[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SALTS OF NITRO COMPOUNDS. I. PREPARATION, ALKYLATION AND ACYLATION OF SALTS OF PHENYLNITROACETONITRILE

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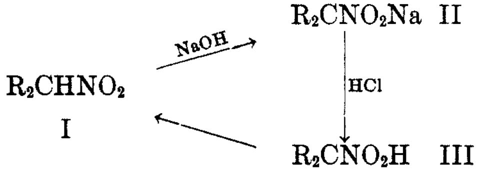
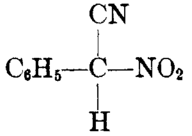
Secondary nitro compounds (I) are interesting chiefly because of their remarkable property of forming salts (II), which, upon acidification, may



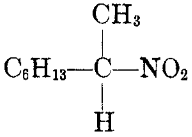
yield either the original nitro compound or an aci-form (III). The latter may then tautomerize to the normal nitro-form (I).

Elucidation of the structures of the salts depends principally on the nature of the derivatives obtained from them by alkylation and acylation. In the special case that the carbon atom holding the hydrogen atom involved in the tautomerization is asymmetric, the optical properties of the salt may aid in indicating its structure. In the present study, a compound of this type—phenylnitroacetonitrile (IV)—has been used. This particular compound was of interest, since both the cyano and the phenyl group



$$C_6H_5-\overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-NO_2$$

IV



$$C_6H_{13}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-NO_2$$

V

are known to promote the mobility of the hydrogen atom, and would enable comparisons to be made with secondary nitro compounds in which only alkyl groups are present, such as 2-nitroöctane (V).

OPTICAL PROPERTIES

The observation that salts of *d*- and *l*-2-nitrobutane[1] and *d*- and *l*-2-nitroöctane[2] were optically active has led to the search[3] for further exam-

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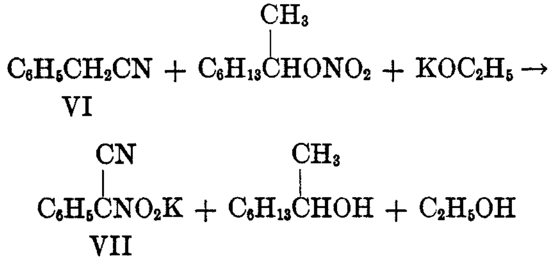
[1] KUHN AND ALBRECHT, *Ber.*, **60**, 1297 (1927).

[2] YOUNG AND SHRINER, *J. Am. Chem. Soc.*, **52**, 3332 (1930).

[3] PARKER AND SHRINER, *ibid.*, **55**, 1242 (1933); HORNE AND SHRINER, *ibid.*, **55**, 4652 (1933); THURSTON AND SHRINER, *ibid.*, **57**, 2163 (1935).

ples of such optically active salts. In the case of phenylnitroacetonitrile, it is not certain whether optically active salts exist. Although the resolution of phenylnitroacetonitrile by brucine, and conversion of the brucine salt into an optically active sodium salt was reported,[4] recent attempts by the same authors to obtain optically active salts have been unsuccessful. It was, therefore, interesting to determine whether optically active sodium salts could be obtained by means of an asymmetric synthesis.[3] Accordingly, phenylacetonitrile (VI) was treated with *d*- and *l*-2-octyl nitrate in the presence of potassium ethoxide. However, the potassium salt (VII)

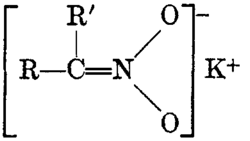


$$\underset{\text{VI}}{C_6H_5CH_2CN} + C_6H_{13}\overset{\overset{CH_3}{|}}{C}HONO_2 + KOC_2H_5 \rightarrow$$

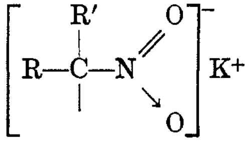
$$\underset{\text{VII}}{C_6H_5\overset{\overset{CN}{|}}{C}NO_2K} + C_6H_{13}\overset{\overset{CH_3}{|}}{C}HOH + C_2H_5OH$$

proved to be optically inactive. The reaction was repeated several times, with changes in the temperature, the ratio, and order of addition of the reactants, but in each case the salts showed no optical activity. One reason for the optical inactivity of the salts may be deduced by a consideration of the factors, which determine whether or not salts of secondary nitro compounds may be optically active.

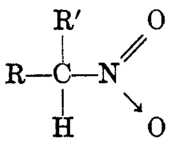
In order to explain both the optical properties and conductivity data on salts of nitro compounds, it was suggested[2] that two forms of the salt



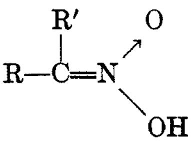
VIII



IX



X



XI

exist, VIII and IX, the latter being the form responsible for the optical activity. Treatment of the salt with acid converts the optically active

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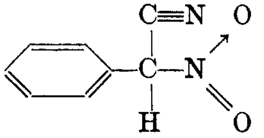
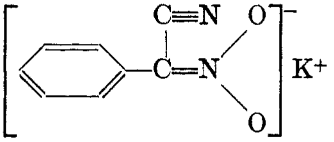
[4] Mills, *J. Soc. Chem. Ind.*, **51**, 750 (1932).

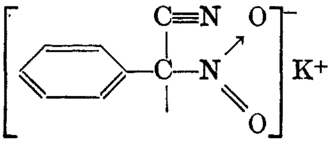
anion (IX), into the optically active nitro form (X), whereas the aci-ion (VIII), yields the inactive aci-modification (XI). Optical activity of the salts is, therefore, dependent on which form of the salt is produced, and this would be determined in part by the character of the R groups. If they are saturated alkyl groups, as in the case of 2- nitrobutane and 2-nitroöctane, both forms would be about equally stable. However, if the R groups contain unsaturated linkages, then forces tending to produce conjugated systems come into play. In the case of phenylnitroacetonitrile (XII),



XII



XIII



XIV

the salt with the aci-structure (XIII) contains a conjugated system, whereas the carbanion (XIV) does not. From studies on many organic reactions, it is known that tautomeric changes and rearrangements tend to produce the conjugated system. Stated in different terms, the resonance of the electrons in these salts would be such as to favor XIII and make the existence of XIV in an optically stable condition rather improbable. No such resonance is possible in the purely aliphatic nitro compounds.

Since the salts were optically inactive, it seems reasonable that, under the conditions of the experiment, the salt possessed the conjugated aci-structure, (XIII). Further evidence bearing out this point was obtained by the alkylation and acylation of this salt.

ALKYLATION

The term alkylation, as used in the present discussion, refers to the treatment of the sodium, potassium, or silver salt of the nitro compound with an alkyl halide. The aci-ion, (VIII), would be expected to produce *O*-alkylation, leading to a nitronic ester; and the carbanion (IX) should produce *C*-alkylation, forming a tertiary nitro compound.

Previous studies on the alkylation of silver salts of secondary nitro compounds have shown that both types of alkylation occur, but the data are somewhat confusing. Nef[5] alkylated 1,1-dinitroethane, and obtained

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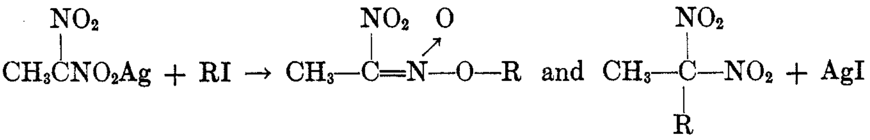
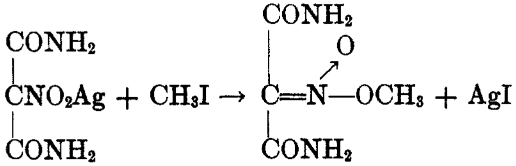
[5] NEF, *Ann.*, **280**, 263 (1894).

both *O*- and *C*-alkylation, whereas Duden[6] reported only *C*-alkylation in the case of dinitromethane.



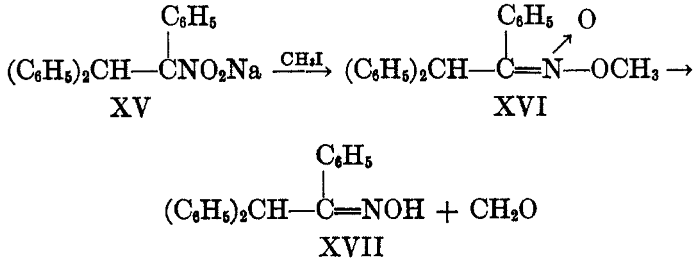
$$CH_3\overset{\displaystyle NO_2}{\overset{|}{C}}NO_2Ag + RI \rightarrow CH_3{-}\overset{\displaystyle NO_2}{\overset{|}{C}}{=}\overset{\displaystyle O}{\overset{\nearrow}{N}}{-}O{-}R \text{ and } CH_3{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle NO_2}{|}}{C}}{-}NO_2 + AgI$$

Ratz[7a] on the other hand, obtained *O*-alkylation upon treatment of silver nitromalonamide with methyl iodide, but Ulpiani[7b] reports *C*-alkylation in the case of ammonium nitromalonic ester.



$$\underset{\underset{\displaystyle CONH_2}{|}}{\overset{\overset{\displaystyle CONH_2}{|}}{C}}NO_2Ag + CH_3I \rightarrow \underset{\underset{\displaystyle CONH_2}{|}}{\overset{\overset{\displaystyle CONH_2}{|}}{C}}{=}\overset{\displaystyle O}{\overset{\nearrow}{N}}{-}OCH_3 + AgI$$

Kohler and Stone[8] obtained no evidence for *C*-alkylation upon treating sodium triphenylnitroethane (XV) with methyl iodide. The product was the oxime (XVII), indicating *O*-alkylation to the nitronic ester (XVI) as the intermediate, since this decomposition of the nitronic ester to the oxime and aldehyde or ketone had been shown to be characteristic of this structure.[9] Nenitzescu and Isacescu[10] obtained fluorenone oxime by alkylation of potassium 9-nitrofluorene, and later isolated the methyl nitronic ester. The silver salt of 2-bromo-9-nitrofluorene also undergoes *O*-alkylation to produce a nitronic ester.[3]



$$\underset{\text{XV}}{(C_6H_5)_2CH{-}\overset{\overset{\displaystyle C_6H_5}{|}}{C}NO_2Na} \xrightarrow{CH_3I} \underset{\text{XVI}}{(C_6H_5)_2CH{-}\overset{\overset{\displaystyle C_6H_5}{|}}{C}{=}\overset{\displaystyle O}{\overset{\nearrow}{N}}{-}OCH_3} \rightarrow$$

$$\underset{\text{XVII}}{(C_6H_5)_2CH{-}\overset{\overset{\displaystyle C_6H_5}{|}}{C}{=}NOH} + CH_2O$$

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[6] DUDEN, *Ber.*, **26**, 3008 (1893).

[7] (*a*) RATZ, *Monatsh.*, **25**, 55 (1904); (*b*) ULPIANI, *Atti. acad. Lincei, Rom.*, [5], **13**, II, 346 (1904).

[8] KOHLER AND STONE, *J. Am. Chem. Soc.*, **52**, 761 (1930).

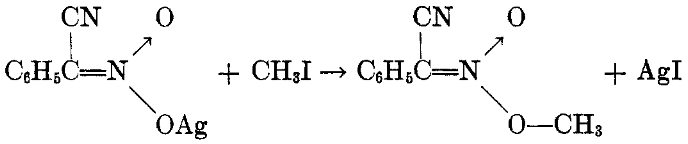
[9] ARNDT AND ROSE, *J. Chem. Soc.*, **1935**, 1.

[10] NENITZESCU AND ISACESCU, *Ber.*, **63**, 2484 (1930); *Bull. soc. chim. Rom.*, **14**, 53 (1932).

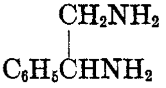
Wislicenus and Elvert[11] obtained the nitronic ester from the silver salt of *p*-bromophenylnitroacetonitrile, whereas Wieland and Höchtlen[12] report *C*-alkylation of phenylnitroacetonitrile by treatment of the silver salt with diphenylbromomethane and triphenylchloromethane.

A survey of these previous studies shows that there are no consistent differences obtained when the sodium, potassium or silver salts are used, and no correlation with the presence or absence of conjugated systems.

In the present investigation it was found that the action of methyl iodide on silver phenylnitroacetonitrile (XVIII) at 0° produced the nitronic ester (XIX). The structure of this nitronic exter was established by catalytic reduction of it in acetic anhydride. The reduction product was the diacetyl derivative of phenylethylenediamine (XX). If *C*-alkylation had taken place, the reduction product should have been 2-phenyl-1,2-propylenediamine (XXI). The diacetyl derivative (XXII) of phenylethylene diamine (XX) was characterized by comparison with a synthetic sample prepared by the following reactions:

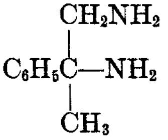


XVIII XIX



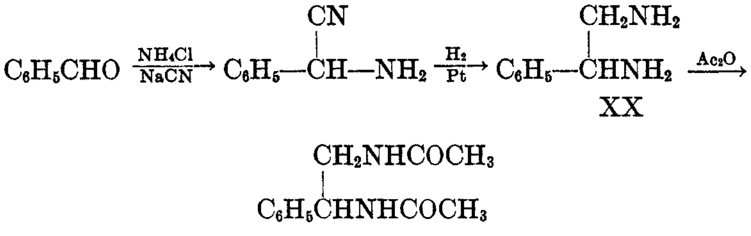
$$C_6H_5CH(NH_2)CH_2NH_2$$

XX



$$C_6H_5C(CH_3)(NH_2)CH_2NH_2$$

XXI



$$C_6H_5CHO \xrightarrow[NaCN]{NH_4Cl} C_6H_5\text{—}CH(CN)\text{—}NH_2 \xrightarrow[Pt]{H_2} C_6H_5\text{—}CH(NH_2)CH_2NH_2 \xrightarrow{Ac_2O} C_6H_5CH(NHCOCH_3)CH_2NHCOCH_3$$

XX

XXII

Treatment of silver phenylnitroacetonitrile with benzyl chloride produced a very unstable nitronic ester (XXIII) which could not be isolated,

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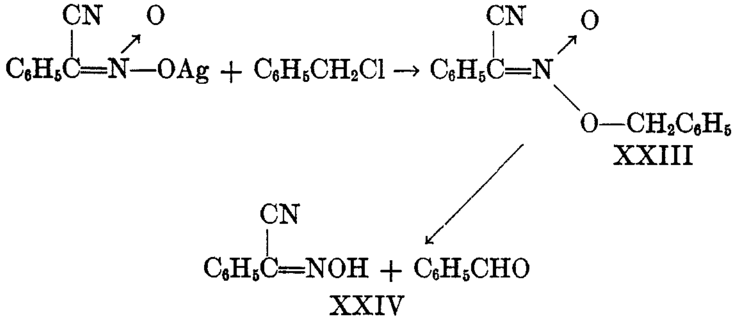
[11] WISLICENUS AND ELVERT, *Ber.*, **41**, 4121 (1908).

[12] WIELAND AND HÖCHTLEN, *Ann.*, **505**, 237 (1933).

since it immediately decomposed into benzoyl cyanide oxime (XXIV) and benzaldehyde. The latter was characterized by its phenylhydrazone, and

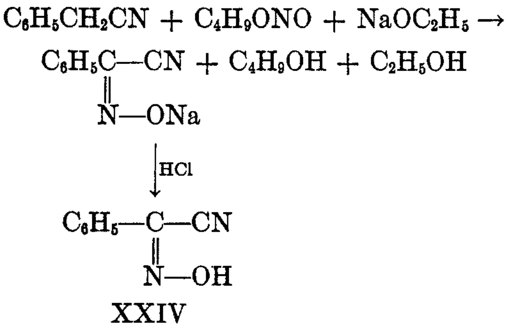


$$C_6H_5\overset{\overset{CN}{|}}{C}=\overset{\overset{O}{\nearrow}}{N}-OAg + C_6H_5CH_2Cl \rightarrow C_6H_5\overset{\overset{CN}{|}}{C}=\overset{\overset{O}{\nearrow}}{N}\searrow O-CH_2C_6H_5 \quad \text{XXIII}$$

$$\swarrow$$

$$\underset{\text{XXIV}}{C_6H_5\overset{\overset{CN}{|}}{C}=NOH} + C_6H_5CHO$$

the former by comparison with an authentic sample synthesized as follows:



$$C_6H_5CH_2CN + C_4H_9ONO + NaOC_2H_5 \rightarrow$$

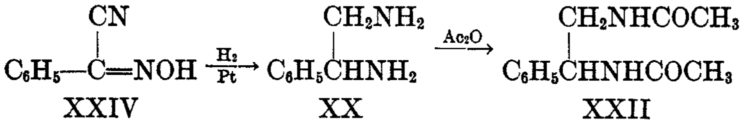
$$C_6H_5\underset{\underset{N-ONa}{\|}}{C}-CN + C_4H_9OH + C_2H_5OH$$

$$\downarrow HCl$$

$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-CN$$

XXIV

Catalytic reduction of benzoyl cyanide oxime (XXIV) in acetic anhydride yielded the diacetyl derivative (XXII) of phenylethylenediamine (XX). This reduction not only confirms the structure of the benzoyl



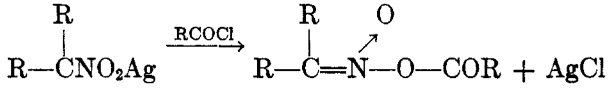
$$\underset{\text{XXIV}}{C_6H_5-\overset{\overset{CN}{|}}{C}=NOH} \xrightarrow[Pt]{H_2} \underset{\text{XX}}{C_6H_5\overset{\overset{CH_2NH_2}{|}}{C}HNH_2} \xrightarrow{Ac_2O} \underset{\text{XXII}}{C_6H_5\overset{\overset{CH_2NHCOCH_3}{|}}{C}HNHCOCH_3}$$

cyanide oxime, but furnishes another independent synthesis of diacetylphenylethylenediamine (XXII) described above.

In both of these alkylations the alkyl group appeared on the oxygen atom, and not on the carbon atom, indicating that the silver salt of phenylnitroacetonitrile had the structure XVIII derived from XIII; *i.e.*, the conjugated aci-structure was the preferred form. The only indication that the other structure, XIV, may also be present is the *C*-alkylation obtained by Wieland and Höchtlen[12] by the action of diphenylbromomethane and triphenylchloromethane on the silver salt. This reaction is now being studied.

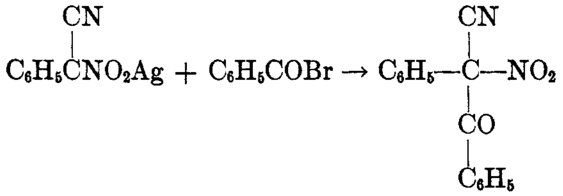
ACYLATION

Several investigators have acylated the salts of secondary nitro compounds. Nef[5] obtained the acyl derivatives of silver 1,1-dinitroethane, and Nenitzescu and Isacescu[10] prepared the acetyl and benzoyl derivatives



$$R_2CNO_2Ag \xrightarrow{RCOCl} R_2C{=}N(\rightarrow O){-}O{-}COR + AgCl$$

of 9-nitrofluorene from the potassium 9-nitrofluorene. These acyl derivatives were indicated as having the acyl group attached to oxygen, but no proof of structure was given other than hydrolysis. Wieland and Höchtlen[12] treated silver phenylnitroacetonitrile with benzoyl bromide, and ascribed the structure XXV to the acyl derivative, which is an example

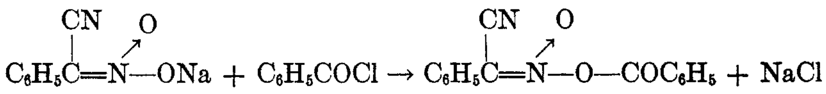


$$C_6H_5C(CN)NO_2Ag + C_6H_5COBr \rightarrow C_6H_5{-}C(CN)(NO_2){-}CO{-}C_6H_5$$

XXV

of *C*-acylation; in fact, it is the only example of *C*-acylation of a salt of a secondary nitro compound. The only evidence for its structure was the fact that it was readily cleaved by alkalies to sodium benzoate and sodium phenylnitroacetonitrile. The structure XXV would certainly be expected to be unstable to alkalies, but the alternative structure XXVI, the *O*-acylation product, would also cleave upon treatment with alkali. Hence, alkaline hydrolysis cannot be used as a method for distinguishing between the two possibilities.

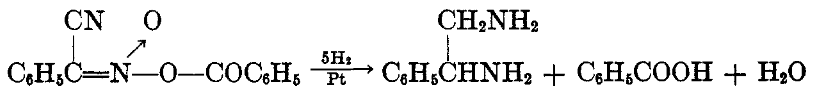
In the present work, the benzoyl derivative of phenylnitroacetonitrile was prepared by the action of benzoyl chloride on both the sodium and silver salts of the nitro compound. Its structure was definitely established



$$C_6H_5C(CN){=}N(\rightarrow O){-}ONa + C_6H_5COCl \rightarrow C_6H_5C(CN){=}N(\rightarrow O){-}O{-}COC_6H_5 + NaCl$$

XXVI

as that of the *O*-acylated compound (XXVI) by catalytic reduction with platinum and hydrogen at room temperature in acetic anhydride. The reduction products were shown to be benzoic acid and the diacetyl deriva-

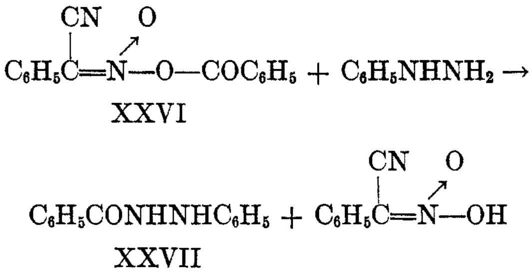


$$C_6H_5C(CN){=}N(\rightarrow O){-}O{-}COC_6H_5 \xrightarrow[Pt]{5H_2} C_6H_5CH(CH_2NH_2)NH_2 + C_6H_5COOH + H_2O$$

XX

tive (XXII) of phenylethylenediamine (XX), previously obtained by catalytic reduction of the methyl nitronic ester. These reduction products could not be obtained from a structure such as XXV under the mild conditions employed for the reduction. The water produced in the reduction was taken up by the acetic anhydride used as the solvent, hence hydrolysis of XXV and then reduction to XX is precluded.

Moreover, treatment of the benzoyl derivative in chloroform solution with phenylhydrazine at 20° did not produce a hydrazone of the ketone (XXV), but instead cleaved the product to β-phenyl benzhydrazide (XXVII). This behavior is further evidence in favor of the *O*-benzoyl linkage, XXVI, since this structure is essentially that of a mixed anhydride of the nitronic acid and benzoic acid.



$$\underset{\text{XXVI}}{C_6H_5\overset{\overset{\displaystyle CN}{|}}{C}{=}\overset{\overset{\displaystyle O}{\nearrow}}{N}{-}O{-}COC_6H_5} + C_6H_5NHNH_2 \rightarrow$$

$$\underset{\text{XXVII}}{C_6H_5CONHNHC_6H_5} + C_6H_5\overset{\overset{\displaystyle CN}{|}}{C}{=}\overset{\overset{\displaystyle O}{\nearrow}}{N}{-}OH$$

The benzoyl derivative of phenylnitroacetonitrile, therefore, possesses the structure XXVI, and, like the two alkyl derivatives, is derived from the aci-structure XIII.

EXPERIMENTAL

Potassium salt of phenylnitroacetonitrile.—One gram of potassium was dissolved in 10 cc. of absolute alcohol and 30 cc. of absolute ether. The solution was cooled to 0°, and a solution, consisting of 3 g. of benzyl cyanide, 6.7 g. *dl*-2-octyl nitrate, 25 cc. absolute ether and 25 cc. petroleum ether was added slowly with stirring. The potassium salt started to precipitate after about one-third of the solution had been added. The precipitated salt was filtered, washed twice with 30-cc. portions of equal parts of ordinary ether and low-boiling petroleum ether, and finally recrystallized by dissolving in 30 cc. of methyl alcohol, then pouring into a solution composed of 50 cc. of ordinary ether and 100 cc. of low-boiling petroleum ether. The slightly yellow potassium salt, obtained in yields of 80 per cent. of the theoretical amount, decomposed at 265°.

Anal. Calc'd for $C_8H_5KN_2O_2$: K, 19.54. Found: K, 19.27.

The above procedure was repeated, using both *d*-2-octyl nitrate ($[\alpha]_D^{25}$ +15.37°) and *l*-2-octyl nitrate ($[\alpha]_D^{25}$ −15.00°), prepared as previously described, and in each case absolute alcohol solutions of the salts showed no sign of optical activity. The order of mixing the reactants was changed, and also the molar ratio, but no optically active salts were produced.

Salt from *d*-2-octyl nitrate:

Anal. Calc'd for $C_8H_5KN_2O_2$: K, 19.54. Found: K, 19.45.

Salt from *l*-2-octyl nitrate:

Anal. Calc'd for $C_8H_5KN_2O_2$: K, 19.54; N, 14.00.
Found: K, 19.52; N, 14.27.

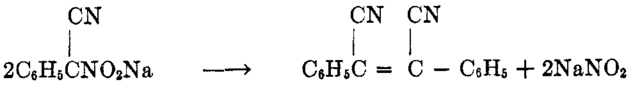
On acidification of a cold, dilute, aqueous solution of the potassium salt with acetic acid, the aci-form separated as a yellow, pasty solid. A solution of this solid in alcohol gave a brownish color with ferric chloride. The aci-form, on standing, changed to an oil, the free nitro form, which did not give a color with ferric chloride. This oil was extracted with ether, the solution dried and the ether distilled. An alcohol solution of the residual phenylnitroacetonitrile showed no optical activity.

Treatment of an absolute alcohol solution of the potassium salt from the preparations in which *d*- and *l*-2-octyl nitrate were used with one mole of bromine produced an oil which Wislicenus and Schafer[13] have shown to be phenylbromonitroacetonitrile. An alcohol solution of this derivative was also optically inactive.

Attempted alkylation of potassium and sodium salts.—Treatment of the potassium or sodium salts of phenylnitroacetonitrile with alkyl halides gave no alkyl derivatives. Decomposition products were produced, among which were benzoyl cyanide oxime and the aldehyde corresponding to the alkyl group. However, treatment of 5 g. of the sodium salt with 4 g. of methyl sulfate and 1.3 g. of sodium hydroxide in 75 cc. of methanol at room temperature for three weeks gave a crystalline precipitate. Recrystallization produced yellow needles melting at 161–162°. This compound was finally identified as dicyanostilbene,[14] and the melting point of a mixture with a synthetic sample showed no depression.

Anal. Calc'd for $C_{16}H_{10}N_2$: N, 12.17. Found: N, 12.00.

This compound resulted from the decomposition of the sodium salt.



$$2C_6H_5\overset{CN}{\overset{|}{C}}NO_2Na \longrightarrow C_6H_5\overset{CN}{\overset{|}{C}} = \overset{CN}{\overset{|}{C}} - C_6H_5 + 2NaNO_2$$

Silver salt of phenylnitroacetonitrile.—To 7 g. of the potassium salt dissolved in 250 cc. of distilled water was slowly added, with stirring, an aqueous solution of silver nitrate prepared by dissolving 6 g. of silver nitrate in 100 cc. of water. The precipitated salt was washed three times with alcohol, and finally with ether. A yield of 9 g., which was nearly quantitative, was obtained.

Methyl aci-*phenylnitroacetonitrile.*—To 12 g. of the silver salt was added ten times the theoretical amount (68 g.) of methyl iodide, diluted with an equal volume of ether. During the addition of the methyl iodide, the pasty mass was stirred and cooled in an ice-salt bath. After standing one and one-half hours at this temperature, the reaction mixture was shaken for fifteen hours at room temperature. The excess methyl iodide and the ether solution of the methylated compound were filtered from the silver iodide. The solvent and methyl iodide were removed under vacuum at room temperature, leaving a heavy oil. Ten cubic centimeters of ether was added and warmed slightly. On cooling in an ice-salt mixture and diluting with low-boiling petroleum ether, the product crystallized in the form of colorless needles. These darkened on standing, and finally turned to a heavy oil. The crystals melted at 41 to 42°, and weighed 3.5 g., which corresponds to a yield of 50 per cent.

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[13] Wislicenus and Shafer, *Ber.*, **41**, 4169 (1908).

[14] Wislicenus and Enders, *ibid.*, **35**, 1755 (1902).

Anal. Calc'd for $C_9H_8N_2O_2$: N, 15.91. Found: 16.10.

The nitronic ester was unstable, and decomposed on standing to form an oil which possessed an odor of formaldehyde. This type of decomposition has been noted by Nenitzescu and Demitrie,[10] and by Arndt and Rose.[9]

Catalytic reduction of methyl aci-*phenylnitroacetonitrile.*—A solution of 1.5 g. of the nitronic ester in 35 cc. of acetic anhydride and 0.15 g. of platinum oxide were shaken with hydrogen under three atmospheres pressure. After fifteen hours, five molecular equivalents of hydrogen had been absorbed. The mixture was filtered, the filtrate poured into 50 cc. of 30 per cent. sodium hydroxide solution, and the product extracted with chloroform. Evaporation of the chloroform left an oil which crystallized on standing. Recrystallization from ethyl acetate gave colorless crystals which melted sharply at 155 to 155.5°.

Anal. Calc'd for $C_{12}H_{16}N_2O_2$: N, 12.72. Found: 12.30.

Since the melting point of the diacetyl derivative of phenylethylenediamine is given as 152° in the literature,[15] a sample was synthesized for comparison.

Synthesis of diacetyl derivative of phenylethylenediamine.—The intermediate phenylaminoacetonitrile was prepared by vigorously stirring a mixture of 20 g. of benzaldehyde, 50 g. of sodium cyanide and 54 g. of ammonium chloride dissolved in 350 cc. of water. After three hours, an equal volume of water was added, and the oil was extracted with two 75-cc. portions of benzene. The combined benzene extracts were shaken with two 75-cc. portions of hydrochloric acid (1:1), which were then poured into 500 cc. of 20 per cent. sodium hydroxide solution. The phenylaminoacetonitrile was extracted with ether, and the ether evaporated. Nine grams of the product was dissolved in 75 cc. of acetic anhydride and reduced with hydrogen in the presence of 0.26 g. of platinum oxide. The reduction mixture was filtered, and the filtrate poured into 100 cc. of 30 per cent. sodium hydroxide solution to decompose the excess acetic anhydride. Extraction with chloroform by distillation gave a gummy solid. After several recrystallizations from ethyl acetate, colorless crystals which melted at 155–155.6° were obtained. The melting point of a mixture with the diacetyl phenylethylenediamne, obtained by reduction of the methyl nitronic ester described above, showed no depression.

Anal. Calc'd for $C_{12}H_{16}N_2O_2$: N, 12.72. Found: N, 12.30.

Benzylation of the silver nitro salt.—By warming at 40–50°, a suspension of 8 g. of the silver salt in 7.5 cc. of benzyl chloride and 15 cc. of ether for one and one-half hours, then filtering and evaporating the solvent at diminished pressure, an oily residue was obtained. This residue was taken up in 10 cc. of low-boiling petroleum ether and cooled in an ice-salt bath. The crystals which separated were purified by recrystallization from hot water. Colorless plates which melted at 129° were obtained. The melting point of a mixture with benzoyl cyanide oxime, prepared as described below, showed no depression.

Anal. Calc'd for $C_8H_6N_2O$: N, 19.19. Found: N, 19.19.

Treatment of the petroleum ether solution from the above crystallization with phenylhydrazine gave the phenylhydrazone of benzaldehyde, which melted at 156.5°, and the melting point of a mixture with an authentic specimen showed no depression.

Benzoyl cyanide oxime.—To 2.3 g. of freshly cut sodium in 25 cc. of absolute alcohol was added 11.7 g. of benzyl cyanide, followed by 10.3 g. of butyl nitrite. The yellow sodium salt immediately precipitated and, after thirty minutes, it was filtered,

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[15] FEIST AND ARNSTEIN, *ibid.*, **28**, 426, 3172 (1895).

washed with ether and dried in a desiccator. The yield was 8.5 g. or 69 per cent of the theoretical. The free oxime was obtained by acidification of an aqueous solution of the salt. After recrystallization from water, the crystals melted at 129.5°, which checked the value given by Zimmerman.[16]

Reduction of benzoyl cyanide oxime.—A solution of 3.7 g. of the oxime in 35 cc. of acetic anhydride was shaken with 0.3 g. of platinum oxide and hydrogen under pressure. The reduction proceeded very slowly, and forty-eight hours was required for absorption of four molecular equivalents of hydrogen. A very low yield of the diacetyl derivative of phenylethylene diamine was isolated by the same procedure given above and found to melt at 155–155.5°.

Benzoylation of the salts of phenylnitroacetonitrile.—Three methods were used in order to obtain the benzoyl derivative.

(*A*) To 1.25 g. of the sodium nitro salt in 10 cc. of water was added 2 cc. of benzoyl chloride. After shaking for a few minutes and keeping the solution alkaline by addition of 10 per cent. sodium hydroxide solution, the product was filtered, washed with alcohol and recrystallized from benzene and low-boiling petroleum ether. The colorless solid melted at 116°, while the recorded melting point[12] is 118°.

Anal. Calc'd for $C_{15}H_{10}N_2O_3$: N, 10.51. Found: N, 1055.

(*B*) To 5 g. of the sodium nitro salt, suspended in 25 cc. of dry benzene, was added 4 cc. of benzoyl chloride. After shaking for thirty-six hours, the filtrate was evaporated under diminished pressure, and the remaining 15 cc. of solution was poured into low-boiling petroleum ether. The precipitate, after recrystallization from ethyl acetate, melted at 116° and gave no depression in melting point when mixed with the product prepared above.

(*C*) The best yield of the benzoylated derivative was obtained as follows. To 8 g. of the silver salt, suspended in 50 cc. of dry benzene, was added 4.5 g. of benzoyl chloride. After vigorous stirring for three hours, the benzene was filtered, concentrated under diminished pressure, and the yellow product recrystallized from ethyl acetate. The yield of colorless prisms melting with decomposition at 116° was 6.8 g., or 85 per cent. of the theoretical amount. The melting points of mixtures with the benzoylated derivatives described above gave no depression.

Properties of the benzoyl derivative.—This compound failed to yield an oxime or semicarbazone, even after standing three months with the reagents.

Treatment of a chloroform solution of the benzoyl derivative with phenylhydrazine gave pale yellow crystals of a compound which melted at 170° after recrystallization from alcohol. This product was identified as β-phenylbenzhydrazide by means of a mixture melting-point comparison with an authentic sample prepared according to the method of Fischer.[17]

Treatment of the benzoyl derivative with warm, 5 per cent. sodium hydroxide hydrolyzed it to benzoic acid and phenylnitroacetonitrile.

Catalytic reduction of the benzoyl derivative.—A solution of 4 g. of the benzoyl-*aci*-phenylnitroacetonitrile in 35 cc. of acetic anhydride absorbed five molecular equivalents of hydrogen in nine hours when shaken with hydrogen and 0.25 g. of platinum oxide. The catalyst was removed by filtration, and the solution was poured into 50 cc. of 30 per cent. sodium hydroxide solution. The product was extracted with ether, and the ether was removed by distillation. Recrystallization of the residue from benzene gave colorless crystals of diacetylphenylethylenediamine, which melted at

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[16] ZIMMERMAN, *J. prakt. Chem.*, **66**, 353 (1902).

[17] FISCHER, *Ann.*, **190**, 125 (1877).

155–155.5°, and did not depress the melting point of the samples of this compound described above.

The above sodium hydroxide solution was acidified and cooled. Crystals of benzoic acid, melting at 120°, were obtained.

SUMMARY

Treatment of benzyl cyanide with *d*- and *l*-2-octyl nitrates in the presence of potassium or sodium ethoxide yielded the potassium or sodium salts of phenylnitroacetonitrile, which were optically inactive.

The silver salt of phenylnitroacetonitrile reacted with methyl iodide to yield the methyl nitronic ester whose structure was established by catalytic reduction to phenylethylenediamine.

Benzyl chloride and the silver salt yielded benzoyl cyanide oxime and benzaldehyde.

Both the sodium and silver salts reacted with benzoyl chloride to produce a benzoyl derivative whose structure as an oxygen acylated derivative was established by catalytic reduction to benzoic acid and phenylethylenediamine.