705. *Reactions of Nitroparaffins. Part III. The Reaction of Primary Nitroparaffins with Acetic Anhydride.*

By T. URBAŃSKI.

Primary nitroparaffins, such as nitromethane, nitroethane, 1-nitropropane, and phenylnitromethane react vigorously with acetic anhydride in the presence of basic compounds, and it is suggested that they are isomerised first to hydroxy-nitroso-compounds, then to hydroxamic acids. The latter are subjected to cleavage and acetolysis, the final product from all nitroparaffins being ONN-*triacetylhydroxylamine.*

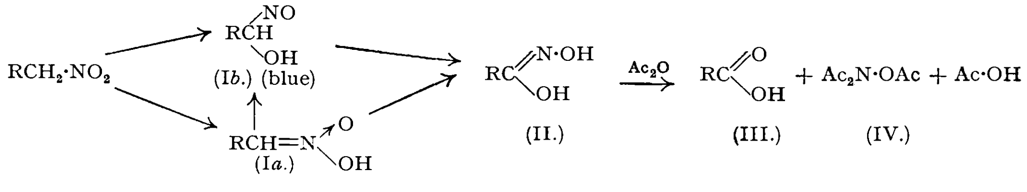
To explain the hydrolysis of primary nitroparaffins to fatty acids and hydroxylamine Bamberger and Brüst (*Ber.*, 1902, **35**, 45) suggested that they isomerised to hydroxamic acids. These authors prepared benzhydroxamic and *p*-nitrobenzhydroxamic acids, by the reaction of phenylnitromethane and *p*-nitrophenylnitromethane, respectively, with sulphuric acid. They also suggested the isomerisation of primary nitroparaffins to secondary hydroxy-nitroso-compounds (I), thus explaining the transient blue colour formed when alkaline solutions of primary nitroparaffins are acidified.

Further experimental proof of the isomerisation of primary nitroparaffins to hydroxamic acids has been given by Nenitzescu and Isacescu (*Bull. Soc. Chim. Roumanie*, 1932, **14**, 53), Junell (*Arkiv Kemi, Min., Geol.*, 1934, *B*, **11**, no. 30), and Lipincott and Hass (*Ind. Eng. Chem.*, 1939, **31**, 118).

Primary nitroparaffins have been suggested (Turski, B.P. 564,610; U.S.P. 2,401,525) as aminating agents. The mechanism of the reaction consists probably in the isomerisation of the nitroparaffins to hydroxamic acids under the action of concentrated sulphuric acid. These in turn hydrolyse to hydroxylamine which effects the amination.

The present author has examined the action of milder reagents, such as acetic anhydride, on primary nitroparaffins, in order to follow their isomerisation and cleavage. It has been found, that nitroparaffins do not react with hot acetic anhydride alone, but a vigorous reaction occurs when anhydrous sodium acetate is added to nitroparaffins dissolved in acetic anhydride, and the mixture is gently warmed. The ease of reaction varies: nitromethane $<$ nitroethane $<$ 1-nitropropane $<$ phenylnitromethane.

The reaction is accompanied by a sudded change of colour, to pale blue (nitromethane) or deep blue (nitroethane and 1-nitropropane). In all three cases the coloured product is volatile and can be distilled off together with acetic acid and acetic anhydride, but the paler-bluish product formed from phenylnitromethane is involatile. This colour disappears when the solution is heated for 20—30 minutes, and ONN-*triacetylhydroxylamine* (IV) and the carboxylic acid (III) are formed. The following sequence of reactions is suggested:

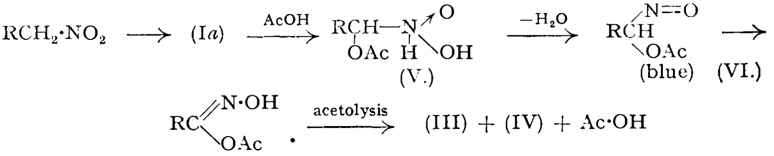


Although the reaction is presumed to proceed by both routes simultaneously, there is probably a preferential formation of the *aci*-form (I*a*) because of the basic medium produced by sodium acetate.

A somewhat different behaviour was noted when sodium acetate was replaced by pyridine. The reaction which started when heated was less vigorous, and no blue colour of the mixture or the refluxing vapour was observed. It is suggested that either the reaction follows the route through (I*a*), without formation of the blue compound (I*b*), or pyridine reacts with (I*b*) to give a colourless addition product.

The transformation of nitroparaffin into (I*b*) and the *aci*-form (I*a*) into (I*b*) or (II) involves oxygen migration from the nitrogen of the nitro-group to carbon. This type of migration is already known, *e.g.*, in the transformation of nitrobenzaldehyde into *o*-nitrosobenzoic acid (Ciamician and Silber, *Ber.*, **1901**, **34**, 2040; **1902**, **35**, 1080).

Another explanation, not involving this oxygen migration, is based on Nenitzescu and Isacescu's (*loc. cit.*) suggestions for the reaction between primary nitroparaffins and hydrochloric acid:



This explanation assumes addition of acetic acid to the double bond of the *aci*-form (I*a*). Acetic acid is present in acetic anhydride probably in sufficient quantity to initiate the reaction.

The preparation of (IV) from nitromethane gave the lowest yield (about 6%), but the yields from nitroethane (76—79%), 1-nitropropane (75—76%) and phenylnitromethane (56—60%) were much higher, and the best figure was obtained when warming of the solution was interrupted as soon as the blue colour of the refluxing liquid disappeared. On prolonged heating decomposition occurred with evolution of gas and a lower yield of (IV).

That the product from 1-nitropropane was not diacetylpropiohydroxamic acid was apparent as acetic acid but no propionic acid was formed on hydrolysis of the product with sodium hydroxide. The triacetyl compound (IV) was also prepared by direct acetylation of hydroxylamine hydrochloride with excess of acetic anhydride. The product of this direct acetylation has been described as acetylacetohydroxamic acid, Me·C(OH)⁚N·OAc or AcNH·OAc (Miolati, *Ber.*, 1892, **25**, 699; Hantzsch, *ibid.*, p. 701). Acetohydroxamic acid results from hydrolysis of acetylacetohydroxamic acid originally formed.

A partial acetolysis of nitroethane by using smaller proportion of acetic anhydride has been attempted. This was unsuccessful: only (IV) resulted, and unreacted nitroethane was recovered.

That (IV) contains a hydroxylamine nucleus has been proved by its use in the direct amination of aromatic compounds, by Turski's method (D.R.-P. 287,756; *loc. cit.*).

Triacetylhydroxylamine is readily hydrolysed by alkalis (*e.g.*, 10% Na_2CO_3), and by long (at least 4 weeks') exposure to air, the product in the latter case being crystalline acetylacetohydroxamic acid.

EXPERIMENTAL.

Reaction of 1-*Nitropropane with Acetic Anhydride in the Presence of Sodium Acetate.*—1-Nitropropane (0·2 mole, 17·8 g.) was dissolved in acetic anhydride (50 c.c.) and sodium acetate (10 g.) was added. The mixture was gently warmed, and reaction soon occurred with considerable heat-evolution and boiling of the reaction mixture. The liquid in the flask and the refluxing vapours acquired an intense blue colour. After about 5 minutes the reaction subsided and the liquid was gently boiled for 30 minutes by which time the blue colour had disappeared. All this time there was a very slow evolution of gas, containing carbon dioxide but no monoxide. The rate of the gas-evolution increased considerably on further heating and there was a considerable drop in yield.

After completion of the reaction, the excess of acetic anhydride and acetic acid was distilled off under reduced pressure, the almost solid residue in the flask was dissolved in water (ca. 200 c.c.), and the oily product extracted with ether. The ethereal extract was neutralised (litmus) with aqueous sodium carbonate, and dried (Na_2SO_4), and the residue from the evaporation of the ether was distilled under reduced pressure. ONN-*Triacetylhydroxylamine* (IV) (24·0 g., 75%), b. p. 96—98°/12 mm.), was a colourless oil with a faint aromatic smell, and was soluble in most organic solvents and in hot water, but insoluble in cold water. After being redistilled it had b. p. 216° (decomp.), 112°/17 mm., 98°/12 mm.; d_4^{20} = 1·168, n_D^{20} = 1·4441 (Found: C, 45·1; H, 6·3; N, 8·8; Ac, 82·2. $C_6H_9O_4N$ requires C, 45·3; H, 5·7; N, 8·8; Ac, 81·1%).

Reaction of Nitroethane and of Nitromethane with Acetic Anhydride in Presence of Sodium Acetate.—(IV) was likewise obtained from nitroethane and from nitromethane, in 78·6 and 6·3% yield, respectively. Partial acetolysis of nitroethane gave only (IV).

Reaction of Nitroethane with Acetic Anhydride in Presence of Pyridine.—Nitroethane (0·1 mole, 7·5 g.) was dissolved in acetic anhydride (25 c.c.) and pyridine (5 c.c.) was added. When the solution was warmed a moderate reaction occurred without the formation of the blue colour. After the reaction had subsided, the contents of the flask were gently boiled for 2 hours; and the product (IV) was isolated by fractional distillation under reduced pressure (yield, 4 g.).

Reaction of Phenylnitromethane with Acetic Anhydride in Presence of Sodium Acetate.—The reaction of phenylnitromethane was much more vigorous than with aliphatic nitroparaffins, and to moderate it a larger quantity of acetic anhydride was used.

Phenylnitromethane (0·1 mole, 13·7 g.) was dissolved in acetic anhydride (75 c.c.), and sodium acetate (10 g.) was added. The reaction started when the mixture was heated. The colour of the solution was slightly blue, but the refluxing vapours were colourless. The reaction ended within 30 minutes.

The reaction mixture was treated as in the previous experiments and gave (IV) (8·5 g., 56%) and benzoic acid (10·2 g., 84%).

Hydrolysis of ONN-*Triacetylhydroxylamine* (IV).—(a) *Hydrolysis with sodium hydroxide.* When (IV) was mixed with 30% NaOH (25 c.c.) a violent exothermic reaction occurred. After this had subsided the reaction mixture was evaporated to dryness on the water-bath, and the product covered with ether, and acidified with concentrated sulphuric acid (10 c.c.). Evaporation of the ether, and distillation of the residue gave acetic acid (10 g., 88%).

(b) *Hydrolysis with sodium carbonate.* A less violent reaction occurred with the same result.

(c) *Hydrolysis by air.* A sample of (IV) was exposed to air for a few weeks. The resulting crystalline white solid was crystallised from chloroform, and identified as acetylacetohydroxamic acid, *i.e.*, *ON*-diacetylhydroxylamine, m. p. 87—88°, unchanged when mixed with the sample prepared by Hantzsch's method, as below.

Complete Acetylation of Hydroxylamine.—Dry hydroxylamine hydrochloride (0·2 mole, 13·9 g.) and acetic anhydride (0·7 mole, 71 g.) were warmed to initiate reaction, and when this had subsided, the solution was boiled; hydrogen chloride being evolved during the reaction, which was completed in about 1 hour. The excess of acetic anhydride and acetic acid was distilled off under reduced pressure, and the oily residue distilled, yielding *ONN*-triacetylhydroxylamine (IV) (27 g., 85%), b. p. 96—98°/12 mm., n_{D}^{20} = 1·4441 (after redistillation) (Found: C, 45·7; H, 5·9; N, 9·0; Ac, 82·8%).

Partial Acetylation of Hydroxylamine to the ON-*Diacetyl Derivative* (*Acetylacetohydroxamic acid*) (*cf. Hantzsch*).—Dry hydroxylamine hydrochloride (0·2 mole, 13·9 g.) and acetic anhydride (0·43 mole, 44 g.) were warmed for 1 hour. The excess of acetic anhydride and acetic acid was distilled off under reduced pressure; when kept, the residue (23·5 g.) partly solidified. The crystals of *ON*-diacetylhydroxylamine (acetylacetohydroxamic acid) (13·7 g., 42%) were separated on a porous tile from the oily product (IV).

The solid was recrystallised from chloroform, and then had m. p. 88—89°, and properties the same as those of Hantzsch's product.

Amination of Anthraquinone with ONN-*Triacetylhydroxylamine by Turski's Method.*—Anthraquinone (0·04 mole, 8·7 g.) was dissolved in concentrated sulphuric acid (100 g.) containing vanadium pentoxide (0·025 g.) and *ONN*-triacetylhydroxylamine (0·04 mole, 6·2 g.) was added. The solution was heated, with stirring, at 130—140° for 8 hours, and after cooling, water (25 c.c.) was added to precipitate the unchanged anthraquinone, which was filtered off (2·6 g.). 1-Aminoanthraquinone (5·9 g.) was then precipitated by addition of more water.

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INSTITUTE OF TECHNOLOGY, WARSAW.

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