7 grams of the cyanohydrine. This was condensed with 49 grams of sodiumbenzylcyanide. Reaction:



$$C_6H_5{-}\overset{H}{\underset{OH}{C}}{-}CN + C_6H_5{-}\overset{Na}{\underset{H}{C}}{-}CN = \begin{array}{c} H \\ | \\ C_6H_5{-}C{-}CN \\ | \\ C_6H_5{-}C{-}CN \\ | \\ H \end{array} + NaOH.$$

The heavy black tarry mass resulting from the condensation was heated over the steam bath for several hours with a slight excess of sulphuric

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[1] J. Chem. Soc., 89, 1455.

acid. On cooling, the mass became thick and showed the presence of crystals. These crystals, insoluble in benzene, were washed free from the oily, foreign substance with benzene, and then purified by recrystallization from glacial acetic acid. The first melting point on what appeared to be the pure substance was 188–190°. Several recrystallizations raised the melting point to 232°. It is recorded by Knoevenagel[1] that there are two isomeric modifications of this nitrile. One melts at 160° and may be changed to the other isomer melting at 239–240° C. After treating the compound in the manner described by Knoevenagel[2] the isomer melting at 239–240° was obtained.

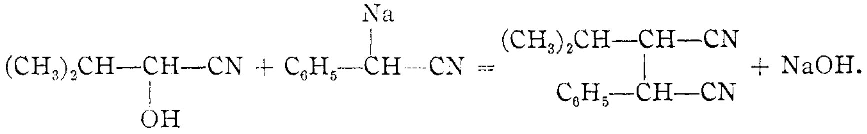
A nitrogen determination gave 12.28 per cent. N. Calculated for $C_{16}H_{12}N_2$, 12.09 per cent.

The nitrile was saponified by heating in a bomb for five hours with hydrochloric acid. The resulting crystals were purified out of alcohol and melted at 229°.

Titration.—0.10475 gram required 7.73 cc. N/10 sodium hydroxide; calculated for two acid hydrogens in $C_{16}H_{14}O_4$, 7.75 cc.

Since both the acid[3] and the nitrile[4] are known and are fully described in the literature, and since the analytical data given clearly indicate that the desired end has been reached, no further examination of this succinic acid was made.

In order to test this reaction, using an aldehyde of the aliphatic series, 25 grams of isobutyl aldehyde were converted to the cyanohydrine and condensed with sodiumbenzylcyanide. It was assumed that the nitrile of phenylisopropylsuccinic acid would be formed according to the equation:



$$(CH_3)_2CH-\underset{\mathrm{OH}}{\underset{|}{CH}}-CN + C_6H_5-\overset{\mathrm{Na}}{\overset{|}{CH}}-CN = \begin{array}{c}(CH_3)_2CH-CH-CN\\ |\\ C_6H_5-CH-CN\end{array} + NaOH.$$

The light brown oily condensation product was heated on the water bath for some time with a slight excess of sulphuric acid. On standing several days and with occasional stirring the mass showed evidences of forming crystals. When it had entirely solidified the crystals were purified by crystallization, first from alcohol and then from a mixture of petroleum ether and chloroform. White, feathery crystals, melting at 126°, were obtained.

A nitrogen determination gave 7.21 per cent. N. Calculated for $C_{13}H_{14}N_2$, 14.16 per cent.

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[1] Ber., **25**, 289.

[2] *Ibid.*, **25**, 295.

[3] Ann., **258**, 87; Ber., **14**, 1802; Ber., **23**, 117.

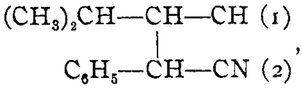
[4] *Ibid.*, **25**, 289.

A titration at this point gave a similar result. 0.0856 gram required 3.82 cc. N/10 sodium hydroxide; calculated for one acid hydrogen in $C_{13}H_{15}O_2N$, 4.38 cc. N/10 sodium hydroxide.

These results seemed to indicate that the nitrile was partially saponified. Some of the nitrile was boiled with dilute sodium hydroxide and the crystals that came down on acidification were purified by crystallizing from a mixture of alcohol and a little petroleum ether.

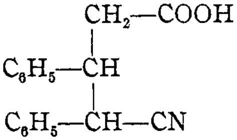
Titration.—0.0756 gram required 3.45 cc. N/10 sodium hydroxide. Calculated for one acid H in $C_{13}H_{15}O_2N$, 3.48 cc.

Apparently one nitrile group had undergone saponification during the progress of the reaction. In this connection it may be noted that in the various cyanogen compounds studied, the readiness with which saponification took place was greatly influenced by the neighboring groups. Thus in the intermediate compound,



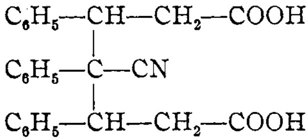
$$\begin{array}{l}(CH_3)_2CH{-}CH{-}CH\ (1)\\ \qquad\qquad\quad\ \ |\\ \qquad\quad C_6H_5{-}CH{-}CN\ (2)\end{array},$$

(1) is apparently very easily saponifiable, while (2) saponifies with more difficulty. The compound



$$\begin{array}{l}\qquad\quad CH_2{-}COOH\\ \qquad\qquad |\\ C_6H_5{-}CH\\ \qquad\qquad |\\ C_6H_5{-}CH{-}CN\end{array}$$

contains a cyanogen group that saponifies with great difficulty, while the compound



$$\begin{array}{l}C_6H_5{-}CH{-}CH_2{-}COOH\\ \qquad\qquad |\\ C_6H_5{-}C{-}CN\\ \qquad\qquad |\\ C_6H_5{-}CH{-}CH_2{-}COOH\end{array}$$

contains a cyanogen group that appears to resist the ordinary methods of saponification. The influence of neighboring groups, especially the phenyl group, in retarding saponification will be studied in detail later.

Some of the half nitrile of the phenylisopropyl succinic acid was converted to the dibasic acid by heating in a bomb with hydrochloric acid. The resulting mixture was extracted with hot water from which fine, pure white crystals of the phenylisopropyl succinic acid were deposited on cooling. These were recrystallized from benzene containing a little petroleum ether. The acid has a white powdery appearance in the mass but under the microscope shows very minute colorless plates, melting at 178°.

The acid is very soluble in ether, alcohol and acetic ether, moderately soluble in benzene, chloroform and hot water, and almost insoluble in petroleum ether and cold water.

Titration.—0.0868 gram of the acid required 7.80 cc. N/10 sodium hydroxide. Calculated for 2 acid H. in $C_{13}H_{16}O_4$, 7.88 cc. N/10 sodium hydroxide. Combustion, 0.1238 gram substance gave 0.3005 gram CO_2. This analysis gave: C, 66.2; H, 6.6. Calculated for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8.

Conclusions.—(1) The data here given show that succinic derivatives, made by reactions that leave no doubt as to their composition, are different compounds from the isomers described in the foregoing article. Hence these latter are in all cases glutaric derivatives.

(2) Sodium benzyl cyanide resembles sodium cyanacetic ester in its action with aldehyde cyanhydrines. As in the case of the deportment of benzyl cyanide with cinnamic ester, so here also there is a tendency toward partial saponification. Having determined the deportment of benzyl cyanide in this respect, since we were using benzyl cyanide in the synthesis of alkyl glutaric and succinic acids when the article by Higson and Thorpe appeared, it is not our intention to make any closer approach to the field of work of Thorpe and his pupils.

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INFLUENCE OF FERTILIZERS UPON THE COMPOSITION OF WHEAT.

BY HARRY SNYDER.

Received January 23, 1908.

There are a number of factors which are known to materially influence the composition of wheat as (1) seed, (2) soil, (3) climatic conditions, and (4) storage. These have been studied by a number of investigators, and in general it can be said that while the composition of wheat, like that of all seeds, is fairly constant it is possible by increasing the fertility of the soil, by seed selection, control of the soil moisture, systematic cultivation or irrigation, and by control of the chemical changes incident to storage to favorably influence its composition and nutritive value.

In order to study the influence of fertilizers upon the composition of wheat, sixty samples grown at 12 different localities in Minnesota and fertilized with different kinds of fertilizers were analyzed. At each of the twelve different places where the fertilizer tests were made a uniform piece of land was selected and five quarter acre plots were staked off. Each plot received similar treatment as to cultivation and seeding. On one of the plots no fertilizer was used and on the remaining plots, complete, potash, superphosphate and nitrogen fertilizers were applied. The grain from each of the plots was harvested and threshed separately, and bushel samples were shipped to the Chemical Laboratory of the Minnesota Experiment Station for analysis and milling and technical tests.

Influence on Physical Qualities of Grain.—In many instances the fer-