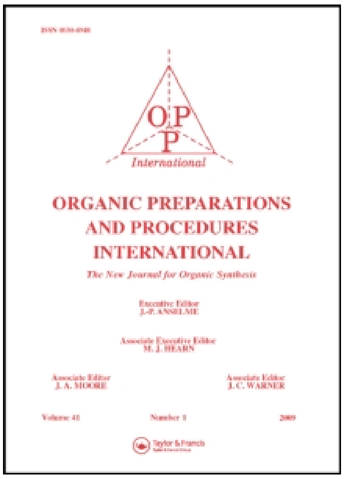

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F. Minisci[a]; A. Quilico[a]
[a] Istituto di Chimica del Politecnico, Milano

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PREPARATION AND REACTIVITY OF THE 2-NITROSO-2-NITROCYCLOHEXANONE

F.Minisci and A.Quilico
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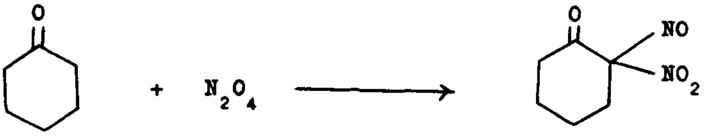
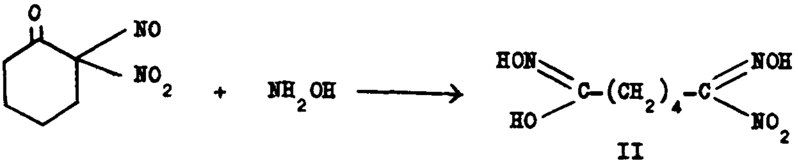


I

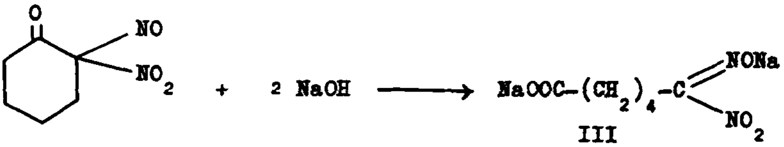
Preliminary reports[1] indicated that the reaction between ketones and dinitrogen tetroxide under suitable conditions could be stopped at α-nitroso-α-nitroketones.This reaction is particularly useful in the case of cyclohexanone:the reaction product I is obtained in good yields under very simple experimental conditions;the reactivity of I is unusually high and permits new syntheses of hydroxamic and nitrolic acids,amides,amidoximes and phenylhydrazones.

The nitrosonitroketone I with hydroxylamine leads to the hydroxamic acid II :



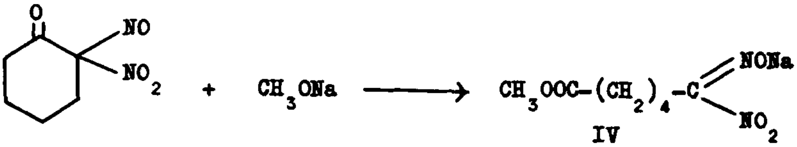
II

The nitrolic acid III is formed with alkaline hydroxides :



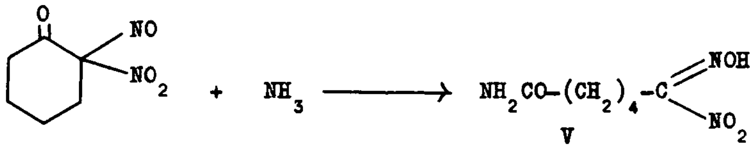
III

The corresponding ester IV is formed with sodium methoxide :



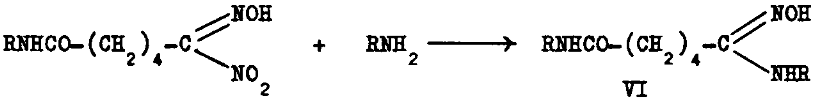
IV

Ammonia and aliphatic amines at first lead to the amide V,



V

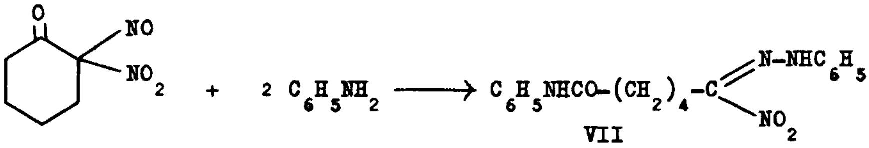
and afterwards to the amidoxime VI :



$$\mathrm{RNHCO{-}(CH_2)_4{-}C}\Big\langle\begin{matrix}\mathrm{NOH}\\ \mathrm{NO_2}\end{matrix} + \mathrm{RNH_2} \longrightarrow \mathrm{RNHCO{-}(CH_2)_4{-}C}\Big\langle\begin{matrix}\mathrm{NOH}\\ \mathrm{NHR}\end{matrix}$$

VI

On the contrary the nitrophenylhydrazone VII is formed with aniline :



VII

Experimental

2-Nitroso-2-nitrocyclohexanone (I). To a solution of 29 g. of cyclohexanone and 30 ml. of acetic anhydride[2] in 160 ml. of carbon tetrachloride, is added at 0° 27 ml. of dinitrogen tetroxide. The solution is maintained at 5-10° for 3 hrs. and the precipitated product, weighing 16.5 g. is collected. After cooling overnight at -10°, the filtrate is kept at 5-10° for an additional 6 hrs. : other 15 g. of product is obtained. After a further 48 hrs. at -10°, an additional 5 g. of product is collected. The total yield of 2-nitroso-2-nitrocyclohexanone amounts to 36.5 g.(72%).The product melts at 98°(dec.). Anal. Calcd. for $C_6H_8N_2O_4$: C, 41.86 ; H, 4.68 ; N, 16.28 . Found : C, 41.75 ; H, 4.62 ; N, 16.30 .

I.R. bands : 1740 cm^{-1}(C=O), 1350 and 1570 cm^{-1}(NO_2), 1290 cm^{-1}(NO). The pure product, colourless cristals (dimer), dissolves in organic solvents with a blue colour (monomer). It slowly deteriorates giving acidic products, with adipic acid as final product; it can be purified by washing with a solution of sodium bicarbonate. The deterioration occurs rapidly, with development of nitrogen oxides, by warming in organic solvents or in acid solutions.

5-Nitroformyloxime of valerohydroxamic acid (II). To a mixture of 5.4 g. of I and 50 ml. of methanol, is added 3 g. of hydroxylamine hydrochloride and 3.6 g. of sodium acetate. The mixture is stirred at room temperature until complete dissolution of I (2 hrs.). The methanol solution is stripped under aspirator vacuum and the residue is crystallized from water; 5.7 g. of product is obtained (89%), m.p.136°(dec.). Anal. Calcd. for $C_6H_{11}N_3O_5$: C, 35.12 ; H, 5.40 ; N, 20.48 . Found : C, 35.18; H, 5.48 ; N, 20.36 .

The product dissolves in alkali with a red colour (nitrolic acid) and it is precipitated unaltered by acids. A violet solution is obtained with ferric chloride and a green precipitate with cupric acetate (hydroxamic acid). Acid hydrolysis leads to adipic acid.

Benzoylderivative, m.p. 126° (dec.) .

Anal. Calcd. for $C_{20}H_{19}N_3O_7$: C, 58.11 ; H, 4.63 ; N, 10.17 . Found : C, 58.08 ; H, 4.56 ; N, 10.18 .

Benzoyl derivative of 5-nitroformyloxime of valeric acid (III). To a solution of 1.2 g. of potassium hydroxide in 30 ml. of water, is added 2 g. of I . After stirring at room temperature for 30 minutes, a red solution is obtained; 2 g. of benzoyl chloride is added at 0° with stirring. The solid precipitate is filtered and washed with ether to remove benzoic acid. The residue is crystallized from aqueous methanol giving 2.9 g. of product melting at 136° (dec.) (85%). Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06 ; H, 4.80 ; N, 9.52 . Found : C, 53.19 ; H, 4.91 ; N, 9.37 .

Final confirmation of the structure of III is provided by synthesis (benzoylation of the known nitrolic acid[3]).

Benzoyl derivative of 5-nitroformyloxime of methyl valerate (IV). To a solution of sodium methoxide, obtained from 0.2 g. of sodium and 20 ml. of methanol, is added 1.5 g. of I . After stirring at room temperature for 20 minutes, a red solution is obtained. The methanol solution is stripped under aspirator vacuum and the residue is dissolved in 20 ml. of water. 1.2 g. of benzoyl chloride is added at 0° with stirring. The solid precipitate is collected and washed with sodium bicarbonate solution to remove the benzoic acid. The residue is crystallized from methanol. The yield is 2.1 g. , m.p. 83° (dec.) (78%).

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.54 ; H, 5.23 ; N, 9.09 . Found : C, 54.68 ; H, 5.23 ; N, 9.02 .

Confirmation of the structure of IV is provided by synthesis from methyl 6-nitrocaproate[4] (nitrosation and benzoylation).

5-Nitroformyloxime of valeroamide (V). To 10 ml. of concentrated ammonia solution, is added 1.2 g. of I with stirring at 0° . The red solution is rapidly evaporated to dryness under reduced pressure and the solid residue is crystallized from water. The yield is 0.8 g. , m.p. 98° (dec.) (39%).

Anal.Calcd. for $C_6H_{11}N_3O_4$: C, 38.09 ; H, 5.86 ; N, 22.21 . Found : C, 38.12 ; H, 5.94 ; N, 22.12 .

Benzoyl derivative, m.p. 122° (dec.) .

Anal.Calcd. for $C_{13}H_{15}N_3O_5$: C, 53.24 ; H, 5.16 ; N, 14.33 . Found : C, 53.36 ; H, 5.24 ; N, 14.15 .

5-Aminoformyloxime (amidoxime) of valeroamide (VI). The reaction is carried out as in the preparation of V except that the reaction is allowed to proceed at room temperature for 48 hrs. The solution is then concentrated under reduced pressure until some white cristals are visible. 10 ml. of acetone is added and 0.9 g. of solid is collected (44%). The product crystallizes from aqueous acetone and melts at 161°.

Anal.Calcd. for $C_6H_{13}N_3O_2$: C, 45.27 ; H, 8.23 ; N, 26.40 . Found : C, 45.32 ; H, 8.41 ; N, 26.23 .

VI is also obtained from V and ammonia under the same conditions. The structure of VI is confirmed by synthesis from the amide of 4-cyanovaleric acid and hydroxylamine.

5-Methylaminoformyloxime (amidoxime) of N-methylvaleroamide (VI). The reaction is carried out as in the preceding case with a concentrated solution of methylamine. From 4 g. of I 1.9 g. of VI is obtained (26%); the product crystallizes from ethanol-ether and melts at 119° .

Anal. Calcd. for $C_8H_{17}N_3O_2$: C, 51.31 ; H, 9.15 ; N, 22.44 . Found : C, 51.46 ; H, 9.14 ; N, 22.39 .

5-Nitroformylphenylhydrazone of valeroanilide (VII). 7.6 g. of I is added with stirring to 12.4 g. of aniline ; the temperature spontaneously rises from 20° to 60° . The reaction is allowed to proceed at room temperature for 24 hrs. ; 50 ml. of ether is added and a yellow precipitate is collected. The product crystallizes from ethanol and melts at 129° . The yield is 5 g. (33%).

Anal. Calcd. for $C_{18}H_{20}N_4O_3$: C, 63.51 ; H, 5.92 ; N, 16.46 . Found : C, 63.59 ; H, 6.01 ; N, 16.55 .

The structure of VII is confirmed by synthesis from known reactions : 6-bromocaproic acid[5] is converted in the anilide by thionyl chloride and aniline, m.p. 81° .

Anal. Calcd. for $C_{12}H_{16}NOBr$: C, 53.26 ; H, 5.93 ; N, 5.18 ; Br, 29.64 Found : C, 53.24 ; H, 5.87 ; N, 5.15 ; Br, 29.41 .

The bromoanilide leads to the corresponding nitroderivative using silver nitrite, m.p. 83° .

Anal.Calcd. for $C_{12}H_{16}N_2O_3$: C, 61.18 ; H, 6.78 ; N, 11.87 . Found : C, 61.24 ; H, 6.72 ; N, 11.83 .

The anilide of 6-nitrocaproic acid with benzendiazonium chloride yields the same product obtained from I and aniline.

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