CXIII.—*The Action of Benzenediazonium Chloride on β-Nitroethyl Alcohol and its Derivatives.*

By Edward Charles Snell Jones and James Kenner.

In a previous paper (J., 1928, 2697) it was pointed out that a large proportion of the reactions of nitroso-compounds can be referred to their tendency to pass into oximino-derivatives, and the perception of this, illuminating the nature of Piloty and Ruff's synthesis of glycerol, permitted the generalisation that compounds in which a nitroso- and a methylol group are attached to the same quaternary carbon atom will decompose immediately they are produced, with the formation of an oximino-compound and formaldehyde :

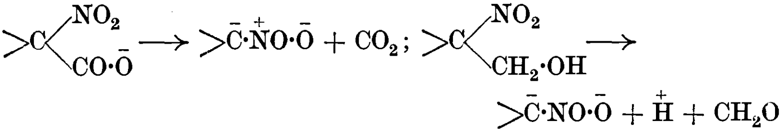
$$>C(NO)\cdot CH_2\cdot OH \longrightarrow >C{:}NOH + CH_2O.$$

Considering now the methylol rather than the nitroso-group, the reaction in question corresponds to the loss of carbon dioxide undergone when, for example, methylacetoacetic and *iso*succinic acids are treated with nitrous acid :

$$COMe\cdot CHMe\cdot CO_2H \longrightarrow [COMe\cdot CMe(NO)\cdot CO_2H] \longrightarrow COMe\cdot CMe{:}NOH + CO_2$$

$$CHMe(CO_2H)_2 \longrightarrow CMe(NO)(CO_2H)_2 \longrightarrow CMe(NOH)\cdot CO_2H + CO_2$$

Similarly the familiar decomposition of the nitroacetate ion, and its homologues, into the nitro-compound and carbon dioxide corresponds to the elimination of formaldehyde from derivatives of β-nitroethyl alcohol under the influence of sodium methoxide (Schmidt and Wilkendorf, *Ber.*, 1919, **52**, 389) :



$$>C\begin{array}{l}\diagup NO_2\\ \diagdown CO\cdot\overset{-}{O}\end{array}\longrightarrow\ >\overset{-}{C}\cdot\overset{+}{N}O\cdot\overset{-}{O}+CO_2;\ >C\begin{array}{l}\diagup NO_2\\ \diagdown CH_2\cdot OH\end{array}\longrightarrow$$

$$>\overset{-}{C}\cdot NO\cdot\overset{-}{O}+\overset{+}{H}+CH_2O$$

A similar correspondence was observed when the sodium salts of β-nitroethyl alcohol and its derivatives were treated with benzenediazonium chloride in place of nitrous acid. For instance, the *ω-nitroacetaldehydephenylhydrazone* (I) resulting from the interaction of the sodium salt of nitroethane with benzenediazonium chloride was also obtained by the action of the same reagent on the sodium salt of β-nitropropyl alcohol :

$$OH\cdot CH_2\cdot\overset{-}{C}Me\cdot\overset{+}{N}O\cdot\overset{-}{O}\longrightarrow OH\cdot CH_2\cdot CMe(N\colon NPh)\cdot NO_2\longrightarrow$$

$$\text{(I.) } CMe(N\cdot NHPh)\cdot NO_2\longleftarrow\overset{-}{C}HMe\cdot\overset{+}{N}O\cdot\overset{-}{O}$$

The formaldehyde produced was identified as usual in the form of methylene*bis*-β-naphthol.

Similarly, β-nitrotrimethylene glycol was converted into a compound corresponding in composition to ω-nitroglycollaldehydephenylhydrazone (II) :

$$(CH_2\cdot OH)_2\overset{-}{C}\cdot\overset{+}{N}O\cdot\overset{-}{O}\longrightarrow\text{(II.) } OH\cdot CH_2\cdot C(N\cdot NHPh)\cdot NO_2+CH_2O.$$

In this instance, however, the product melted at 117°, whereas Demuth and Meyer record a melting point of 104° for the compound obtained from β-nitroethyl alcohol itself (*Annalen*, 1890, **256**, 30) and a repetition of their work confirmed their result with the exception that the melting point was raised to 108°. Whereas the specimen of Demuth and Meyer's substance was orange-red and became discoloured after a day or two at the ordinary temperature, (II) was yellow and remained unchanged for a considerable period. Each compound exhibited the normal molecular weight in chloroform solution, and satisfied Bülow's reaction for hydrazones (*Annalen*, 1886, **236**, 195). Furthermore, (II) was converted into its isomeride by treatment with aqueous sodium hydroxide or with methylalcoholic sodium methoxide, followed by acidification, whereas the isomeride was recovered unchanged after similar treatment. We therefore regard them as stereoisomerides, assigning the *cis*-configuration to the lower-melting isomeride, and thus relating its instability to that of the nitrolic acids, which are also regarded as *cis*-compounds (Graul and Hantzsch, *Ber.*, 1898, **31**, 2863).

In no other of the cases investigated and referred to later, did we isolate definite stereoisomerides, although there was some evidence of their formation: for instance, the hydrazones (III) and (IV) were isolated in the first place as red oils, which crystallised only very slowly when inoculated with the pure material (compare also Lapworth, J., 1903, **83**, 1114), but were at once obtained in the solid condition by solution in alkali and precipitation by acid:

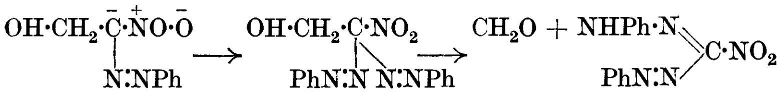
$$OH\cdot CH_2\cdot CHEt\cdot NO_2 \longrightarrow CEt(N\cdot NHPh)\cdot NO_2 \quad \text{(III.)}$$

$$OH\cdot CH_2\cdot CHPr^{a}\cdot NO_2 \longrightarrow CPr^{a}(N\cdot NHPh)\cdot NO_2 \quad \text{(IV.)}$$

$$COMe\cdot C(N\cdot NHPh)\cdot CO_2C_{10}H_{19} \quad \text{(V.)}$$

Bamberger and Schmidt have described two forms of nitroformaldehydephenylhydrazone, melting respectively at 74·5° and 84·5° (*Ber.*, 1901, **34**, 2001), but since the two forms are interconvertible by treatment with solvents their relationship would seem to be of a physical rather than a chemical character. Moreover, in a repetition of the preparation of this compound from nitromethane we were able to raise the melting point to 92°.

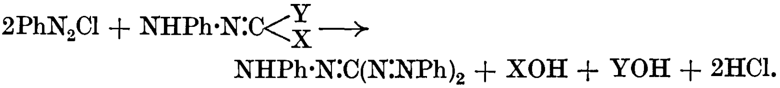
Although the hydrazone formula for the products of coupling nitro- and other reactive compounds with benzenediazonium chloride has probably been universally accepted since it was put forward by V. Meyer (*Ber.*, 1888, **21**, 11), this would appear to be the first occasion on which the stereoisomerism it involves has received definite experimental verification. The slow mutarotation of menthyl benzeneazoacetoacetate (V) observed by Lapworth (*loc. cit.*) is an indication of isomerism which might, however, be structural rather than spatial. The possibility of structural isomerism in fact is indicated by the behaviour of the above stereoisomeride towards alkali. For the transition of (II) into its isomeride must be regarded as indicating the formation from each of an anion (VI), in which the double bond of the hydrazone group has given place to a single bond. Further evidence on this point is supplied by the behaviour of the hydrazones towards benzenediazonium ions. Thus the formula (VI) shows a negative centre available for coupling:



$$OH\cdot CH_2\cdot\underset{N:NPh}{\overset{-}{C}}\cdot\overset{+}{N}O\cdot\overset{-}{O} \longrightarrow OH\cdot CH_2\cdot\underset{PhN:N\ \ N:NPh}{C}\cdot NO_2 \longrightarrow CH_2O + \begin{matrix}NHPh\cdot N\\PhN:N\end{matrix}\!\!>\!C\cdot NO_2$$

(VI.) (VII.) (VIII.)

In the light of the foregoing considerations, however, it is clear that the first product (VII) of such a reaction would at once pass into nitroformazyl (VIII) by the loss of formaldehyde. Indeed this series of changes was observed by Demuth and Meyer (*loc. cit.*) when they studied the interaction of the sodium salt of nitroethyl alcohol with benzenediazonium chloride, and, as we have found, occurs so readily that the nitroacetaldehydephenylhydrazone initially formed can be satisfactorily isolated only when the solution of sodium salt is added to that of the diazonium compound so that no opportunity is afforded for salt formation on the part of the hydrazone. Demuth and Meyer attributed their result to the presence in nitroethyl alcohol (prepared in the usual manner by means of silver nitrite) of a considerable proportion of nitroacetic acid, and suggested that it originated from the action of nitrous acid on the alcohol. This explanation was not challenged either by Bamberger (*Ber.*, 1892, **25**, 3201, 3547; 1894, **27**, 147, 155), who first assigned the correct constitution to nitroformazyl, or by von Pechmann (*Ber.*, 1892, **25**, 3190), who, simultaneously with Bamberger, made an extensive study of the displacement of other groups by the benzeneazo-group, according to the scheme:



$$2PhN_2Cl + NHPh{\cdot}N{:}C{<}^{Y}_{X} \longrightarrow NHPh{\cdot}N{:}C(N{:}NPh)_2 + XOH + YOH + 2HCl.$$

(X or Y = *e.g.*, $\cdot H, \cdot CO_2H, \cdot CHO, \cdot COMe, \cdot CO{\cdot}CO_2H$)

The course of this reaction is presumably analogous to that represented above by the formulæ (VI), (VII), and (VIII).

This property of the methylol group asserts itself in still another direction. For although β-hydroxy-acids in general readily undergo loss of water with formation of αβ-unsaturated acids, β-hydroxy-αα-dimethylpropionic acid, lacking an α-hydrogen atom, undergoes in part a thermal decomposition (Blaise, *Compt. rend.*, 1902, **134**, 552; Marcilly, *Bull. Soc. chim.*, 1904, **31**, 120) strictly analogous to that of the malonic acids and of various aldols: *

$$OH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2H \longrightarrow CH_2O + CHMe_2{\cdot}CO_2H$$
$$CO_2H{\cdot}CMe_2{\cdot}CO_2H \longrightarrow CO_2 + CHMe_2{\cdot}CO_2H$$

Similarly, by analogy with the decomposition of nitroacetic acid into nitromethane and carbon dioxide, it might be expected that the thermal decomposition of the hydrazone (II) and its isomeride would, in part, follow the course:

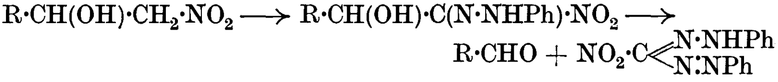
$$OH{\cdot}CH_2{\cdot}C(N{\cdot}NHPh){\cdot}NO_2 \longrightarrow CH_2O + CH(N{\cdot}NHPh){\cdot}NO_2$$

In the case of the *trans*-isomeride, there is no difficulty in observing the production of formaldehyde, but careful regulation of the temperature is requisite in the case of the *cis*-compound to enable the

* [Added to proof.] The thermal decomposition of ethyl di(hydroxymethyl)-malonate (Welch, this vol., p. 257) is a further example of this reaction.

odour of formaldehyde to be detected before the main portion of the material undergoes a complete decomposition, doubtless analogous to that of the nitrolic acids into nitrogen peroxide, nitrogen, and carboxylic acids.

The thermal decomposition of β-hydroxy-acids already mentioned is also exhibited by higher acids, containing alkylol in place of methylol groups (compare, for example, Beilstein's " Handbuch der Organischen Chemie," 4th edition, III, pp. 330—353), and accordingly we have found that quite generally the saturated group X·CH·OH can be displaced from nitro-compounds in the same manner as the unsaturated groups already enumerated. Thus the reactions represented by the following scheme have been carried out in a number of cases, the ultimate product in each instance being nitroformazyl :

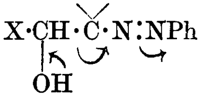


$$R\cdot CH(OH)\cdot CH_2\cdot NO_2 \longrightarrow R\cdot CH(OH)\cdot C(N\cdot NHPh)\cdot NO_2 \longrightarrow R\cdot CHO + NO_2\cdot C{<}\begin{matrix}N\cdot NHPh\\ N{:}NPh\end{matrix}$$

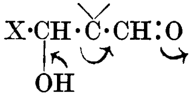
($R = Me, Et, Pr^{\alpha}, CHMe_2\cdot CH_2, Ph, CCl_3$.)

In each case the intermediate hydrazone was isolated and shown to be recovered unchanged from its solution in alkali.

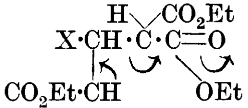
A comparison of (IX), (X), and (XI) shows that the decomposition of the product initially formed from (IX) is formally analogous to the reversals of the aldol condensation (compare, for example, Houben–Weyl, " Methoden der Organischen Chemie," 2nd edition, 1922, **2**, 466) and the Michael reaction (compare Knoevenagel, *Annalen*, 1894, **285**, 27 ; Kohler and Conant, *J. Amer. Chem. Soc.*, 1917, **39**, 1411) :



(IX.)



(X.)



(XI.)

This comparison assists in substantiating the view that in (X) and (XI), as well as in the thermal decomposition of malonic acids, the initiation of the decomposition is due to an effect transmitted from the carbonyl oxygen atom (compare Cooper, Ingold, and Ingold, J., 1926, 1870), just as in the case of (IX) it is clearly determined by the nitrogen atom attached to the phenyl group. At the same time, however, it must not be overlooked that the cyanohydrins, α-hydroxy-acids, and, quite generally, compounds of the type X·CH(OH)Y tend to decompose into X·CHO and HY, and that the reversal of the aldol change can be formulated in this manner.

There is also an evident analogy between the aldol condensation and that of aldehydes with nitro-compounds. Correspondingly, we have found that with increase in complexity of the groups X and Y the stability of the compound $X{\cdot}CH(OH){\cdot}CHY{\cdot}NO_2$ towards alkali diminishes, as has been observed in the case of aldols. For instance, whereas the methylol derivatives prepared from nitroethane, α-nitropropane, and α-nitrobutane are convertible into their sodium salts, analysis of those prepared from the ethylol derivatives shows that *γ-nitropentan-β-ol* (XII) and *γ-nitrohexan-β-ol* (XIII) suffer decomposition by alkali:

$$\begin{aligned} Me{\cdot}CH(OH){\cdot}CHEt{\cdot}NO_2 \text{ (XII.)} &\longrightarrow Me{\cdot}CHO + CHEt{:}NO_2Na \\ Me{\cdot}CH(OH){\cdot}CHPr^{a}{\cdot}NO_2 \text{ (XIII.)} &\longrightarrow Me{\cdot}CHO + CHPr^{a}{:}NO_2Na \\ OH{\cdot}CH_2{\cdot}CHEt{\cdot}NO_2 \text{ (XIV.)} &\longrightarrow OH{\cdot}CH_2{\cdot}CEt{:}NO_2Na \end{aligned}$$

Under the same conditions, however, the desired sodium salt was obtained from *β-nitrobutyl alcohol* (XIV).

These various salts, on treatment with benzenediazonium chloride, yielded hydrazones in accordance with the principles already discussed.

EXPERIMENTAL.

ω-Nitroacetaldehydephenylhydrazone from β-Nitropropyl Alcohol.—A solution of the sodium salt of β-nitropropyl alcohol (J., 1928, 2697) (12·7 g.) in water (125 c.c.) was gradually added to a solution prepared from aniline (9·3 g.), water (125 c.c.), hydrochloric acid (*d* 1·17; 22 c.c.), and sodium nitrite (6·9 g.). The product (17 g.), isolated by extraction with ether, crystallised from methyl alcohol in yellow plates, m. p. 149° (Found: C, 53·5; H, 5·15. Calc. for $C_8H_9O_2N_3$: C, 53·6; H, 5·1%). By the procedure previously described (*loc. cit.*), formaldehyde in the aqueous liquor was identified in the form of methylene*bis*-β-naphthol, m. p. 205°, which did not depress the melting point of an authentic specimen.

The phenylhydrazone was also directly prepared for purposes of comparison by gradual addition of a solution of nitroethane (7·5 g.) and sodium hydroxide (4 g.) in water (100 c.c.) to a diazonium solution prepared as above. The product (16·2 g.) also melted at 149° (Bamberger, *Ber.*, 1898, **31**, 2629, gives 141—142°) and did not depress the melting point of the above material. Each product was recovered unchanged from its solution in sodium hydroxide.

ω-Nitroglycollaldehydephenylhydrazones.—(1) When a solution of the sodium salt of β-nitrotrimethylene glycol (8·3 g.) in water (50 c.c.) was gradually added to a solution (50 c.c.) prepared from aniline (3·73 g.), hydrochloric acid (*d* 1·17; 8 c.c.), and sodium nitrite (2·76 g.), a crystalline separation (7·6 g.) was soon produced. On recrystallisation from acetone, stout yellow prisms (II), m. p. 117—118°, were obtained (Found: C, 49·0; H, 4·9; N, 21·6;

M, 187. $C_8H_9O_3N_3$ requires C, 49·2; H, 4·65; N, 21·6%; *M*, 195). Methylene*bis*-β-naphthol, prepared from the aqueous liquor as in the previous case, melted at 205—206°, as also did a sample prepared from the solution obtained by carefully heating the hydrazone in a water-bath at 85° under reduced pressure and absorbing the gases evolved in water. At 110°, oxides of nitrogen accompanied the formaldehyde. This decomposition of the hydrazone also asserted itself when its methyl-alcoholic solution was concentrated.

(2) A solution of the sodium salt of β-nitroethyl alcohol (3·9 g.) (compare J., 1928, 269) was gradually added to a diazonium solution (70 c.c.) prepared from aniline (3·2 g.), hydrochloric acid (*d* 1·17; 7 c.c.), water and sodium nitrite (2·4 g.). The product (6·3 g.) melted at 108—109° after crystallisation from methyl alcohol (Found: C, 49·4; H, 4·7; N, 21·6%; *M*, 201, 189). Formaldehyde could not be detected as a product of treatment of the hydrazone with warm methyl-alcoholic sodium methoxide or aqueous sodium hydroxide, and the material was recovered unchanged. The same compound was obtained by acidifying a solution of the isomeride, m. p. 117—118°, in aqueous sodium hydroxide or in sodium methoxide. A mixture of the isomerides melted at 100—102°. When the hydrazone was very cautiously heated, the odour of formaldehyde was distinctly perceptible, but further decomposition supervened so closely that it was not possible to collect and identify the aldehyde as was done in the previous instance.

By treating the hydrazone (1·95 g.) with a solution of sodium hydroxide (0·4 g.) in water (20 c.c.) and mixing the whole with a diazonium solution (40 c.c.) prepared from aniline (0·93 g.), nitroformazyl (2·1 g.), m. p. 162—163°, was obtained; this did not depress the melting point of an authentic specimen prepared from nitromethane. The odour of formaldehyde was very noticeable in the concentrated ethereal extract, and it was identified as in previous cases. A similar experiment was performed with (II), and nitroformazyl was also produced when a diazonium solution was gradually added to an aqueous solution of the sodium salt of β-nitrotrimethylene glycol.

Nitroformaldehydephenylhydrazone.—When a diazonium solution from aniline (9·3 g.), hydrochloric acid (*d* 1·17; 24·4 c.c.), water (125 c.c.), and sodium nitrite (6·9 g.) was gradually added to a solution of nitromethane (6·1 g.) and sodium hydroxide (4 g.) in water (100 c.c.), a mixture of the desired hydrazone with nitroformazyl was produced. The latter was removed by repeated crystallisation from methyl alcohol and the hydrazone was ultimately obtained in orange prisms, m. p. 92° (Found: C, 50·7; H, 4·5; N, 25·7. Calc. for $C_7H_3O_2N_3$: C, 50·9; H, 4·3; N, 25·4%).

Other Examples of the Elimination of Formaldehyde from Nitromethylol Derivatives.—β-Nitrobutyl alcohol, b. p. 122—125°/24 mm. (Pauwels, *Bull. Acad. Sci. Belg.*, 1897, **34**, 651), was converted into its sodium salt (Na, 15·8%), which was coupled with benzenediazonium chloride in the manner described for the case of β-nitropropyl alcohol. The oily phenylhydrazone had only partly crystallised after 4 days, but by precipitation of its solution in aqueous sodium hydroxide the solid hydrazone was at once obtained; it melted at 103—104° after crystallisation from methyl alcohol and did not depress the melting point of the product prepared from nitropropane in brilliant red needles, m. p. 103—104° (N, 21·9%). In the latter case no difficulty was experienced in regard to the solidification of the hydrazone. Bamberger (*Ber.*, 1898, **31**, 2631) gives m. p. 98—99°.

β-*Nitroamyl alcohol*, prepared by adding a few grains of potassium carbonate to a mixture of nitrobutane (12 g.) and formaldehyde (40% solution; 8·75 c.c.) and leaving the mixture for 12 hours after the initial reaction was over, boiled at 130—136°/28 mm. (Found: N, 10·4. $C_5H_{11}O_3N$ requires N, 10·5%). From its *sodium* salt (Found: Na, 15·1. $C_5H_{10}O_3NNa$ requires Na, 14·8%), an oily *phenylhydrazone* was obtained which did not crystallise when inoculated with the solid material. This was, however, readily obtained by acidifying the solution of the oil in aqueous alkali, and separated from methyl alcohol in brilliant red needles, m. p. 63—66° (Found: N, 20·6. $C_{10}H_{13}O_2N_3$ requires N, 20·3%). The same compound was obtained directly from the sodium salt of nitrobutane, the crude hydrazone solidifying as in the case of that prepared from nitropropane.

β-*Nitro*-β-*hydroxymethylamyl alcohol*, also formed in small amount in the preparation of the nitroamyl alcohol just described, was isolated as the non-volatile residue from the distillation of the nitroamyl alcohol. After crystallisation from alcohol it melted at 80—83° (Found: N, 8·9. $C_6H_{13}O_4N$ requires N, 8·6%), and its constitution was established by treatment with sodium ethoxide, the sodium salt of the nitroamyl alcohol (Na, 15·0%), itself identified by conversion into the phenylhydrazone, m. p. 63—66°, just described, being produced.

Displacement of Other Aldehydes as a Consequence of Coupling.—The sodium salt of nitro*iso*propyl alcohol (Henry, *Bull. Acad. Roy. Belg.*, 1895, **15**, 999), on treatment with benzenediazonium chloride, was converted into a *phenylhydrazone*, $CHMe(OH)\cdot C(NO_2):N\cdot NHPh$, which formed felted orange needles, m. p. 126—127° (Found: C, 51·65; H, 5·5. $C_9H_{11}O_3N$ requires C, 51·65; H, 5·3%).

From α-*nitrobutan*-β-*ol* (Henry, *ibid.*, 1896, **15**, 1223) in the same way, a *sodium* salt (Found: Na, 16·3. $C_4H_8O_3NNa$ requires Na, 16·3%) and a *phenylhydrazone*, CHEt(OH)·C(NO_2):N·NHPh, bright red needles, m. p. 100—102° (Found: N, 18·9. $C_{10}H_{13}O_3N_3$ requires N, 18·9%), were successively obtained.

α-*Nitropentan*-β-*ol* was prepared by condensation of nitromethane (33 g.) with *n*-butaldehyde (39 g.) in presence of water (10 c.c.) and potassium carbonate (0·2 g.). Since no particular rise in temperature was observed, the mixture was heated for some time at 60°, until the aqueous layer (originally the lower) was displaced by the specifically heavier condensation product. After 12 hours, the mixture was worked up and the alcohol (44 g.) isolated as a viscous oil, b. p. 117°/17 mm. (Found: N, 10·8. $C_5H_{11}O_3N$ requires N, 10·5%). From the *sodium* salt (Found: Na, 14·6. $C_5H_{10}O_3NNa$ requires Na, 14·8%), α-*chloro*-α-*nitropentan*-β-*ol* was prepared by direct chlorination; it separated from a mixture of equal volumes of chloroform and ethyl acetate in fine needles, m. p. 38° (Found: N, 8·6. $C_5H_{10}O_3NCl$ requires N, 8·4%). The *phenylhydrazone* obtained from the sodium salt crystallised from methyl alcohol in brilliant red needles, m. p. 92—94° (Found: N, 18·1. $C_{11}H_{15}O_3N_3$ requires N, 17·7%).

α-Nitrohexan-β-ol (Mousset, *Bull. Acad. Roy. Belg.*, 1901, **26**, 622) yielded a *sodium* salt (Found: Na, 13·3. $C_6H_{12}O_3NNa$ requires Na, 13·6%), and a *phenylhydrazone*, which separated from methyl alcohol in bright red needles, m. p. 108—111° (Found: N, 16·7. $C_{12}H_{17}O_3N_3$ requires N, 16·7%). The chloro-derivative, analogous to that described above, was obtained as an oil which could not be induced to crystallise.

γγγ-Trichloro-α-nitropropan-β-ol, m. p. 48—49° (Henry, *Bull. Acad. Roy. Belg.*, 1896, **15**, 1223, gives m. p. 42—43°), was for obvious reasons not converted into its sodium salt, but coupled in dilute aqueous solution immediately after addition of sodium hydroxide (1 mol.). The resulting *phenylhydrazone* crystallised from methyl alcohol in red prisms, m. p. 129° (Found: N, 13·6. $C_9H_8O_3N_3Cl_3$ requires N, 13·5%).

The sodium salt of β-nitro-α-phenylethyl alcohol (Rosenmund, *Ber.*, 1913, **46**, 1037) yielded a *phenylhydrazone*, which crystallised from methyl alcohol in fine red needles, m. p. 126° (Found: N, 15·8. $C_{14}H_{13}O_3N_3$ requires N, 15·5%).

The following details are typical of the procedure followed in converting each of the above-mentioned phenylhydrazones into nitroformazyl: a diazonium solution (100 c.c.) prepared from aniline (0·93 g.), hydrochloric acid (*d* 1·12; 2·2 c.c.), water, and sodium nitrite (0·69 g.) was added to a cold solution of the phenylhydrazone from methylnitropentanol (2·5 g.) and sodium hydroxide (0·4 g.)

in water (100 c.c.), and the precipitate purified by crystallisation from methyl alcohol.

γ-Nitrobutan-β-ol (Henry, *Bull. Acad. Roy. Belg.*, 1896, **15**, 1224) yielded a *sodium* salt which was purified by addition of ether to its solution in methyl alcohol (Found : Na, 16·7. $C_4H_8O_3NNa$ requires Na, 16·3%), from which a phenylhydrazone, m. p. 148—149°, was prepared (Found : N, 23·5%). The liquor from the coupling process exhibited reducing properties and responded to Simon's test for acetaldehyde, and the phenylhydrazone did not depress the melting point of the phenylhydrazone prepared from nitroethane.

*Decomposition of Derivatives of Nitro*iso*propyl Alcohol by Alkali.*—When a solution of γ-nitropentan-β-ol (Henry, *Bull. Acad. Roy. Belg.*, 1896, **15**, 1223) (Found : N, 10·3%) (13·5 g.) in alcohol (25 c.c.) was treated with a solution of sodium (2·3 g.) in alcohol (42 c.c.), a *sodium* salt was precipitated (Found : Na, 19·9%), and the presence of acetaldehyde in the liquor was demonstrated by Simon's test. The salt was purified by addition of ether to its solution in methyl alcohol (Found : Na, 20·7. $C_3H_6O_2NNa$ requires Na, 20·7%).

γ-*Nitrohexan*-β-*ol* (36·5 g.), b. p. 122·5°/17 mm. (Found : N, 10·0, 10·2. $C_6H_{13}O_3N$ requires N, 9·5%), was prepared by addition of two drops of aqueous potassium hydroxide solution (50%) to a mixture of nitrobutane (50 g.), acetaldehyde (22 g.), and water (10 c.c.). A *sodium* salt was prepared in the same manner as in the previous instance (Found : Na, 18·2. $C_4H_8O_2NNa$ requires Na, 18·4%), and the presence of acetaldehyde in the mother-liquor was again indicated by Simon's test.

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