Tetrahedron, 1958, Vol. 2, pp. 296–299. Pergamon Press Ltd., London

ON ISOMERISATION OF NITROPARAFFINS

T. URBAŃSKI
Institute of Technology (Politechnika), Warsaw 10, Poland

(*Received* 4 *October* 1957)

Abstract—The investigation deals with the isomerisation of primary nitroparaffins into hydroxamic acids under influence of acetic anhydride or ketene, in presence of basic catalysts.

A practical application of the hydrolysis of 1:2-dinitroethane to hydroxylamine sulphate is described.

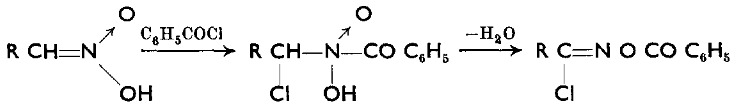
Another application is the preparation of caprolactam by the reaction of *cyclo*hexanone with 1:2-dinitroethane in presence of concentrated sulphuric acid.

INTRODUCTION

It is well known, that primary nitroparaffins can be hydrolysed to hydroxylamine.[1,2] Bamberger and Rüst[3] elucidated the mechanism of this reaction. They showed that primary nitroparaffins are isomerised in acid medium into hydroxamic acids and the latter can be hydrolysed to carboxylic acids and hydroxylamine.

Geuther[4] attempted to explain the mechanism of formation of hydroxylamine from primary nitroparaffins by ascribing them a structure of "amidoxydes". Taking into account the German terminology, this might signify "hydroxyamide" which is one of the desmotropic forms of hydroxamic acids. Also it would be interesting to point out that a number of authors[5,6,7] prior to Bamberger, found that a relation exists between primary nitroparaffins and hydroxamic acids, namely, that acid chlorides can react with sodium salts of *aci*-nitroparaffins yielding mono- or di-acylderivatives of hydroxamic chlorides.

This reaction was investigated by Wieland and Kitasato.[8] They treated *aci*-nitroparaffins with acid chlorides in presence of pyridine and suggested that the mechanism of the reaction consists in adding acid chloride to the double bond of the aciform of nitroparaffins. The additive compound then loses water and acylhydroxamic chloride results:



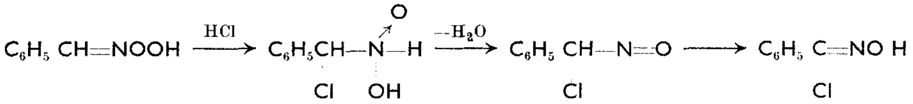
$$\mathrm{R\,CH{=}N}\begin{smallmatrix}\nearrow \mathrm{O}\\ \diagdown \mathrm{OH}\end{smallmatrix} \xrightarrow{C_6H_5COCl} \mathrm{R\,\underset{Cl}{CH}{-}\underset{OH}{\overset{\overset{O}{\nearrow}}{N}}{-}CO\,C_6H_5} \xrightarrow{-H_2O} \mathrm{R\,\underset{Cl}{C}{=}N\,O\,CO\,C_6H_5}$$

Nenitzescu and Isacescu[9] also investigated this reaction, and found that the mechanism suggested by Wieland and Kitasato occurred when anhydrous HCl reacted with

---

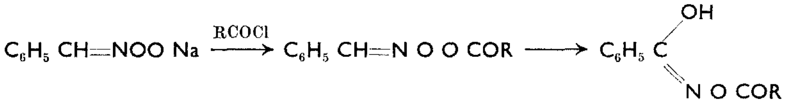
[1] R. Preibisch *J. Prakt. Chem.* **7**, 480 (1873).
[2] V. Meyer *Ber. Dtsch. Chem. Ges.* **8**, 29 (1875); V. Meyer and J. Locher *Liebigs Ann.* **180**, 163 (1876).
[3] E. Bamberger and E. Rüst *Ber. Dtsch. Chem. Ges.* **35**, 45 (1902).
[4] A. Geuther *Ber. Dtsch. Chem. Ges.* **7**, 1620 (1874).
[5] J. U. Nef *Ber. Dtsch. Chem. Ges.* **29**, 1218 (1896).
[6] A. T. Holleman *Rec. Trav. Chim. Pays-Bas* **15**, 356 (1896).
[7] A. van Raalte *Rec. Trav. Chim. Pays-Bas* **18**, 378 (1898).
[8] H. Wieland and Z. Kitasato *Ber. Dtsch. Chem. Ges.* **62**, 1250 (1929).
[9] C. D. Nenitzescu and D. A. Isacescu *Bull. Soc. Chim. Roumanie* **14**, 53 (1932).

phenyl-*aci*-nitromethane. An additive compound was first formed, and after losing water it was transformed into a blue nitroso compound which was isomerised to benzohydroxamic chloride:



$$C_6H_5\,CH{=}NOOH \xrightarrow{HCl} C_6H_5\underset{Cl}{CH}-\overset{O}{\underset{OH}{N}}-H \xrightarrow{-H_2O} C_6H_5\,\underset{Cl}{CH}-N{=}O \longrightarrow C_6H_5\,\underset{Cl}{C}{=}NO\,H$$

Primary *aci*-nitroparaffins react with acid chlorides in the same way as indicated by Wieland. However, when sodium salts of *aci*-nitroparaffins were used, acyl derivatives of hydroxamic acids resulted:



$$C_6H_5\,CH{=}NOO\,Na \xrightarrow{RCOCl} C_6H_5\,CH{=}N\,O\,O\,COR \longrightarrow C_6H_5\,C\begin{matrix}OH\\ N\,O\,COR\end{matrix}$$

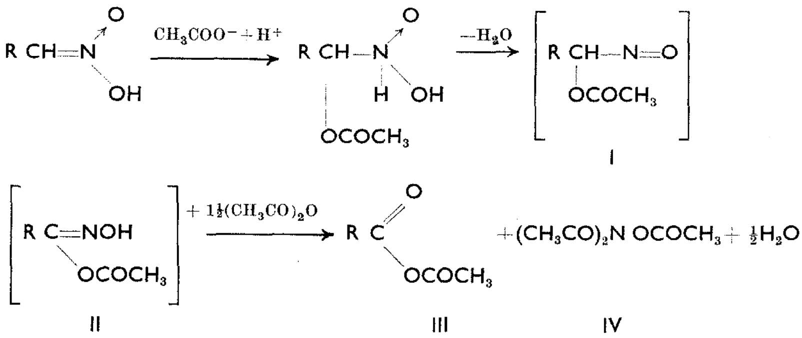
Further experiments on formation of hydroxamic acids from primary nitroparaffins were carried out by Melnikov[10] who confirmed the earlier statement by Geuther[4] that ammonium salts are also formed in addition to hydroxylamine.

Junell[11] examined the kinetics of transformation of nitroethane into acethydroxamic acid and found it to be a reaction of the first order. Lippincott and Haas[12] investigated the conditions of hydrolysis of primary nitroparaffins and determined the yield of hydroxylamine (86–91 per cent), ammonia (6–7 per cent) and carboxylic acids (90–96 per cent).

Using the fact that primary nitroparaffins furnish hydroxylamine, Turski[13] worked out new conditions for his reaction of direct amination of aromatic compounds.[14]

The author of the present paper also investigated[15] the isomerisation of primary nitroparaffins using acetic anhydride in presence of basic agents such as sodium acetate or pyridine. The presence of a basic agent is essential, the reaction does not occur without it. This indicates that the *aci*-form is an intermediate in formation of the final product, which is diacetylacethydroxamic acid, or O,N,N-triacetylhydroxylamine (IV).

The author suggested a mechanism similar to that of Wieland[8] or Nenitzescu:[9]



$$R\,CH{=}N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} \xrightarrow{CH_3COO^- + H^+} R\,\underset{OCOCH_3}{CH}-N\begin{matrix}\nearrow O\\ H\ \ OH\end{matrix} \xrightarrow{-H_2O} \underset{I}{\left[R\,\underset{OCOCH_3}{CH}-N{=}O\right]}$$

$$\longrightarrow \underset{II}{\left[R\,C\begin{matrix}{=}NOH\\ OCOCH_3\end{matrix}\right]} \xrightarrow{+\,1\frac{1}{2}(CH_3CO)_2O} \underset{III}{R\,C\begin{matrix}{=}O\\ OCOCH_3\end{matrix}} \underset{IV}{+(CH_3CO)_2N\,OCOCH_3} + \tfrac{1}{2}H_2O$$

---

[10] N. V. Melnikov *J. Gen. Chem., Moscow* **4,** 1061 (1934).

[11] R. Junell *Ark. Kemi. Min. Geol.* **B 11,** No 30 (1934).

[12] S. B. Lippincott and H. B. Haas *Industr. Engng. Chem.* (*Industr.*) **31,** 118 (1939).

[13] J. S. Turski *Brit. Pat.* 564 610 (1944); *U.S. Pat.* 2 401 525 (1946).

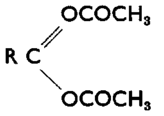
[14] J. S. Turski *Ger. Pat.* 287 756 (1915).

[15] T. Urbański *J. Chem. Soc.* 3374 (1949).

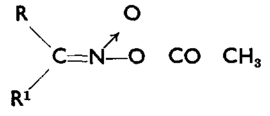
The blue intermediate is probably a nitroso compound (I), which would isomerise to another hypothetical intermediate—II. Acetolysis of (II) would yield an anhydride (III), and the final compound (IV).

Urbański and Gurzyńska[16] investigated also the action of ketene on primary nitroparaffins. The reaction also takes place in presence of basic agents, but it is evidently milder, than with acetic anhydride.

Thus, the hypothetical intermediate compound (II) was subjected to acetylation, the diacetyl derivative (V) of hydroxamic acid being formed:



V



VI

By acting on secondary nitroparaffins with acetic anhydride or ketene, in presence of sodium acetate, an acetyl derivative of *aci*-form (VI) was obtained. It can also be considered as a mixed anhydride of acetic anhydride and *aci*-nitroparaffin.

It should be pointed out, that Nenitzescu and Isacescu[9] tried to act with ketene on primary nitroparaffins. They obtained a definite compound—acetylbenzohydroxamic acid—only in the case of *aci*-phenylnitromethane. Other nitroparaffins did not furnish definite compounds.

EXPERIMENTAL

Isomerisation and hydrolysis of 1:2-*dinitroethane*

1:2-Dinitroethane is the cheapest among primary nitroparaffins. It can easily be prepared as described by Levy, Scaife and Smith[17] who investigated the hydrolysis of dinitroethane with hydrochloric acid, and the yield of hydroxylamine hydrochloride which remained in solution was found to be 90·8 per cent of theoretical.

The author of the present paper in collaboration with T. Dobosz carried out a number of experiments using 1:2-dinitroethane as a starting material to produce hydroxylamine salts. Experiments by Levy *et al.* have been repeated. Hydrolysis of slightly larger quantities of dinitroethane (e.g. 2 g) with hydrochloric acid led to vigorous reaction accompanied by a considerable increase of pressure owing to decomposition of oxalic acid formed in the reaction.

Better results have been obtained when concentrated sulphuric acid was used, 2 mol. for 1 mol. of dinitroethane. The reaction was carried out in an open vessel at 100°.

The reaction is vigorous and to moderate it, dinitroethane was dissolved in glacial acetic acid, e.g. in the ratio 50 : 50 prior to introduction into sulphuric acid. The acetic acid can be recovered by increasing the temperature to 120° at the end of the reaction.

Hydroxylamine sulphate $(NH_2OH)_2 \cdot H_2SO_4$ was isolated in a crystalline form with a yield of 75–79 per cent.

When sulphuric acid of lower concentration was used, the reaction was slow and required a higher temperature. The yield was lower.

Oxalic acid could not be isolated from the reaction since most of it was decomposed during the reaction.

---

[16] T. Urbański and W. Gurzyńska *Roczn. Chem.* **25**, 213 (1951).

[17] N. Levy, C. W. Scaife and A. E. Wilder Smith *J. Chem. Soc.* 1096 (1946).

A patent was obtained[18] for the preparation of hydroxylamine sulphate from 1:2-dinitroethane.

Preparation of caprolactam from cyclo*hexanone and* 1:2-*dinitroethane*

Novotný[19] suggested a new method of preparing caprolactam, which consists in warming a solution of *cyclo*hexanone and a primary nitroparaffin in concentrated sulphuric acid. This method was examined and confirmed by Piotrowski[20]—one of the present authors' collaborators.

In collaboration with Piotrowski a possibility of using 1:2-dinitroethane as primary nitroparaffin was now examined. Dinitroethane dissolved in glacial acetic acid was introduced into concentrated sulphuric acid at 120°, and *cyclo*hexanone was then introduced into the solution. Acetic acid was distilled and after cooling caprolactam separated. The yield was ca. 72 per cent calculated on *cyclo*hexanone used.

A patent was obtained for this reaction.[21]

Preparation of hydroxylamine sulphate

Two grammes of 1:2-dinitroethane was added in small portions to 3·5 g of concentrated sulphuric acid (98 per cent) previously heated to 100°C and stirred. The reaction was very vigorous due to decomposition of oxalic acid formed during the reaction.

The reaction mixture was cooled below room temperature (5–10°C) and 8–10 ml of ethyl alcohol was added. A precipitate of hydroxylamine sulphate was filtered, washed with alcohol and ether. The yield was 2·13 g (79 per cent of theoretical).

Preparation of caprolactam

Ten grammes of 1:2-dinitroethane was dissolved in an equal weight of glacial acetic acid. The solution was introduced dropwise during 20 min into 35 g of concentrated sulphuric acid, the temperature being maintained between 120–125°C. The reaction flask was kept in a bath of calcium chloride solution boiling at 120°.

*Cyclo*hexanone (12·5 mg) was added dropwise during 24 min to the reaction mixture, the temperature being still kept at 120°.

Acetic acid was removed by distillation.

After the reaction was completed (this was marked by a fall of temperature in the reaction flask), the reaction mixture was carefully neutralised by introducing it into cold aqueous 25% solution of ammonia, the temperature being kept below 50°. The mixture separated into two layers, the lower one consisted of a saturated aqueous solution of ammonium sulphate, the upper layer consisted of caprolactam, which was dissolved in ether, dried over anhydrous sodium sulphate, and purified by distillation b.p. 138–9°/11–12 mm Hg.

The yield was 10·5 g of caprolactam, i.e. ca. 72 per cent (calculated on *cyclo*hexanone).

Acknowledgements—The author thanks Mr. T. Dobosz and Mr. A. Piotrowski for carrying out experiments with 1:2-dinitroethane.

---

[18] T. Urbański and T. Dobosz *Polish Pat.* 40008 (1956).

[19] A. Novotný *Swiss Pat.* 273402 (1952); *U.S. Pat.* 2 569 114 (1952); A. Stoy and A. Novotný *Nova Syntetická Vlákna.* Statní Nakladatelstvi Technické Literatury, Prague (1953).

[20] A. Piotrowski *Przem. Chem.* **12**, 405 (1956).

[21] T. Urbański and A. Piotrowski *Polish Pat.* 40009 (1956).