5. Evidence is presented for the presence of the monomethyl ene-diol common to tetramethylmannose and tetramethylglucose.

6. The ring structures of the normal forms of tetramethylmannose and tetramethylglucose are indicated to be identical.

7. The prediction of the ene-diol theory as applied to the action of dilute alkali upon tetramethylmannose has been confirmed.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

# REACTIONS OF ALPHA, BETA-UNSATURATED DINITRILES

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Malononitrile, by virtue of its methylene group, readily condenses with carbonyl compounds to yield α,β-unsaturated dinitriles.[1] In several instances we obtained two products, the usual α,β-unsaturated dinitrile (I) and a dimer (II) whose structure we are still investigating.

$$C_6H_5CHO + CH_2(CN)_2 \longrightarrow \underset{\text{I}}{C_6H_5CH{=}C(CN)_2} \quad \text{also} \quad \underset{\text{II}}{C_{20}H_{12}N_4}$$

This paper deals with condensation products corresponding to I.

There is a close resemblance between the reactions of α,β-unsaturated dinitriles and those of α,β-unsaturated aldehydes and ketones, the resemblance being due to the presence in both classes of substances of a reactive conjugated system, $C{=}C(C{\equiv}N)_2$ and $C{=}C{-}C{=}O$, respectively.

We have studied this resemblance in four reactions which are typical of α,β-unsaturated aldehydes and ketones, namely, the reaction with sodium bisulfite, oxidation by permanganate, reversal of reaction of formation (aldol or ketol condensation) by means of sodium hydroxide and the addition of the elements of hydrocyanic acid.

Benzalmalononitrile (I) and similar substances dissolve in sodium bisulfite solution—slowly in the cold, rapidly when warmed. The product thus formed (III) resembles the sulfonates (IV)[2] obtained from the reaction

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[1] (a) Heuck, *Ber.*, **28**, 2251 (1895); (b) Walter, *Ber.*, **35**, 1320 (1902); (c) Hinrichsen, *Ann.*, **336**, 323 (1904); (d) Sachs and Appenzeller, *Ber.*, **41**, 102 (1908); (e) Heller and Wunderlich, *Ber.*, **47**, 1617 (1914); (f) Ostling, *Ofversich Finska Vetenskaps. Soc. Forhandl.*, **57A**, No. 11, 1 (1915); (g) Kauffmann, *Ber.*, **49**, 1324 (1916); (h) **50**, 526, 1618 (1917); (i) **52**, 1422 (1919); (j) Diels, Gärtner and Kaack, *Ber.*, **55**, 3439 (1922); (k) Diels and Conn, *Ber.*, **56**, 2076 (1923); (l) Rosenmund and Boehm, *Ann.*, **437**, 125 (1924); (m) Fischer and Nenitzescu, *Ann.*, **439**, 175 (1924).

[2] (a) Pinner, *Ber.*, **15**, 592 (1882); (b) Kerp, *Ann.*, **290**, 123 (1896); (c) Knoevenagel, *Ber.*, **37**, 4038 (1904); (d) Hofmann, *Ann.*, **201**, 81 (1880); (e) Harries, *Ann.*, **330**, 188 (1903); (f) Tiemann, *Ber.*, **31**, 3297 (1898); (g) **32**, 823 (1899); (h) **33**, 561 (1900); (i) Baeyer and Henrich, *Ber.*, **28**, 652 (1895); (j) Labbé, *Bull. soc. chim.*, [3] **23**, 280 (1900); (k) Looft, *Ber.*, **15**, 1538 (1882); (l) *Ann.*, **275**, 377 (1893).

between α,β-unsaturated aldehydes and ketones and sodium bisulfite in that it is not reversed into the original components by means of acid or base. Lapworth and McRae[3] assumed a similar structure (V) for the product formed in the reaction between benzalcyano-acetic ester and sodium bisulfite.

$[C_6H_5CH(SO_3Na)CH(CN)_2]$
III

$C_6H_5CH(SO_3Na)CH_2COC_6H_5$
IV

$[C_6H_5CH(SO_3Na)CH(CN)CO_2C_2H_5]$
V

We were unable to isolate the sodium salt (III) in pure condition; Lapworth and McRae did not isolate V. However, by titration of the excess sodium bisulfite with iodine solution we found that one molecule of dinitrile reacted with one molecule of sodium bisulfite.

These α,β-unsaturated dinitriles are readily oxidized by potassium permanganate in acetone solution. Thus, benzalmalononitrile (I) yields benzoic acid; *m*-nitrobenzalmalononitrile, *m*-nitrobenzoic acid; *o*-methoxy benzalmalononitrile, *o*-methoxybenzoic acid.

It has long been known that acid, and especially alkali, reverses the reaction of formation of α,β-unsaturated compounds such as mesityl oxide. Likewise, the reaction of formation of these dinitriles is readily reversed. Benzalmalononitrile (I) shaken for ten minutes at room temperature with *N*/5 sodium hydroxide, produces benzaldehyde in good yield.

These α,β-unsaturated dinitriles add the elements of hydrocyanic acid. Hydrocyanic acid has been added to other α,β-unsaturated compounds by means of alkali cyanides[3,4] but the metallic derivatives of the addition products have not been isolated heretofore. Their appearance in this case is probably due to favorable solubility relations.

The general procedure was to treat the dinitrile with potassium cyanide solution, warm the mixture for a few minutes and acidify with hydrochloric acid. When the mixture was acidified, trinitrile was obtained. On the other hand, if the reaction mixture was allowed to stand without acidification, a potassium derivative was deposited. For example, starting with *p*-methoxybenzalmalononitrile (VI) we obtained a 95% yield of trinitrile (VII) if we acidified the solution after the reaction with potassium cyanide had taken place. However, if the reaction mixture was allowed to stand without acidification, a 90% yield of a potassium deriva-

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[3] Lapworth and McRae, *J. Chem. Soc.*, 121, 1704 (1922).

[4] (a) Pinner, *Ber.*, **14**, 1072 (1881); (b) Lapworth, *J. Chem. Soc.*, **85**, 1214 (1904); (c) **83**, 995 (1903); (d) **89**, 945, 1869 (1906); (e) Clarke and Lapworth, *ibid.*, **89**, 1869 (1906); (f) Knoevenagel, *Ber.*, **37**, 4065 (1904); (g) Anschütz, *Ber.*, **26**, 827 (1893); (h) Higginbotham and Lapworth, *ibid.*, 121, 49 (1922); (i) Baker and Lapworth, *ibid.*, **127**, 560 (1925); (j) Lapworth and Baker, "Organic Syntheses," John Wiley and Sons, Inc., New York, **8**, 89 (1928).

tive was obtained whose nitrogen and potassium content agreed with the percentage composition of compound VIII

$$\begin{tikzcd}
 & \underset{\text{VII}}{p\text{-}CH_3OC_6H_4CH(CN)CH(CN)_2} \\
\underset{\text{VI}}{p\text{-}CH_3OC_6H_4CH{=}C(CN)_2} + KCN + HOH \arrow[ur] \arrow[dr] & \\
 & \underset{\text{VIII}}{C_{12}H_8ON_3K}
\end{tikzcd}$$

These trinitriles function as weak acids, dissolving in bases to form salts. The trinitrile (VII) obtained by the addition of the elements of hydrocyanic acid to *p*-methoxybenzalmalononitrile (VI) dissolves easily, even in such weakly alkaline solutions as potassium cyanide or dilute ammonium hydroxide solution. Recovery of trinitrile was practically quantitative from the potassium and from the ammonium salts. The yield from the silver salt was 73% of the theoretical amount.

$$p\text{-}CH_3OC_6H_4CH(CN)CH(CN)_2 \xrightleftharpoons[HCl]{NH_4OH} C_{12}H_8ON_3^- + NH_4^+$$

A white silver salt precipitates when dilute silver nitrate solution is added to a dilute solution of either the potassium or the ammonium salt. We analyzed several potassium and silver salts but the percentage of metal was usually high (around 5% high). The high values for silver and potassium may be due to the presence of some di-salt, for example, $p$-$CH_3OC_6H_4CAg(CN)CAg(CN)_2$.

The potassium derivative alkylates to give a carbon–carbon linkage. The potassium salt (IX) corresponding to $\alpha$-phenyl-$\alpha,\beta,\beta$-tricyano-ethane (XV) reacts with methyl iodide to form a methyl derivative (X) whose structure was established by conversion into the corresponding succinic acid (XI).

$$\underset{\text{IX}}{C_{11}H_6N_3K} \longrightarrow \underset{\text{X}}{C_6H_5CHCNCCH_3(CN)_2} \longrightarrow \underset{\text{XI}}{C_6H_5CH(CO_2H)CH(CH_3)CO_2H}$$

The melting point of this acid (XI) agreed with that given in the literature but since only a small amount of the product was obtained it seemed wise to synthesize a larger amount for purification and comparison. This was accomplished by means of the following series of transformations.

$$\begin{tikzcd}
\underset{\text{XII}}{C_6H_5CH{=}C(CN)CO_2CH_3} \arrow[r] & \underset{\text{XIII}}{C_6H_5CHCNCH(CN)CO_2CH_3} \arrow[dl] \\
\underset{\text{XIV}}{C_6H_5CHCNCCH_3(CN)CO_2CH_3} \arrow[r] & \underset{\text{XI}}{C_6H_5CH(CO_2H)CH(CH_3)CO_2H}
\end{tikzcd}$$

There is nothing certain about the constitution of these salts. We see no evidence to justify any conclusion as to their structure, whether they be carbides or nitrides, that is, $C_6H_5CH(CN)CK(CN)_2$ or $C_6H_5CH(CN)$-$C{=}C{=}NK(CN)$, respectively.

The structure of the trinitriles was established by relating it to that of succinic acid. The structure of the $\alpha,\beta$-unsaturated dinitriles follows from their method of formation and also from their relationship to the trinitriles.

$$RCHO + CH_2(CN)_2 \longrightarrow RCH{=}C(CN)_2 \longrightarrow RCHCNCH(CN)_2 \longrightarrow RCH(CO_2H)CH_2CO_2H$$

Incidentally, this is a very convenient set of reactions for use in proof of structure of many substances with the following constitutions, $RCH{=}C(CN)CO_2R$ and $RCH{=}C(CN)_2$. The nitrile groups in such substances are very resistant to hydrolysis.[5]

In order to hydrolyze a nitrile group so situated, hydrogen must first be introduced into the molecule in a position alpha to the nitrile group. This can be accomplished by reduction, which leads to complications because the product is apt to be a mixture of cyano and amino compounds.[5b]

$$RCH{=}C(CN)CO_2R \longrightarrow RCH_2CH(CN)CO_2R + RCH_2CH(CH_2NH_2)CO_2R$$

The better method for the introduction of alpha hydrogen is that employed in the present instance, namely, the addition of the elements of hydrocyanic acid to the $\alpha,\beta$-unsaturated nitrile.

## Experimental Part

### I. Dinitriles

**Preparation.**—Equivalent quantities of aldehyde and malononitrile were dissolved in a suitable solvent and a few drops of piperidine added with shaking. The solution warmed up somewhat and became more or less reddish. Within fifteen minutes the mixture was solid with crystalline condensation product. It is advisable to carry out the reaction in an open beaker in order to facilitate removal of the solid. These condensations can be run without solvent but the products are apt to be dark colored. Solvent is desirable.

In the case of furfural the condensation must be run in a high dilution of water and in the presence of a weak catalyst (a pinch of sodium acetate). When the usual procedure was followed, the product was a sticky red gum with which we could do nothing. However, it is only in the condensation of furfural that special precautions are necessary.

For catalyst we usually used piperidine. However, other alkaline reagents also bring about condensation, for example, sodium methylate, sodamide, sodium acetate, ammonium carbonate, diethylamine and aniline. Reaction proceeded slowly in the presence of small amounts of formic and acetic acids. We have run several condensations between benzaldehyde and malononitrile without addition of any catalyst. Without catalyst the reaction required a day or so, whereas with piperidine the reaction was done in fifteen minutes. However, it is not to be concluded from this experiment that the condensation really takes place without the aid of a catalyst. Our materials were not sufficiently pure to preclude the presence of a trace of some basic or acidic impurity which might act as catalyst.

The condensation procedure can be best illustrated by the two following sets of directions, one for the preparation of piperonalmalononitrile (XIX), the other for furfuralmalononitrile (XXIII).

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[5] (a) Heller and Wunderlich, *Ber.*, **47**, 1617 (1914); (b) Kohler and Corson, THIS JOURNAL, **45**, 1975 (1923); (c) Rosenmund and Boehm, *Ann.*, **437**, 125 (1924).

**Condensation of Piperonal with Malononitrile.**—To a solution of 30 g. of piperonal (0.2 mole) and 15 g. of malononitrile (0.24 mole) in 130 cc. of *n*-butyl alcohol was added with stirring, 8 drops or so of piperidine. The solution became somewhat reddish and warmed up a little. Within five minutes the mixture was solid. After cooling to room temperature the product was jammed up, filtered by suction, washed with water containing a small amount of acetic acid and finally air dried. The yield was 38 g. or 96% of the theoretical amount. A small yield (±1 g.) slowly crystallized from the mother liquor. The product is lemon yellow; it has no irritant action upon the nose or eyes. The analytical sample was crystallized 3 times from acetic acid and dried at 100° in a vacuum over quicklime. It melts at 199–200°.[6]

**Condensation of Furfural with Malononitrile.**—Forty-eight g. of furfural (0.5 mole) and 33 g. of malononitrile (0.5 mole) was added to 250 cc. of water contained in a wide-mouthed Erlenmeyer flask equipped with a mechanical stirrer. The stirrer was started and a pinch of sodium acetate added to catalyze the condensation reaction. A flocculent yellow solid soon appeared. There was perhaps a slight rise in the temperature of the reaction mixture. At the end of half an hour the mixture was filtered by suction. After air drying the product weighed 70 g., which corresponds to 80% of the theoretical amount. The mother liquor slowly deposited 2 g. more of the product. The analytical sample was crystallized 4 times from carbon tetrachloride and finally air dried. Furfuralmalononitrile (XXIII) is straw yellow and melts at 72.5–73°.

**Physiological Properties.**—Certain of these dinitriles have the effect of sneeze and tear gases. They are harmless when wet but to handle the dry powder is diastrous. When crystallizing *m*-nitrobenzalmalononitrile, for instance, the alcohol solution should not be boiled very much since the alcohol vapor has a peppery sting. In sneezing caused by *m*-nitrobenzalmalononitrile (XVIII) the mucous discharge from the nose becomes bright yellow on exposure to air. In sneezing caused by *o*-chlorobenzalmalononitrile (XX) the face smarts, especially if damp. The smarting is intensified by washing. Most of the discomfort can be avoided if a gas mask is worn whenever dry solid is to be handled. However, the majority of the dinitriles reported in this paper have no irritant effect, as furfuralmalononitrile (XXIII) and *p*-methoxybenzalmalononitrile (VI).

**Solubilities of Dinitriles.**—As a general rule these substances are very soluble in acetic acid, acetone, benzene, chloroform and methyl acetate; less soluble in the higher alcohols, carbon tetrachloride and ether; sparingly soluble in carbon bisulfide, petroleum ether and water. The crystallizing properties of these dinitriles are excellent—they crystallize readily from a variety of solvents.

**Solubility in Sodium Bisulfite Solution.**—All these $\alpha,\beta$-unsaturated dinitriles are soluble in sodium bisulfite solution with the exception of cyclohexylidene malononitrile (XXI). One and one-half grams of finely ground benzalmalononitrile (I) was suspended in 100 cc. of saturated sodium bisulfite solution and the mixture mechanically shaken at room

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[6] All melting points reported in this paper are corrected for exposed thread and were read from a thermometer which had been calibrated against one which had been examined by the U. S. Bureau of Standards.

TABLE IA

α,β-UNSATURATED DINITRILES

| No. | Malononitrile | Reaction solvent | Crystallizing solvent |
|---|---|---|---|
| I | Benzal-[a] | *Tert.*-$C_5H_{11}OH$ | *n*-$C_3H_7OH$, *n*-$C_4H_9OH$, *tert.*-$C_4H_9OH$, *tert.*-$C_5H_{11}OH$ |
| VI | *p*-Methoxybenzal-[b] | $CH_3OH$ | $CH_3CO_2H$ |
| XVI | *o*-Methoxybenzal- | *Tert.*-$C_4H_9OH$ | *Iso*-$C_5H_{11}OH$ |
| XVII | *p*-Hydroxybenzal- | $CH_3OH$ | $CH_3CO_2H$, $H_2O$, *tert.*-$C_5H_{11}OH$ |
| XVIII | *m*-Nitrobenzal- | $C_2H_5OH$ | Any alcohol |
| XIX | 3,4-Dioxymethylene- | *n*-$C_4H_9OH$ | *Iso*-$C_3H_7OH$, *n*-$C_4H_9OH$ |
| XX | *o*-Chlorobenzal- | *Tert.*-$C_5H_{11}OH$ | Any alcohol, $CS_2$, $CCl_4$ |
| XXI | Cyclohexylidene- | None | $C_2H_5OH$, *iso*-$C_3H_7OH$ |
| XXII | 3-Methoxy-4-hydroxy-benzal- | $C_6H_6$ | $CH_3CO_2H$, $C_6H_6$, $C_6H_4(CH_3)_2$ |
| XXIII | Furfural-[c] | $H_2O$ | $CCl_4$ |

[a] Reported as melting at 87° by Heuck, *Ber.*, **28**, 2251 (1895).

[b] Reported as colorless and melting at 110° by Hinrichsen, *Ann.*, **336**, 323 (1904).

[c] Reported by Heuck as melting at 76°.

TABLE IB

α,β-UNSATURATED DINITRILES

| No. | Formula | Color | Physiol. action | Yield, % | M. p., °C. | Nitrogen, %[a] Calcd. | Found |
|---|---|---|---|---|---|---|---|
| I | $C_6H_5CH{=}C(CN)_2$ | None | Sneeze and tear | 96 | 83.5–84 | 18.2 | 18.0 |
| VI | *p*-$CH_3OC_6H_4CH{=}C(CN)_2$ | Corn | None | 93 | 114.5–115 | 15.2 | 15.1 |
| XVI | *o*-$CH_3OC_6H_4CH{=}C(CN)_2$ | Straw | None | 90 | 84–84.5 | 15.2 | 15.1 |
| XVII | *p*-$HOC_6H_4CH{=}C(CN)_2$ | Lemon | None | 77 | 188.5–189.5 | 16.5 | 16.4 |
| XVIII | *m*-$NO_2C_6H_4CH{=}C(CN)_2$ | Light cream | Sneeze | 90 | 104.5–105 | 21.2 | 21.3 |
| XIX | 3,4-$CH_2O_2C_6H_3CH{=}C(CN)_2$ | Lemon | None | 96 | 199–200 | 14.1 | 14.0 |
| XX | *o*-$ClC_6H_4CH{=}C(CN)_2$ | None | Sneeze and skin irritant | 85 | 95–96 | 14.9 | 14.7 |
| XXI | $C_6H_{10}{=}C(CN)_2$ | Pale straw | None | ±30 | 173.5–174.5 | 19.2 | 19.0 |
| XXII | 3,4-$CH_3O(HO)C_6H_3CH{=}C(CN)_2$ | Lemon | None | 85 | 133.5–134.5 | 14.0 | 14.1 |
| XXIII | $C_4H_3OCH{=}C(CN)_2$ | Pale straw | None | 80 | 72.5–73 | 19.5 | 19.6 |

[a] Kjeldahl analysis with mercury catalyst.

temperature. At the end of twenty-four hours the substance had gone into solution. The same substance dissolved immediately when the mixture was warmed to 70° or so.

It would seem that the salts of sulfonic acids are formed since the dinitriles are not regenerated on addition of excess acid or base. In spite of several attempts we were unable to isolate any of these sodium salts. However, by determining the amount of bisulfite used we were able to show that one molecule of sodium bisulfite reacted with one molecule of dinitrile. Two examples follow.

To a warm solution (±65°) of 1.657 g. of sodium bisulfite in about 50 cc. of water was added 1.443 g. of benzalmalononitrile. The mixture was shaken for fifteen minutes or so until all the dinitrile had dissolved. The solution was then cooled to room temperature and diluted to 100 cc. A portion of this solution was titrated against a solution of iodine, 1 cc. of which was equivalent to 0.00506 g. of sodium bisulfite. The excess of bisulfite was found to be 0.567 g. since 17.63 cc. of the solution required 19.88 cc. of iodine solution. Therefore, 1.443 g. of benzalmalononitrile used up 1.091 g. of sodium bisulfite, which is in the molecular ratio of 1.00 to 1.12.

Using the same analytical procedure, 2.014 g. of furfuralmalononitrile was treated with 1.976 g. of sodium bisulfite. After dilution to 100 cc., 27.66 cc. required 19.99 cc. of iodine solution. Therefore, 2.014 g. of furfuralmalononitrile had used up 1.610 g. of sodium bisulfite, which is in the molecular ratio of 1.00 to 1.09.

**Oxidation with Permanganate.**—$\alpha,\beta$-Unsaturated dinitriles are readily oxidized in acetone solution by means of potassium permanganate. These substances break at the ethylene double linkage. We isolated benzoic and substituted benzoic acids. Our method is illustrated by the following procedure.

One gram of *m*-nitrobenzalmalononitrile (XVIII) was dissolved in 200 cc. of acetone. To this solution was added with shaking a hot aqueous solution of 2 g. of potassium permanganate (25% excess) in 100 cc. of water. Manganese dioxide appeared as soon as the solutions were mixed. The mixture was warmed on a steam-bath for fifteen minutes and then filtered; permanganate color had disappeared. The filtrate was freed from acetone by heating on a steam-bath. Norite was added and the solution filtered. The solution was cooled and then extracted with ether in order to remove non-acidic organic material and next heated over a flame and evaporated to a volume of 50 cc. This 50 cc. of solution was poured with stirring into 50 cc. of concentrated hydrochloric acid. The *m*-nitrobenzoic acid was extracted with ether and the ether extract dried with anhydrous sodium sulfate. After evaporation of the ether the organic acid was crystallized from 50 cc. of 1% hydrochloric acid. Crystallization yielded 0.32 g. of pure *m*-nitrobenzoic acid; ether extraction of the mother liquor gave an additional yield of 0.13 g. The total yield was 0.45 g. or 50% of the theoretical amount. The product melted at 140° and was identified by comparison with an authentic sample of *m*-nitrobenzoic acid prepared by the method of Kamm and Segur.[7]

Using the same procedure we obtained a 60% yield of benzoic acid by the oxidation of benzalmalononitrile (I). The product was identified by means of a mixed melting point comparison. Starting with 0.9 g. of *o*-methoxybenzalmalononitrile (XVI) and 1.6 g. of potassium permanganate, we obtained 0.43 g. of impure *o*-methoxybenzoic acid (60% yield). Crystallization from water yielded pure *o*-methoxybenzoic acid melting at 100.5–101°. The melting point of *o*-methoxybenzoic acid is recorded in the literature as 98.5, 98.5–99 and 99°.[8] We had no authentic sample on hand for a mixed melting point comparison.

**Reversal by Means of Sodium Hydroxide.**—Benzalmalononitrile decomposes readily in the presence of sodium hydroxide. A good yield of benzaldehyde is obtained after shaking for ten minutes at room temperature in contact with *N*/5 aqueous sodium hydroxide.

In order to obtain an idea as to the extent of this reversal, we carried out the following procedure. To a dilute solution of sodium hydroxide contained in a 250cc. distilling flask connected to a water condenser was added a known amount of dinitrile. The alkaline mixture was boiled and about 50 cc. of distillate collected. The odor of ammonia was apparent after distillation had proceeded for a few minutes. The benzaldehyde in the distillate was precipitated by means of an acidic aqueous solution of phenylhydrazine hydrochloride. The precipitate was collected in a fretted glass

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[7] Kamm and Segur, "Organic Syntheses," John Wiley and Sons, Inc., New York, **3**, 73 (1923).

[8] (a) Graebe, *Ann.*, **139**, 139 (1866); (b) Bromwell, *Am. Chem. J.*, **19**, 577 (1897); (c) Lander, *J. Chem. Soc.*, **77**, 745 (1900).

Gooch, dried and weighed. The product thus obtained was shown to be benzaldehyde phenylhydrazone by means of a mixed melting point comparison with an authentic sample. We obtained 1.48 g. of benzaldehyde phenylhydrazone from 1.93 g. of benzalmalononitrile; this corresponds to 60% of the theoretical amount. We ran a blank with pure benzaldehyde against our phenylhydrazine reagent in order to test the analytical procedure. Starting with 0.6194 g. of benzaldehyde we obtained 0.8847 g. of benzaldehyde phenylhydrazone, 77.3% of the theoretical amount. This indicates that the yield of phenylhydrazone in the reversal experiment was 60/77.3 × 100% or 77.6%.

In like manner we obtained 2.80 g. of *p*-methoxybenzaldehyde phenylhydrazone from 3.58 g. of *p*-methoxybenzalmalononitrile. This corresponds to 45% of the theoretical amount. The identity of the product was established by means of a mixed melting point comparison with an authentic sample.

## II. Trinitriles

We obtained trinitriles from four of the unsaturated dinitriles, namely, benzal- (I), *p*-methoxybenzal- (VI), *o*-methoxybenzal- (XVI) and dioxymethylene benzalmalononitrile (XIX). The crude trinitriles from *p*- and *o*-methoxybenzalmalononitrile were fairly pure and the yields almost quantitative. The crude yield from piperonalmalononitrile was the smallest and the least pure. The general procedure follows.[9]

**Addition of Hydrocyanic Acid to *p*-Methoxybenzalmalononitrile.**—To 13.5 g. (0.74 mole) of finely ground *p*-methoxybenzalmalononitrile (VI) wet with 15 cc. of ethyl alcohol was added a hot, filtered solution of 9.5 g. (1.5 moles) of potassium cyanide in 15 cc. of water. The mixture was stirred and heated for two to three minutes on a steam-bath. The dinitrile dissolved. The red solution was then diluted with an equal volume of water. If the reaction had proceeded to completion the solution remained clear on dilution. Sometimes, however, a flocculent, tan-colored precipitate appeared. This substance seemed to be neither the original dinitrile nor the trinitrile sought. This precipitate should be removed by filtration before proceeding. Usually, however, the solution remained clear. A large excess of concentrated hydrochloric acid was stirred into the clear solution. A milkiness appeared, then a rather dark, heavy oil which quickly solidified and granulated (stirring should be continued for a few minutes after precipitation). The mixture was filtered by suction and the solid air dried. The crude product weighed 15.5 g.; one crystallization cut the yield down to 14.5 g. or 95% of the theoretical amount. The analytical sample was recrystallized several times from tertiary amyl alcohol with one or two treatments with Norite and finally dried in a vacuum at 80° over concentrated sulfuric acid. The pure substance is light cream colored and melts at 122–122.5°.

**Solubility, Color and Physiological Action of Trinitriles.**—The solubilities of the trinitriles are similar to those of the dinitriles, usually very soluble in acetic acid, acetone, benzene, chloroform and methyl acetate; less soluble in alcohols, carbon tetrachloride and ether; sparingly soluble in carbon bisulfide, petroleum ether and water. The trinitriles are lighter colored than the dinitriles. It may be that further purification would totally decolorize them. None of the trinitriles have the irritant physiological action of the dinitriles.

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[9] This is practically the procedure outlined by Lapworth and Baker (ref. 4j) for the addition of hydrocyanic acid to ethyl benzalcyano-acetate.

TABLE IIA

TRINITRILES

| No. | Tricyano-ethane | Crystallizing solvent |
|---|---|---|
| XV | $\alpha$-Phenyl-$\alpha,\beta,\beta$- | *n*-$C_4H_9OH$ |
| VII | $\alpha$-(*p*-Methoxyphenyl)-$\alpha,\beta,\beta$- | *Tert.*-$C_5H_{11}OH$ |
| XXIV | $\alpha$-(*o*-Methoxyphenyl)-$\alpha,\beta,\beta$- | Aq. $CH_3CO_2H$, *iso*-$C_3H_7OH$, *iso*-$C_5H_{11}OH$, *tert.*-$C_5H_{11}OH$ |
| XXV | $\alpha$-(3,4-Dioxymethylenephenyl)-$\alpha,\beta,\beta$- | *n*-$C_4H_9OH$ |

TABLE IIB

TRINITRILES

| No. | Formula | Color | Yield, % | M. p., °C. | Nitrogen, % Calcd. | Found |
|---|---|---|---|---|---|---|
| XV | $C_6H_5CH(CN)CH(CN)_2$ | None | 90 | 124.5–125 | 23.2 | 23.0 |
| VII | *p*-$CH_3OC_6H_4CH(CN)CH(CN)_2$ | Cream | 95 | 122–122.5 | 19.9 | 19.7 |
| XXIV | *o*-$CH_3OC_6H_4CH(CN)CH(CN)_2$ | Cream | 95 | 140.5–141 | 19.9 | 20.0 |
| XXV | 3,4-$CH_2O_2C_6H_3CH(CN)CH(CN)_2$ | Light orange | 80 | 153–153.5 | 18.7 | 18.4 |

**Potassium Derivative as Intermediate.**—When the reaction with potassium cyanide was carried out according to the preceding directions, the trinitrile was obtained directly without the intermediate appearance of a potassium salt. However, when the following modified procedure was employed a potassium derivative could be isolated.

Benzalmalononitrile (I) and potassium cyanide were mixed as in the preparation of trinitrile. The mixture was stirred and warmed for two to three minutes. The solution was then quickly filtered by suction. Large pink crystals of the potassium derivative (IX) crystallized from the filtrate. We were unable to purify this potassium salt by recrystallization. We could, however, remove the greater part of the pink color by grinding in a mortar with dry ether or *n*-butyl acetate. The salt darkens and shrivels around 180°; it partially melts around 190°. It is very soluble in water; rather soluble in acetone and acetic acid (the acetic acid solution soon deposits trinitrile); less soluble in the alcohols; insoluble in benzene, ether, *n*-butyl acetate and carbon bisulfide. It crystallizes poorly from *n*-butyl alcohol. The analytical sample was washed with ether and dried in a vacuum at 100°.

*Anal.* Calcd. for $C_{11}H_6N_3K$: N, 19.2; K, 17.8. Found: N, 19.0; K, 17.6.

Starting from *p*-methoxybenzalmalononitrile (VI), the corresponding potassium derivative was obtained in 88% yield. The high figures for potassium suggest that a second active hydrogen has undergone partial salt formation.

*Anal.* Calcd. for $C_{12}H_8ON_3K$: N, 16.9; K, 15.7. Found: N, 16.7; K, 17.5, 17.6.

These potassium salts decompose slowly in water solution. A water solution was made by dissolving 1.6 g. of the potassium derivative of $\alpha$-phenyl-$\alpha,\beta,\beta$-tricyanoethane in 12 cc. of water. There resulted a clear, red solution, alkaline to litmus. In three hours considerable brown sediment had settled out. We were unable to identify this solid. It reminds one of the flocculent precipitate which occasionally appears on diluting the reaction mixture in the preparation of the trinitriles. This water solution was allowed to stand for two months and became thick with dark solid. A strong odor of ammonia developed and *perhaps* there was an odor of hydrocyanic acid.

**Neutralization of Trinitriles.**—The trinitriles, as acids, dissolve in bases—even in such weakly alkaline solutions as potassium cyanide solution and dilute ammonium hydroxide. Solution takes place readily.

**Acidification of Salts.**—Trinitrile is obtained pure and in quantitative yield on acidification of the corresponding potassium or ammonium salt. Three grams of the potassium derivative of $\alpha$-phenyl-$\alpha,\beta,\beta$-tricyano-ethane ($C_{11}H_6N_3K$, IX) was dissolved in 50 cc. of water and the red solution was acidified with a slight excess of acetic acid. Trinitrile (XV) was precipitated immediately. The yield of pure, dry trinitrile was 2.55 g., the theoretical amount being 2.50 g.

In another instance, 1.31 g. of $\alpha$-(*p*-methoxyphenyl)-$\alpha,\beta,\beta$-tricyano-ethane (VII) was dissolved in a mixture consisting of 10 cc. of concentrated ammonia water and 50 cc. of water. The resulting solution of ammonium salt was slightly yellow. Trinitrile was precipitated by addition of 20 cc. of concentrated hydrochloric acid. The yield of dry trinitrile was 1.29 g., which corresponds to 98.5% of the theoretical amount.[10]

**Silver Salt.**—To a dilute solution of the ammonium salt of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$ was added, in the dark, with stirring, a dilute solution of silver nitrate. The silver salt immediately appeared. The salt is pure white at first but soon darkens, especially if exposed to the light. The solid was washed, first with methyl alcohol, finally with ether. It was dried, in the dark, over sulfuric acid in a vacuum desiccator. Choking fumes were given off during ignition of the silver salt.

*Anal.* Calcd. for $C_{12}H_8ON_3Ag$: Ag, 33.9. Found: Ag, 39.9.

Another sample of the silver derivative of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$ was made by adding silver nitrate solution to a solution of the potassium salt.

*Anal.* Calcd. for $C_{12}H_8ON_3Ag$: Ag, 33.9. Found: Ag, 38.0.

Both of these analyses are high and they also disagree between themselves to the extent of 2%.

The silver salt behaves like the potassium and ammonium salts in that it regenerates the corresponding trinitrile upon acidification. The yield, however, is not quantitative. A sample of the silver salt (which had become dark upon standing) of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$ was acidified with dilute nitric acid. The product was contaminated with so much silver (from previous decomposition of the salt) that the quantitative results were of no significance. We recrystallized the product and showed that trinitrile (*p*-$CH_3OC_6H_4CHCNCH(CN)_2$) was present.

Better results were obtained by acidifying the silver salt before it had a chance to darken. Trinitrile (1.105 g. of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$) was dissolved in dilute ammonia water and the excess of ammonia neutralized with dilute nitric acid. To the clear solution of ammonium salt was added silver nitrate solution in excess. A white precipitate of silver salt appeared. The silver salt was immediately decomposed by the addition of dilute nitric acid. The precipitated trinitrile was filtered on a fretted glass crucible, dried and weighed. The product was pure *p*-$CH_3OC_6H_4CHCN\cdot CH(CN)_2$, 0.800 g. (73% of the theoretical amount). There was no odor of hydrocyanic acid upon acidification.

**Alkylation of Potassium Derivative to Form $C_6H_5CHCNCCH_3(CN)_2$.**—Eighteen grams of the potassium derivative of $C_6H_5CHCNCH(CN)_2$ was suspended in 25 cc. of methyl alcohol. The mixture was treated under a reflux with 6 cc. of methyl iodide. Within five minutes the alcohol had come to a boil. After the force of the reaction

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[10] In a recent interesting investigation by Rising and Zee, THIS JOURNAL, **50**, 1699 (1928), (see Rising and Zee, *ibid.*, **49**, 541 (1927)), certain sodium derivatives (seemingly similar to the salts encountered in this work but of smaller molecular weight) were found to yield hydrocyanic acid on treatment with acid. This was construed as evidence for the nitride formula, that is, $C_6H_5CH{=}C{=}NNa$ and $C_6H_5C(C_2H_5){=}C{=}NNa$.

had subsided, an additional 10 cc. of methyl iodide was added and the mixture allowed to stand for six hours. The reaction mixture was finally poured into water. In the course of a day a white solid appeared. The yield was small. The substance was crystallized several times from *iso*butyl alcohol; it melts at 83–84°. It is soluble in acetone, acetic acid, ether and the alcohols; less soluble in carbon tetrachloride.

*Anal.* Calcd. for $C_{12}H_9N_3$: N, 21.5. Found: N, 21.3.

**Proof of Structure of Alkylated Nitrile, $C_6H_5CHCNCCH_3(CN)_2$.**—In order to establish the structure of the alkylated nitrile we transformed it into the corresponding succinic acid (XI). This was accomplished by refluxing for several hours with 20% hydrochloric acid. An acid was obtained which melted at 182–183° with a little bubbling. This is one of the melting points recorded in the literature for $\alpha$-phenyl-$\beta$-methyl succinic acid.[11]

**Methyl $\alpha$-Phenyl-$\alpha,\beta$-dicyano Propionate, $C_6H_5CHCNCH(CN)CO_2CH_3$.**—The elements of hydrocyanic acid were added to methyl benzalcyano-acetate (XII) in the usual manner. An oil was obtained upon acidification. The mixture of oil and water was aspirated for several hours until the oil had solidified into a hard lump. The product was crystallized three times from *iso*propyl alcohol and, finally, once from methyl alcohol. It melts at 100–101°. It is very soluble in acetone, acetic acid and methyl acetate; rather soluble in benzene, ether and the alcohols; less soluble in carbon bisulfide and carbon tetrachloride; sparingly soluble in petroleum ether and water.

*Anal.* Calcd. for $C_{12}H_{10}O_2N_2$: N, 13.1. Found: N, 12.7.

**Methyl $\alpha$-Phenyl-$\alpha,\beta$-dicyano-$\beta$-methyl Propionate, $C_6H_5CHCNC(CN)CH_3$-$CO_2CH_3$.**—Thoroughly dried nitrile ester (XIII) prepared above was dissolved in a cold methyl alcohol solution of sodium methylate (1 equivalent of sodium methylate, based on $C_6H_5CHCNCH(CN)CO_2CH_3$). The yellowish solution was treated with an excess of methyl iodide. The mixture came to a slight boil. After standing in warm water for one hour, the reaction mixture was poured into water and extracted with ether. An oil was obtained from the ether extract. We tried to distil the product under 5 mm. pressure but it decomposed. However, the crude oil solidified upon long standing. The solid was crystallized from methyl alcohol. We did not have sufficient material to determine its solubility in the various solvents. The colorless crystals melt at 87–88°.

*Anal.* Calcd. for $C_{13}H_{12}O_2N_2$: N, 12.3. Found: N, 12.3.

**$\alpha$-Phenyl-$\beta$-methylsuccinic Acid, XI.**—Methyl $\alpha$-phenyl-$\alpha,\beta$-dicyano-$\beta$-methyl propionate was refluxed for several hours with 20% hydrochloric acid. A good yield of phenylmethylsuccinic acid resulted. It was purified by several crystallizations from hot water. It melted at 182–183° with some effervescence. A mixed melting point comparison showed it to be identical with the acid obtained from $C_6H_5CHCNCCH_3(CN)_2$

*Anal.* Calcd. for $C_{11}H_{12}O_4$; 0.5316 g. requires 25.54 cc. of *N*/5 KOH. Found 25.69 cc. 0.1875 g. requires 18.01 cc. of *N*/10 KOH. Found: 17.88 cc.

The silver salt was prepared, dried in a vacuum and analyzed. It is quite stable toward light as had already been observed by Zelinsky and Buchstab.

*Anal.* Calcd. for $C_{11}H_{10}O_4Ag_2$: Ag, 51.15. Found: Ag, 50.96.

## III. Hydrolysis of Trinitriles to Succinic Acids

The trinitriles were transformed into succinic acids by refluxing for several hours (three to ten hours, depending on the substance) with a con-

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[11] (a) Zelinsky and Buchstab, *Ber.*, **24**, 1876 (1891); (b) Ruhemann, *J. Chem. Soc.*, **81**, 1216 (1902); (c) Upson and Thompson, THIS JOURNAL, **44**, 185 (1922).

siderable excess of 20% hydrochloric acid. The products were recrystallized from hot water.

Ten grams of α-phenyl-α,β,β-tricyano-ethane (XV) yielded upon hydrolysis and decarboxylation 9.6 g. of phenylsuccinic acid (90% of the theoretical amount). Its identity was established by comparison with an authentic sample prepared by the method of Bredt and Kallen.[12]

Ten grams of α-(*p*-methoxyphenyl)-α,β,β-tricyano-ethane (VII) yielded 7 g. of colorless *p*-methoxyphenylsuccinic acid (67% of the theoretical amount). It was recrystallized several times from hot water and finally dried at 100° in a vacuum over sulfuric acid. Its melting point depends upon the speed of heating. Heated slowly it melts at 204–206°; heated rapidly it melts at 207–208°. Uncertain melting point is often characteristic of dibasic acids and is doubtless due to the formation of a small amount of anhydride, the presence of which lowers the melting point. The faster the heating, the less anhydride formed and, therefore, the higher the melting point.

*Anal.* Calcd. for $C_{11}H_{12}O_5$: 0.4448 g. requires 19.85 cc. of $N/5$ KOH. Found: 19.83 cc.

*p*-Methoxyphenylsuccinic acid has been reported by Baker and Lapworth[13] as melting at 194–195° (10° below our melting point). Chrzaszezewska[14] describes it as pale yellow and melting still lower, 189–190°.

Because of this disagreement in melting points we prepared the anhydride for further comparison. The acid was refluxed for one hour with acetyl chloride. The acetyl chloride was removed by vacuum evaporation at room temperature and the residual solid crystallized from chloroform–petroleum ether mixture. The product melts at 91–92°, which agrees well with the melting point of 90.5° observed by Baker and Lapworth.

**Dimethyl *p*-Methoxyphenylsuccinate,** *p*-$CH_3OC_6H_4CH(CO_2CH_3)CH_2CO_2CH_3$.—The dimethyl ester was obtained in 50% yield by refluxing 6.5 g. of the corresponding trinitrile (VII) with a solution of 9 cc. of concentrated sulfuric acid in 25 cc. of 98% methyl alcohol. After boiling for five hours, the solution was poured into ice water and the mixture extracted with ether. The colorless product was recrystallized several times from methyl alcohol. It melts at 93–94°. We were unable to obtain consistent analyses for the carbon content. A qualitative test showed nitrogen to be absent.

*Anal.* Calcd. for $C_{13}H_{16}O_5$: C, 61.9; H, 6.0. Found: C, 57.8, 56; H, 5.5, 5.7.

***o*-Methoxyphenylsuccinic Acid,** *o*-$CH_3OC_6H_4CH(CO_2H)CH_2CO_2H$.—Ten grams of the corresponding trinitrile (XXIV) yielded 6 g. of substituted succinic acid (57% of the theoretical amount).[15] The product, however, was a mixture. Fractional crystallization from water separated it into two fractions. The more soluble fraction melted cloudy around 122°; the melt cleared around 185° and bubbled at about 197°. We did not investigate this fraction. The less soluble fraction was *o*-methoxyphenylsuccinic acid. It melts with slow heating at 182–184°; with rapid heating at 184–185°.

*Anal.* Calcd. for $C_{11}H_{12}O_5$: C, 58.9; H, 5.4. Found: C, 59.1; H, 5.5. Calcd.:

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[12] Bredt and Kallen, *Ann.*, **293**, 342 (1896).

[13] Baker and Lapworth, *J. Chem. Soc.*, **127**, 560 (1925).

[14] Chrzaszezewska, *Roczniki Chem.*, **5**, 1–3, 33–76 (1925); *C. A.*, **20**, 1078 (1926).

[15] Lapworth and McRae, *J. Chem. Soc.*, 121, 1704 (1922), found that a very similar compound, *o*-$CH_3OC_6H_4CHCNCH(CN)CO_2R$, carbonized badly on refluxing with hydrochloric acid.

0.3743 g. requires 16.67 cc. of $N/5$ KOH. Found: 16.67 cc. Calcd.: 0.2106 g. requires 18.79 cc. of $N/10$ KOH. Found: 18.78.

Piperonylphenylsuccinic acid was obtained in poor yield by the alkaline hydrolysis and decarboxylation of $3,4\text{-}CH_2O_2C_6H_3CH(CN)CH(CN)_2$ (XXV). The product was very pale yellow and melted at 210–212°, which agrees with the melting point of 211° observed by Lapworth and McRae.[16]

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## Summary

1. Several new condensation products of malononitrile with aromatic aldehydes are reported.

2. These $\alpha,\beta$-unsaturated dinitriles closely resemble $\alpha,\beta$-unsaturated aldehydes and ketones in that they (a) dissolve in sodium bisulfite solution, (b) are oxidized by potassium permanganate, (c) are reversed into the original components by sodium hydroxide and (d) add the elements of hydrocyanic acid.

3. The trinitriles, resulting from the addition of hydrocyanic acid to the dinitriles, function as weak acids, dissolving in bases to form salts. Acidification of the potassium, ammonium and silver salts results in regeneration of trinitrile. The potassium salt alkylates with methyl iodide to give carbon–carbon alkylation.

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[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

# THE ACTION OF SELENIUM MONOCHLORIDE UPON FATTY OILS

BY ELLERY H. HARVEY AND H. A. SCHUETTE

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The discovery by Parkes[1] that rubber could be vulcanized by immersing it in sulfur monochloride, followed by his observation[1] that "articles having properties analagous to those from india-rubber or gutta percha" could be made from fatty oils by the action of this substance, eventually gave rise to its introduction into the field of analytical chemistry by Warren[2] and then by Fawsitt.[3] Warren's conclusions, which were based upon the nature of the reaction product, were subsequently questioned.[4] Fawsitt's

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[16] Lapworth and McRae, *J. Chem. Soc.*, 121, 1708 (1922).

[1] Parkes, British Patents 11,147, Sept. 25, 1846, and 2359, Oct. 22, 1855.

[2] Warren, *Chem. News*, **55**, 134 (1887); **56**, 222, 231, 243, 262 (1887); **57**, 26, 43, 113 (1888); **58**, 4, 15 (1888).

[3] Fawsitt, *J. Soc. Chem. Ind.*, **7**, 552 (1888).

[4] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan Co., London, 1921, 6th ed., Vol. I, p. 474.