

MECHANISM OF THE REACTION OF AMINE N-OXIDES WITH ACETIC ANHYDRIDE; THE POLONOVSKI REACTION

O. ČERVINKA, A. FÁBRYOVÁ and J. ZIKMUND

*Department of Organic Chemistry,
Institute of Chemical Technology, 166 28 Prague 6*

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Starting from the reaction of N,N-dimethyl-4-pentenylamine N-oxide with acetic anhydride N-methyl-N-(4-pentenyl)acetamide, N,N-dimethylacetamide, 4-pentenal and 2-methylene-4-pentenal were isolated. In the case of using N,N-dimethyl-4-penten-[1-D₂]ylamine N-oxide, N,N-dimethylacetamide free of deuterium, N-methyl-N-(4-penten-1-D₂-yl) acetamide and 2-methylene-4-penten [1-D]al were formed. In this way the generally accepted mechanism of the reaction of amine N-oxides with acetic anhydride was confirmed and the same course without isomerisation was proved, on the contrary to the literature, for the reaction of amine N-oxides possessing one alkyl group unsaturated.

The most common reaction of amine N-oxides is the Cope thermic decomposition¹ leading to alkene and dialkylhydroxylamine. Trialkylhydroxylamines are formed on Meisenheimer rearrangement of amine N-oxides². The reaction of amine N-oxides, known as the Polonovski reaction³, gives the mixture of compounds, the main portion of which being composed of aldehydes corresponding to the alkyl groups originally attached to nitrogen and dialkylamides. Obviously, a complicated mixture of products results within the condition of different alkyl groups. For this reason, only examples showing two equal alkyls, usually methyls, are described in the aliphatic series (1). Recently, the cleavage of dimethyl- ω -alkenylamine N-oxides with the use of acetic anhydride or propionic anhydride⁴ was described. Besides of formaldehyde and of both possible amides a mixture of unsaturated aldehydes was isolated. The main and in the several cases even the sole product was the aldehyde exhibiting the double bond conjugated to the carbonyl group⁴. The aldehyde was identified by the melting point of its dinitrophenylhydrazone. The isolation of α,β -unsaturated aldehydes within the reaction of N,N-dimethyl-3-butenylamine N-oxide and N,N-dimethyl-4-pentenylamine N-oxide with acetic anhydride, which is difficult to explain on the basis of the presently accepted mechanism⁵, forced the authors of this paper to study the mechanism of this reaction in detail. For this purpose the reaction of N,N-dimethyl-4-pentenylamine N-oxide with acetic anhydride was chosen due to the formation of unique α,β -unsaturated aldehyde 2-pentenal besides of the amides and of formaldehyde.

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N,N-dimethylamide with complex hydride prepared *in situ* on partial reduction of ethyl acetate with lithium aluminium hydride. The α,β -unsaturated aldehyde, 2-pentenal, isolated as the sole product in the original work was not found in the reaction mixture.* For the sake of comparison we prepared this aldehyde on reaction of formylmethylenetriphenylphosphorane with propionaldehyde. The reaction of N,N-dimethyl-4-penten-[1-D₂]ylamine N-oxide with acetic anhydride lead to a mixture of N,N-dimethylacetamide, N-methyl-N-(4-penten-[1-D₂]yl)acetamide and 2-methylene-4-penten-[1-D]al. All experiments given above eliminated the shift of the double bond in the course of the reaction and confirmed the mechanism proposed by Renaud and Leith⁵ (2).

EXPERIMENTAL

The given boiling points and melting points are uncorrected. Analytical samples were dried for 8 hours at laboratory temperature and the vacuum of an oil pump.

Starting Compounds

4-Pentenoic acid b.p. 86–87°C/20 Torr was obtained on alkaline hydrolysis of ethyl 4-pentenoate b.p. 142–144°C prepared on acidic hydrolysis of ethyl allylacetoacetate⁶ b.p. 94–96°C/10 Torr. 5-Pentenoyl chloride b.p. 130–133°C (Literature⁷ gives b.p. 129–131°C).

4-Pentenoic acid dimethylamide was prepared from a) ethyl 4-pentenoate and dimethylamino-magnesium iodide b) 4-pentenoyl chloride and dimethylamine. B.p. 100–102°C/10 Torr. For C₇H₁₃NO (127.2) calculated: 66.11% C, 10.30% H, 11.01% N; found: 65.95% C, 10.51% H, 11.42% N.

N,N-Dimethyl-4-pentenylamine was obtained on reducing the amide with LiAlH₄; b.p. 117 to 118°C; the picrate m.p. 79–80°C (ethanol). The physical constants agree with those of the compound obtained on decomposition of N,N-dimethylpiperidinium hydroxide⁸. N,N-dimethyl-4-penten-[1-D₂]ylamine was obtained on reduction of the amide with LiAlD₄; b.p. 118–120°C.

N,N-Dimethyl-4-pentenylamine N-oxide was prepared according to a method described in the literature⁴. The strongly hygroscopic compound m.p. 98–100°C. This compound was after drying at 70–80° directly used in the next step. N,N-dimethyl-4-penten-[1-D₂]ylamine N-oxide was obtained on a similar procedure.

The Reaction of N,N-Dimethyl-4-pentenylamine N-Oxide with Acetic Anhydride

12.2 g of acetic anhydride diluted with 15 ml of ether was added to a suspension of 15 g (70 mmol) of amine N-oxide in 15 ml of ether during 15 minutes on ice-cooling. After 4-hours' standing at laboratory temperature the mixture was decomposed by a saturated solution of sodium carbonate. The ethereal layer was separated. After ether having been distilled off, the residue was frac-

* According to the authors of the original paper⁴ the melting point of supposed 2-pentenal dinitrophenylhydrazone arose after repeated crystallizations. Following this result the dinitrophenylhydrazone described therein does not exhibit the structure supposed.

tionated. The following fractions were obtained: 1) b.p. 70°C/250 Torr was composed of aldehydes (1.6 g). 2) b.p. 50–60°C/20 Torr the main portion of which was N,N-dimethylacetamide (900 mg). 3) b.p. 70–80°C/5 Torr was almost pure N-methyl-N-(4-pentenyl)acetamide (8.2 g). The particular fractions were purified by preparative gas-chromatography. The purification was realized first on Carbowax 20 M and afterwards on poly-(propyleneglycole succinoate).

4-Pental b.p. 104–106°C. Mass spectrum *m/e*: 84 = [M]⁺, 55 = M–(CHO), 41 = M–(CH₂CHO). Dinitrophenylhydrazone m.p. 119–120°C; literature⁹ gives m.p. 119–120°C.

2-Methylene-4-pental mass spectrum *m/e*: 96 = [M]⁺, 41 = M–(C–CHO), 67 = M–(CHO). Dinitrophenylhydrazone m.p. 142–143°C.

$$\begin{array}{c} \parallel \\ \text{CH}_2 \end{array}$$

The Reaction of N,N-Dimethyl-4-penten-[1-D₂]ylamine N-oxide with Acetic Anhydride

From the reaction of 9 g of amine N-oxide on standing overnight, 600 mg of N,N-dimethylacetamide, 5.1 g of N-methyl-N-(4-penten-[1-D₂]yl)acetamide and 250 mg of 2-methylene-4-penten-[1-D]al were isolated.

N,N-Dimethyl-(4-penten-[1-D₂]yl)acetamide mass spectrum *m/e*: 143 = [M]⁺, 46 = M–(C₆H₅O).

2-Methylene-4-penten-[1-D]al mass spectrum *m/e*: 97 = [M]⁺, 41 = M–(C–CDO), 67 = M–(CDO).

$$\begin{array}{c} \parallel \\ \text{CH}_2 \end{array}$$

All compounds described above were identified by IR and NMR spectra and on comparison with authentic samples.

Model Compounds: 4-Pental

From the reduction of 15 g (118 mmol) of 4-pentenoic acid dimethylamide by the agent obtained on partial reduction of ethyl acetate (6.35 g, 72 mmol) with LiAlH₄ (2.74 g, 72 mmol) dissolved in 120 ml of ether, 1.5 g of pure aldehyde b.p. 103–105°C/750 Torr was isolated using preparative gas-chromatography on Carbowax 20 M. Literature⁹ gives b.p. 103–109°C. Dinitrophenylhydrazone m.p. 119–120°C.

2-Pental

On action of 1M ethereal solution of *n*-butyllithium on methyltriphenylphosphonium iodide the ylide was formed, which in subsequent reaction with ethyl formiate resulted in formyl-methylenetriphenylphosphorane m.p. 184–185°C. (Literature¹⁰ gives m.p. 185–186°C). The mixture of 7.3 g (46 mmol) of ylide and 3 g (52 mmol) of propionaldehyde in 100 ml of benzene was boiled for 12 hours. The course of the reaction was monitored gas-chromatographically on Carbowax 20 M. After benzene having been distilled off the aldehyde b.p. 122–124°C was isolated. Literature¹¹ gives b.p. 120–130°C. Dinitrophenylhydrazone m.p. 160°C.

REFERENCES

1. Cope A. C., Trumbull E. R.: *Organic Reactions* Vol. 11, p. 317. Wiley, New York 1960.
2. Johnstone R. A. W. in the book: *Mechanisms of Molecular Migrations* (B. S. Thyagarajan, Ed.), p. 249. Interscience, New York 1969.
3. Russel C. A., Mikol G. J.: ref. 2, p. 157.

4. Ferles M., Jankovský M.: *This Journal* 36, 4103 (1971).
5. Renaud R. N., Leith L. C.: *Can. J. Chem.* 46, 385 (1968).
6. Brühl J. W.: *J. Prakt. Chem.* 50, 119 (1894).
7. Wieland P., Überwasser H., Anner G., Miessner K.: *Helv. Chim. Acta* 36, 376 (1953).
8. Eikmann J. F.: *Ber. Deut. Chem. Ges.* 25, 3071 (1892).
9. Croxall W. J., van Hook J. O.: *J. Amer. Chem. Soc.* 72, 803 (1950).
10. Trippett S., Walker D. M.: *J. Chem. Soc.* 1961, 1266.
11. Schinz H., Rossi A.: *Helv. Chim. Acta* 31, 1953 (1948).

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