610. *Properties and Reactions of Free Alkyl Radicals in Solution. Part IX.* Synthesis and Reactions of Some Tertiary Nitroalkanes.*

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Nitrogen dioxide combines with tertiary aliphatic free radicals in solution to give nitroalkanes, optimum yields being obtained with material containing a little nitric oxide.

α-Nitro*iso*butyronitrile and its analogues are decomposed by caustic alkali, by alcoholic cyanide, and by lithium aluminium hydride with loss of the nitrile group.

In Part VII [1] it was reported that nitric oxide combined with three 2-cyano-2-propyl radicals to give a trisubstituted hydroxylamine and that aromatic nitroso-compounds similarly combined with two such radicals, though the NO_2 group of aromatic nitro-compounds did not add alkyl radicals in a similar way. In continuation of this work we have investigated the combination of nitrogen dioxide with 2-cyano-2-propyl and analogous

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* Part VIII, *J.*, 1955, 4256.

[1] Gingras and Waters, *J.*, 1954, 1920; *Chem. and Ind.*, 1953, 615.

radicals and, as already reported in outline,[2] find that tertiary nitroalkanes are formed in yields (see Table) that indicate that nitrogen dioxide is a less active radical-trapping agent than is nitric oxide.

Optimum yields (30—35% of purified material) are obtained with nitrogen dioxide containing up to 10% of nitric oxide. Treatment of the nitrogen dioxide with oxygen to remove all nitric oxide halves the yield of nitroalkane whilst saturation of the nitrogen dioxide with nitric oxide also lowers the yield. One possible explanation is that free oxygen may diminish yields by combining directly with 2-cyano-2-propyl radicals, as is known from autoxidation studies [3] to occur readily. An alternative, and in our view more probable, interpretation is the suggestion that tertiary nitrosoalkanes are readily formed by reaction (1) and are then oxidised by nitrogen dioxide (reaction 2), so that a little nitric oxide acts as a chain-carrier, though reaction (3) competes with reaction (2) when too much nitric oxide is present.

$$(1) \qquad R\cdot + NO \longrightarrow R\cdot NO$$

$$(2) \qquad R\cdot NO + NO_2 \longrightarrow R\cdot NO_2 + NO$$

$$(3) \qquad 2R\cdot + R\cdot NO \longrightarrow R_2N\cdot OR$$

The ease of oxidation of α-nitroso*iso*butyronitrile has been demonstrated by Piloty and Schwerin [4] who in 1901 found that when moist it decomposed to a mixture of α-nitro*iso*butyronitrile and *NNO*-tri-(2-cyano-2-propyl)hydroxylamine; they failed, however, to identify the latter product, citing only a melting point and analysis which agrees with that of material later synthesised from nitric oxide and 2-cyano-2-propyl radicals by Gingras and Waters.[1] In support of the above mechanism we have demonstrated that, under our general reaction conditions, nitrogen dioxide does oxidise nitrosobenzene to nitrobenzene in high yield.

Metathetical reactions of type (2) have been reviewed by Gray and Yoffe,[5] and a literature review by Gray [6] indicates that in the vapour phase free alkyl radicals combine with nitrogen dioxide to give nitroalkanes rather than nitrites. Our findings accord with his conclusion, for the products that we have prepared from four different alkyl radicals in solution all have the characteristic infrared absorption bands of tertiary nitroalkanes [7] and are not hydrolysed by dilute acids. Minor by-products of these reactions between nitrogen dioxide and free radicals of the type $R_2C(CN)\cdot$ have been isolated chromatographically. Besides the invariable radical dimers of type $R_2C(CN)\cdot C(CN)R_2$, small amounts of substituted amides $R_2CH\cdot CO\cdot NH\cdot CR_2\cdot CN$ (derived from the unsymmetrical dimer $R_2C\colon C\colon N\cdot CR_2\cdot CN$ first mentioned by Talât-Erben and Bywater [8]) and its nitrated product $NO_2\cdot CR_2\cdot CO\cdot NH\cdot CR_2\cdot CN$ are obtainable. Other work in this laboratory [9] has shown that the amide $R_2CH\cdot CO\cdot NH\cdot CR_2\cdot CN$ is regularly formed when a tertiary α-azonitrile is decomposed in a moist solvent, and the direct nitration of this by nitrogen dioxide is not surprising in view of the known reaction between nitrogen dioxide and tertiary C–H groups.[5]

Hydrolyses and Reductions of Tertiary Nitroalkanes.—98% Sulphuric acid converts the tertiary α-nitro-nitriles into α-nitro-amides, whilst treatment with methanolic hydrogen chloride and subsequent hydrolysis converts α-nitro*iso*butyronitrile into methyl α-nitro*iso*butyrate identical with the product obtained directly from nitrogen dioxide and dimethyl αα′-azo*iso*butyrate. This suffices to show that the nitro-group cannot be removed by S_N1 hydrolysis.

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[2] Tilney-Bassett and Waters, *Chem. and Ind.*, 1956, 957.

[3] Davies, Goldsmith, Gupta, and Lester, *J.*, 1956, 4926; Bateman and Morris, *Trans. Faraday Soc.*, 1952, **48**, 1149.

[4] Piloty and Schwerin, *Ber.*, 1901, **34**, 1863.

[5] Gray and Yoffe, *Quart. Rev.*, 1955, **9**, 367.

[6] Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.

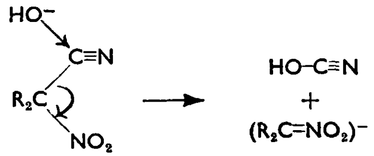
[7] Brown, *J. Amer. Chem. Soc.*, 1956, **78**, 6341.

[8] Talât-Erben and Bywater, *J. Amer. Chem. Soc.*, 1955, **77**, 2240.

[9] Personal communication from Mr. R. M. Haines.

However, concentrated sodium hydroxide rapidly destroys α-nitronitriles. 1-Cyano-1-nitro*cyclo*hexane, when warmed with alcoholic sodium hydroxide, gave sodium cyanate and the sodium salt of *aci*-nitro*cyclo*hexane. Alkaline hydrolysis of α-nitro*iso*butyronitrile similarly gave sodium cyanate as a major product, but acetone and free nitrite were also obtained. Acidification of the hydrolysed solution yields much carbon dioxide, from the breakdown of the cyanate, and a pale blue colour probably due to the condensation of free nitrous acid with 2-nitropropane to give 2-nitroso-2-nitropropane. Thus, although there is evidence for some S_N2 displacement of NO_2 by OH^-, the main hydrolytic reaction in alkali must be represented as :

(4)



This strikingly illustrates the strong electrophilic character of the nitro-group and the difficulty of hydrolysis of nitroalkanes. It is similar to the alkaline hydrolysis of dichlorodinitromethane,[10] $Cl_2C(NO_2)_2 + 2KOH \longrightarrow K{\cdot}CCl(NO_2)_2 + KOCl + H_2O$, and to the decarboxylation of α-nitro-acids in alkali.

Treatment of α-nitro*iso*butyronitrile with alcoholic sodium cyanide yielded a product $C_7H_{12}O_2N_2$ identified as 2-cyano-2 : 3-dimethyl-3-nitrobutane, $NC{\cdot}CMe_2{\cdot}CMe_2{\cdot}NO_2$, both from spectral evidence and from its formation, though in poor yield, on reaction of sodio-2-nitropropane with α-nitro*iso*butyronitrile in dry alcohol—in this case by S_N2 displacement of NO_2 :

Products of reactions between nitrogen dioxide and tertiary aliphatic azo-compounds.

	Yields (%) of products			
Reaction	$R{\cdot}NO_2$ [a]	$R{\cdot}R$	$R_2N{\cdot}OR$	$NO_2{\cdot}CR_2{\cdot}CO{\cdot}NH{\cdot}CR_2{\cdot}CN$
*αα′-Azo*iso*butyronitrile with :*				
(*a*) 0·5 equiv. NO_2 (+ some NO)	43 (31) [b]	43	6·4	1·0
(*b*) 2 equiv. NO_2 (+ some NO)	42 (27)	10	1·7	1·0 [c]
(*c*) pure NO_2 in PhCl at 100°	(17)	—	—	—
(*d*) pure NO_2 in boiling C_6H_6	12 (8·7)	49	—	—
(*e*) ,, ,,	(18)	38	0·8 [d]	1·4 [e]
(*f*) N_2O_3 in boiling C_6H_6	33 (20)	35	2·9	2·0
(*g*) NO_2; with NO passed through solution in C_6H_6	22 (12)	—	12·6	0·5
3 : 3′-*Azobis*-3-*cyanopentane with :*				
NO_2 (+ some NO) in PhMe at 100°	(21)	14	—	8·4 [d, f]
1 : 1′-*Azobis*-1-*cyano*cyclo*hexane with :*				
(*a*) NO_2 (+ some NO) in boiling PhMe	(24)	30	—	4·3 [g]
(*b*) ,, ,, in boiling PhCl	30	—	—	—
(*c*) pure NO_2	Low	—	—	—
*Dimethyl αα′-azo*iso*butyrate with :*				
NO_2 (+ some NO) in PhMe at 100°	(33)	—	—	—

[a] Crude yields, with pure yields in parentheses. [b] Yields calc. on NO_2 taken; in all other cases calc. on azo-compound used. [c] Also 2·2% of the corresponding acid. [d] Crude. [e] Pure. [f] Also 2·1% of $R_2CH{\cdot}CO{\cdot}NR_2{\cdot}CN$. [g] This product is $C_{21}H_{32}O_4N_4$; also 3·6% of $R_2CH{\cdot}CO{\cdot}NR_2{\cdot}CN$.

$$(5)\quad CN^- + NC{\cdot}CMe_2{\cdot}NO_2 \longrightarrow NC{\cdot}CN + (Me_2C{=}NO_2)^-$$

$$(Me_2C{=}NO_2)^- + Me_2C(CN){\cdot}NO_2 \longrightarrow Me_2C(NO_2){\cdot}CMe_2{\cdot}CN + NO_2^-$$

In reaction (5) a volatile product, thought to be cyanogen, was also obtained. Again, compounds $X_2C(NO_2)_2$ (X = Cl, Br, or I) undergo a similar reaction,[10] $X_2C(NO_2)_2 + KCN \longrightarrow K{\cdot}CX(NO_2)_2 + XCN$.

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[10] Gotts and Hunter, *J.*, 1924, **125**, 442.

Reductions with lithium aluminium hydride in ether follow a similar course, for the cyanide group is displaced and a secondary amine (characterised as its benzoyl derivative) is formed:

$$(6)\quad H^- + NC{\cdot}CR_2{\cdot}NO_2 \longrightarrow HCN + (R_2C{=}NO_2)^- \longrightarrow R_2CH{\cdot}NH_2$$

Methyl α-nitro*iso*butyrate was also decarboxylated by this reducing agent.

However the less drastic, and much less nucleophilic, reducing agent hydrazine in presence of Raney nickel [11] gave, in this case, the corresponding α-amino-ester, the benzoyl derivative of which was identical with material prepared from acetone by a conventional Strecker synthesis.

EXPERIMENTAL

Nitrogen dioxide was prepared by adding saturated aqueous sodium nitrite slowly to fuming nitric acid at 50°, condensing the evolved vapours at −30°, and fractionating the product slowly in a stream of oxygen. The nitrogen dioxide was dried (P_2O_5) and redistilled just before use, further treatment with oxygen being employed when complete removal of lower oxides of nitrogen was important.

*Decompositions of αα′-Azo*iso*butyronitrile in Presence of Nitrogen Dioxide* (cf. Table).—(a) 2-*Cyano-*2-*propyl radicals in* 2 : 1 *excess.* A solution of nitrogen dioxide (9 g., containing a little N_2O_3) in dry benzene (60 c.c.) was added gradually during ½ hr. to a refluxing solution of αα-azo*iso*butyronitrile (30 g.) in benzene (200 c.c.). To minimise the escape of oxides of nitrogen a cold trap was placed at the top of the reflux condenser. After refluxing for a further 5 hr. the benzene was removed and the residue distilled under reduced pressure to separate the crude α-nitro*iso*butyronitrile (9·8 g.; b. p. 69—72°/14 mm.) from other products. The nitro-compound was purified by crystallisation from ether at −30° and then had m. p. 34° (Piloty and Schwerin [4] give 35°) (yield 7 g., 31%) (Found: C, 42·1; H, 5·3; N, 24·6. Calc. for $C_4H_6O_2N_2$: C, 42·1; H, 5·2; N, 24·6%). Its infrared spectrum had strong bands at 6·40, 7·48, and 11·78 μ (NO_2 group [7]) and moderate bands at 7·17, 7·30, and 8·50 μ (Me_2C group), but the weak absorption at 4·45 μ indicative of CN was not observable (it has been noted that strongly electronegative groups in the same molecule often suppress the CN vibration [12]). A direct comparison with the infrared spectra of authentic samples of 2-nitropropane and 2-chloro-2-nitropropane confirmed the assignments of the bands at 6·35—6·50, 7·40—7·50 and 11·55—12·10 μ to vibrations of the nitroparaffin ($C{\cdot}NO_2$) group in this and other nitro-compounds described in this paper. Chromatography of the residue left after separation of the α-nitro*iso*butyronitrile led to the isolation of tetramethylsuccinonitrile, m. p. and mixed m. p. 169° (10·8 g., 43%), tri-(2-cyano-2-propyl)hydroxylamine (2·3 g., 6·5%), m. p. and mixed m. p. 79°,[1] and a small quantity (0·4 g.) of a product, m. p. 135° (from benzene) (Found: C, 48·1; H, 6·5; N, 20·9. $C_8H_{13}O_3N_3$ requires C, 48·2; H, 6·5; N, 21·1%). Its infrared spectrum showed the presence of NO_2, CN, and CO·NH, and CMe_2 groups. Since this substance gave no colour with nitrous acid it contains a tertiary nitro-group, and this evidence together with the identification of the corresponding acid (see below) identifies it as N-(2-*cyano-*2-*propyl*)-α-*nitro*iso*butyramide.*

(b) *Nitrogen dioxide in* 2 : 1 *excess over* 2-*cyano-*2-*propyl radicals.* Repetition of experiment (a) with equal weights (40 g.) of nitrogen dioxide and αα′-azo*iso*butyronitrile gave a similar yield of α-nitro*iso*butyronitrile, 10% of tetramethylsuccinonitrile, 1·7% of tri-(2-cyano-2-propyl)-hydroxylamine, 1% of *N*-(2-cyano-2-propyl)-α-nitro*iso*butyramide, and 2·2% of the corresponding acid, N-(2-*carboxy-*2-*propyl*)-α-*nitro*iso*butyramide*, m. p. 174° (from chloroform–acetone) (Found: C, 44·1; H, 6·6; N, 13·1. $C_8H_{14}O_5N_2$ requires C, 44·0; H, 6·4; N, 12·8%). The infrared spectrum of this compound showed the presence of NO_2, Me_2C, NH·CO, and CO_2H groups. Subsequently it was obtained by treating *N*-(2-cyano-2-propyl)*iso*butyramide (0·5 g.) in benzene (20 c.c.) with nitrogen dioxide (0·55 g.) at 30—40° for 30 min. and then at the b. p. for 30 min. It crystallised, in poor yield, when this mixture was cooled. The amide was prepared from α-amino*iso*butyronitrile and *iso*butyryl chloride and had m. p. 108°. It has been isolated in this laboratory in 10% yield by thermal decomposition of αα′-azo*iso*butyronitrile in boiling water or aqueous alcohol [9] and in smaller amounts when other moist solvents were used.

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[11] Balcon and Furst, *J. Amer. Chem. Soc.*, 1951, **75**, 4334.

[12] Bellamy, " The Infra Red Spectra of Complex Molecules," Methuen, London, 1954, p. 225.

(c) Approximately equivalent concentrations of nitrogen dioxide and 2-cyano-2-propyl radicals were used. Change of solvent has only a minor effect on the yields of products.

(d) The decomposition in boiling benzene of αα-azo*iso*butyronitrile in the presence of an equal weight of oxides of nitrogen of approximate composition N_2O_3 resulted in about 30% reduction of the yield of α-nitro*iso*butyronitrile, but dropwise addition of a cold benzene solution of equivalent amounts of nitrogen dioxide and αα′-azo*iso*butyronitrile to refluxing benzene through which a slow stream of nitrogen admixed with nitric oxide was being passed more significantly reduced the yield of the nitroalkane and increased that of the tertiary hydroxylamine, though the side reaction leading to the nitro-cyanide was not quite eliminated.

Oxidation of Nitrosobenzene with Nitrogen Dioxide.—Nitrogen dioxide (5 g.) in benzene was added slowly to a refluxing solution of nitrosobenzene (10·5 g.) in benzene. Fractionation of the product gave 67% of pure nitrobenzene and a tarry residue.

Decompositions of Other Aliphatic Azo-compounds in the Presence of Nitrogen Dioxide.—These were carried out with slightly impure nitrogen dioxide, as in (a) above, with approximately equivalent amounts of dioxide and organic radicals.

(1) Dimethyl αα′-azo*iso*butyrate in toluene at 100° gave a 33% yield of *methyl α-nitro*iso*butyrate*, b. p. 77—79°/14 mm., m. p. −4° (Found: C, 40·6; H, 6·2. $C_5H_9O_4N$ requires C, 40·8; H, 6·1%). This ester was also prepared from α-nitro*iso*butyronitrile by hydrolysis, *via* the corresponding *imidate hydrochloride*, m. p. 117° (Found: C, 32·7; H, 5·7; N, 15·6; Cl, 19·6. $C_5H_{11}O_3N_2Cl$ requires C, 32·9; H, 6·0; N, 15·3; Cl, 19·45%), with methanolic hydrogen chloride.

Treatment of the ester with saturated ethanolic ammonia gave *α-nitro*iso*butyramide*, m. p. and mixed m. p. 116°, identical with material obtained by dissolving α-nitro*iso*butyronitrile in cold concentrated sulphuric acid, warming the solution slightly, and then pouring it into ice-water (Found: C, 36·6; H, 6·0; N, 21·2. $C_4H_8O_3N_2$ requires C, 36·4; H, 6·1; N, 21·2%). The infrared spectrum of this compound showed bands indicative of NO_2, Me_2C, and CO·NH_2.

(2) 3 : 3′-Azobis-3-cyanopentane, prepared from diethyl ketone,[13] when similarly treated gave a 21% yield of *3-cyano-3-nitropentane*, b. p. 89—92°/11 mm. (Found: C, 50·8; H, 7·1; N, 19·3. $C_6H_{10}O_2N_2$ requires C, 50·7; H, 7·0; N, 19·7%), together with 14% of the radical dimer, m. p. and mixed m. p. 47°,[13] 8% of a compound, m. p. 100° [which since it exhibited infrared absorption indicative of the groups NO_2, CO·NH, and CN is evidently N-(*3-cyano-3-pentyl*)*-1-ethyl-1-nitrobutyramide* (Found: C, 56·3; H, 8·1. $C_{12}H_{21}O_3N_3$ requires C, 56·5; H, 8·2%)], and 2% of N-(*3-cyano-3-pentyl*)*-1-ethylbutyramide*, m. p. 113·5° (Found: C, 68·2; H, 10·1. $C_{12}H_{22}ON_2$ requires C, 68·6; H, 10·1%), which had infrared absorption corresponding to CO·NH. Acid hydrolysis of 3-cyano-3-nitropentane gave *3-carbamoyl-3-nitropentane*, m. p. 59° (from *cyclo*hexane) (Found: C, 45·6; H, 7·3; N, 17·2. $C_6H_{12}O_3N_2$ requires C, 45·0; H, 7·5; N, 17·5%).

(3) 1 : 1′-Azobis-1-cyano*cyclo*hexane [14] in boiling toluene gave 24% of *1-cyano-1-nitro*cyclo*hexane*, m. p. 56° (Found: C, 54·9; H, 6·4; N, 17·7. $C_7H_{10}O_2N_2$ requires C, 54·6; H, 6·5; N, 18·2%), 30% of the symmetrical radical dimer, m. p. 223°, 3·6% of N-(*1-cyano-1-*cyclo*hexyl*)-cyclo*hexanecarboxyamide* (also obtained in 6% yield by decomposition of 1 : 1′-azobis-1-cyano*cyclo*hexane in boiling water), m. p. 156° (Found: C, 72·1; H, 9·6; N, 11·4. $C_{14}H_{22}ON_2$ requires C, 71·8; H, 9·4; N, 12·0%), and a similar amount of an unidentified by-product, m. p. 145°, with analysis corresponding to $C_{21}H_{32}O_4N_4$. Decomposition of this azo-compound in boiling chlorobenzene gave a similar yield of 1-cyano-1-nitro*cyclo*hexane, but this was greatly reduced when freshly purified nitrogen dioxide was used. Hydrolysis of 1-cyano-1-nitro*cyclo*hexane with strong sulphuric acid gave *1-nitro*cyclo*hexane-1-carboxyamide*, m. p. 120°, quantitatively (Found: C, 48·5; H, 7·0; N, 16·7. $C_7H_{12}O_3N_2$ requires C, 48·9; H, 6·9; N, 16·3%).

*Alkaline Hydrolysis of α-Nitro*iso*butyronitrile.*—(1) α-Nitro*iso*butyronitrile dissolved in a few minutes when warmed with 2N-sodium hydroxide. On addition of iodine the solution gave a positive iodoform test, indicating the presence of acetone. Carbon dioxide was liberated on acidification and the solution became blue. This colour could be extracted into ether and was presumed to be due to the nitroso-derivative of 2-nitropropane. Treatment of the acid solution with sulphanilic acid and then alkaline β-naphthol gave a red colour, indicating the presence of some free nitrous acid. However the solution failed to give the Prussian-blue test for free cyanide. (2) α-Nitro*iso*butyronitrile (3 g.) was refluxed for 15 min. with sodium hydroxide (5 g.)

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[13] Dox, *J. Amer. Chem. Soc.*, 1925, **47**, 1471.

[14] Overberger, O'Shaughnessy, and Shalit, *ibid.*, 1949, **71**, 2661.

in water (10 ml.), and 10 ml. of liquid were then distilled off and collected. From this distillate was obtained a solid dinitrophenylhydrazone corresponding to the liberation of only 2% of acetone. The remaining liquid on cooling deposited 1·05 g. of sodium cyanate (61% of theory for eqn. 4, p. 3131), the identity of which was confirmed by the colour test with chloroform, pyridine, and copper sulphate.[15] (3) Nitro*iso*butyronitrile (3 g.) was hydrolysed with sodium hydroxide (5 g.) in ethanol (40 ml.) and water (5 ml.). Sodium cyanate separated in 96% yield. The alcoholic filtrate on evaporation gave a white solid (1·67 g.), containing a little sodium nitrite, that detonated on heating and was possibly the sodium salt of *aci*-2-nitropropane. A similar hydrolysis of 1-cyano-1-nitro*cyclo*hexane gave 85% of sodium cyanate, and by ether-precipitation of the alcoholic filtrate the solid sodium salt of *aci*-nitro*cyclo*hexane (Found : N, 8·4; Na, 15·6. Calc. for $C_6H_{10}O_2NNa$: N, 9·3; Na, 15·2%) which gave the characteristic blue colour test for a secondary nitroparaffin when treated with nitrous acid.

*Reaction of α-Nitro*iso*butyronitrile with Sodium Cyanide.*—α-Nitro*iso*butyronitrile (5 g.) and sodium cyanide (2·5 g.) were refluxed overnight in dry ethanol (50 ml.). The ethanol, which was then distilled off, gave a precipitate with acidified silver nitrate and liberated iodine from potassium iodide but not bromine from potassium bromide. These tests indicate the presence of cyanogen rather than of hydrogen cyanide which has no oxidising properties. The residue, on dilution with water, gave a solid (1·3 g.) which after crystallisation had m. p. 194° and gave an infrared spectrum indicating the presence of NO_2, CN, and Me_2C groups. A test with nitrous acid showed that the compound was a tertiary nitroalkane. It thus seemed to be 2-*cyano*-2 : 3-*dimethyl*-3-*nitrobutane* (Found : C, 54·1; H, 7·7; N, 18·1. $C_7H_{12}O_2N_2$ requires C, 53·9; H, 7·7; N, 18·0%). A later preparation of the same compound by refluxing α-nitro*iso*butyronitrile with the sodium salt of 2-nitropropane in alcohol confirmed this structure.

*Reduction of α-Nitro*iso*butyronitrile and Methyl α-Nitro*iso*butyrate.*—(1) α-Nitro*iso*butyronitrile (3 g.) in dry ether (30 c.c.) was added slowly to a refluxing suspension of lithium aluminium hydride in ether (50 c.c.). After an hour water was added, the resulting amine was extracted from the ether with dilute acid, concentrated in salt form, and then benzoylated : *N*-*iso*propylbenzamide, m. p. and mixed m. p. 98°, was isolated in 62% yield. The same product was obtained by a similar reduction of methyl α-nitro*iso*butyrate; and similarly 1-cyano-1-nitro*cyclo*hexane gave *N*-benzoyl*cyclo*hexylamine, m. p. and mixed m. p. 147°. (2) Methyl α-nitro*iso*butyrate (2 g.) in methanol (15 c.c.) was refluxed with Raney nickel (1 g.) and treated gradually with 50% aqueous hydrazine (3 c.c.). The mixture was then refluxed for 30 min., filtered, acidified, and concentrated. Benzoylation of the residue gave methyl α-benzamido*iso*butyrate (1·3 g.), m. p. and mixed m. p. 120° (Found : C, 65·2; H, 6·8. Calc. for $C_{12}H_{15}O_3N$: C, 65·0; H, 6·7%).

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[15] Vogel, " Text-Book of Qualitative Chemical Analysis," Longmans, London, 1945, p. 256.