NITROSOCHLORINATION REACTION OF SUBSTITUTED IMIDAZOLIN-2-ONES

V. V. Golovko, A. I. Statsenskaya, Yu. A. Baskakov,
and Yu. G. Putsykin

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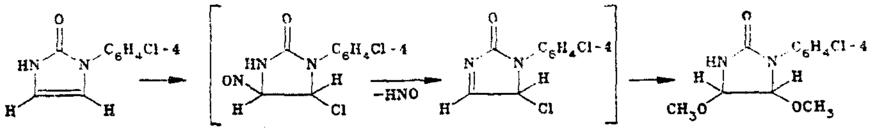
Interaction of nitrosyl chloride with 1-arylimidazolin-2-ones in methanol leads to the formation of 4,5-dimethyoxyimidazolidin-2-ones. Under similar conditions 1,5-diarylimidazolin-2-ones give 1,5-diaryl-4-oximino-5-alkoxyimidazolidin-2-ones. When the reaction is carried out in an aprotic solvent 1,5-diaryl-4-nitrosoimidazolin-2-ones are separated, and when treated with alcohol they give the final reaction products. An increase in temperature and duration of the reaction results in the formation of 1,5-diaryl-5-hydroxyhydantoins.

The familiar electrophilic addition reaction of nitrosyl chloride to the double bond in a number of functionally unsubstituted olefins [1, 2] has no analogous references in the literature for a number of unsaturated heterocycles.

We have studied the nitrosochlorination reaction of 1-aryl- and 1,5-diarylimidazolin-2-ones (I, II). It is shown that when compound Ic undergoes nitrosochlorination in methanol a product is formed, which, according to the data from elemental analysis and IR spectra, corresponds to the structure of 1-(4-chlorophenyl)-4,5-dimethoxyimidazolidin-2-one (III). In fact, the presence in the PMR spectrum of two singlets at 3.18 and 3.31 ppm from the protons of the methoxy groups, two singlets at 4.50 and 4.90 ppm from the protons at the 4- and 5-positions of the ring, a multiplet at 7.40 ppm from the aromatic protons, and finally a broad singlet at 8.40 ppm from the NH group proton supports the proposed structure.



Ic IV III

Evidently, nitrosochlorination of the unsubstituted double bond of the heterocycle involves the intermediate formation of the Δ^3-imidazolin-2-one (IV), in which successive replacement of the chlorine atom by a methoxy group and addition of methanol to the double bond lead to compound III.

On interaction of nitrosyl chloride with compounds II in alcohol products V are obtained which display in their IR spectra intense absorption bands in the region of stretching vibrations of C=N and C=O groups and a monovalent C–O–C bond. In the spectra of these compounds in CCl_4 solution there are intense absorption bands of the free hydroxyl group at 3590-3600 cm^{-1}, which is confirmed also by the data of the PMR spectra (a singlet at 10.20-10.40 ppm from the proton of the HON group). In the PMR spectra of compounds V signals are also observed from the protons of the methoxy and ethoxy groups at 3.20-3.40 ppm or 1.50-1.80 ppm (triplet) and 3.60-4.00 ppm (quartet) (J = 6.0 Hz), respectively, as well as multiplets from the protons of the aromatic rings. This data has made it possible to assign the structure of 1,5-diaryl-4-oximino-5-alkoxyimidazolidin-2-ones to the compounds V obtained. In this case, the conversion route of compounds II to compounds V probably includes the intermediate formation of the nitrosochloride (VI) and nitrosoolefin (VII).

When comparing the results of the reaction of unsaturated heterocycles I and II with NOCl it should be noted that this reaction evidently conforms to the same mechanism as the nitrosochlorination of olefins such as styrene [3] and substituted styrenes [4]. The effect

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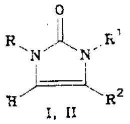
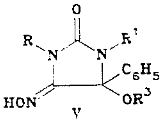
TABLE 1. Properties of Compounds I, II, and V


I, II

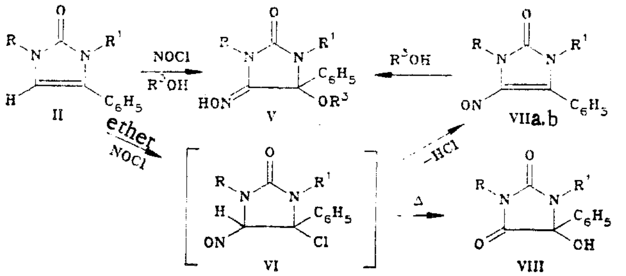

V

Compound*	R^1	mp, °C	IR spectrum (KBr), cm^{-1}				Found, %			Empirical formula	Calculated, %			Yield, %
			C=C	C=O	C=N	C—O—C	C	H	N		C	H	N	
Ia	C_6H_5	126	1680	1670			67,4	4,8	17,8	$C_9H_8N_2O$	67,5	5,0	17,5	82
Ib	3-ClC_6H_4	117	1665	1680			55,4	3,6	14,2	$C_9H_7ClN_2O$	55,5	3,6	14,4	67
Ic	4-ClC_6H_4	154	1670	1690			55,8	3,9	14.2	$C_9H_7ClN_2O$	55,5	3,6	14,4	63
Id	3,4-$Cl_2C_6H_3$	148	1660	1680			47,7	2,4	12,6	$C_9H_6Cl_2N_2O$	47,2	2,7	12,2	87
IIa	CH_3	165	1665	1670			68,5	5.6	16,0	$C_{10}H_{10}N_2O$	68,9	5,8	16,1	72
IIb	C_6H_5	180	1675	1685			76,3	5,4	11,9	$C_{15}H_{12}N_2O$	76,2	5,1	11,9	85
IIc	2-ClC_6H_4	173	1670	1690					10,9	$C_{15}H_{11}ClN_2O$			10,3	88
IId	3-ClC_6H_4	187	1670	1690			67,2	4,3	10,5	$C_{15}H_{11}ClN_2O$	66.5	4,1	10,3	93
IIe	4-ClC_6H_4	193	1685	1690			66,7	4,4	10,2	$C_{15}H_{11}ClN_2O$	66,5	4,1	10,3	95
IIf	C_6H_5	136	1680	1695			77,0	5,8	11,4	$C_{16}H_{14}N_2O$	76,8	5,6	11,2	94
IIg	4-ClC_6H_4	147	1680	1690			67,3	4,3	9,7	$C_{16}H_{13}ClN_2O$	67,5	4,6	9,8	85
Va	C_6H_5	195		1720	1690	1000	64,9	5,2	13,8	$C_{16}H_{15}N_3O_3$	64,6	5,1	14,1	73
Vb	C_6H_5	189		1740	1700	1050	66.1	5,4	13,5	$C_{17}H_{17}N_3O_3$	65,6	5,5	13.5	78
Vc	3-ClC_6H_4	191		1740	1695	1150	58,0	4,5	12,6	$C_{16}H_{14}ClN_3O_3$	57,9	4,3	12,7	85
Vd	4-ClC_6H_4	193		1730	1710	1100	58,0	4,6	12,4	$C_{16}H_{14}ClN_3O_3$	57,9	4,3	12,7	79
Ve	4-ClC_6H_4	190		1720	1700	1050	59,3	4,3	12,1	$C_{17}H_{16}ClN_3O_3$	59,0	4,7	12,2	83
Vf	3,4-$Cl_2C_6H_3$	199		1720	1700	1150	53,9	3.7	11,0	$C_{17}H_{15}Cl_2N_3O_3$	53,7	4,0	11,1	85
Vg	C_6H_5	165		1740	1690	1050	65,7	5,8	13,8	$C_{17}H_{17}N_3O_3$	65.6	5.5	13,5	77
Vh	3-ClC_6H_4	163		1720	1695	1100	58,9	4,7	12,5	$C_{17}H_{16}ClN_3O_3$	59,0	4,7	12,2	81

*Ia-d, IIa-e, Va-f R = H; IIf, g, Vg, h R = CH_3; I R^2 = H; II R^2 = C_6H_5; Va, c, d, g, h R^3 = CH_3; Vb, e, f R^3 = C_2H_5.

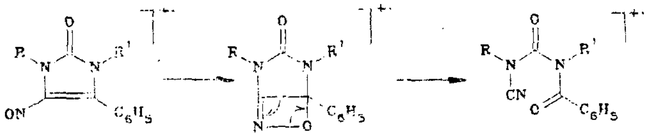
of the N-arylurea fragment of rings I and II on the polarization of the double bond correlates with the effect of the substituent on the $C_{(5)}$ carbon atom of compounds II.

An attempt to isolate compound VI or its isomeric α-chloroxime proved unsuccessful. However, nitrosochlorination of compound IIb dissolved in an aprotic solvent — diethyl ether leads to the separation of a solid crystalline substance VIIa, which displays in its IR spectrum an intense band from vibrations of the C═C and C═O bonds at 1680 cm^{-1} with a shoulder at 1715 cm^{-1}, a bending deformation band of the NH group at 1500 cm^{-1}, and an intense broad band at 1390 cm^{-1} which can be attributed to the nitroso group conjugated with the aromatic ring. In this case, the shift of the band to lower frequency may be related to the formation of hydrogen bonds N—H•••O═N—. On the basis of this information and also the data from elemental analysis compound VIIa was assigned the structure of 1,5-diphenyl-4-nitrosoimidazolin-2-one.



VIIa R=H, R^1=C_6H_5; b R=H, R^1=C_6H_4—Cl-3

Compound VIIb is obtained in a similar manner from compound IId. The monomeric structure of these products, in contrast to, for example, the dimeric structure of styrene nitrosoolefins [4], is supported by the data of the mass spectra, in which the peaks of the molecular ion (M^+) are recorded at values of m/z 265 and 269/271, respectively. The presence of an intense peak from a benzoyl cation in the mass spectra of both compounds makes it possible to propose the following rearrangement of M^+:



Chemical confirmation of the structure of nitroso product VIIa is provided by the formation of compound Va from VIIa on boiling in alcohol solution.

An increase in temperature and duration of the reaction of nitrosyl chloride with compound II leads to the separation of 1,5-diaryl-5-hydroxyhydantoins (VIII), which are evidently products of acid hydrolysis of the intermediate α-chloroxime formed.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 457 instrument in KBr pellets and in CCl_4; PMR spectra were recorded on Tesla BS-487c and Bruker HX-90E instruments using solutions in DMSO-d_6 with internal standard HMDS; mass spectra were recorded on a LKB 2091 mass spectrometer. The properties of the compounds obtained are given in Table 1.

1-Arylimidazolin-2-ones (I). Ten mmole of N-arylcarbamoylaminoacetaldehyde dimethyl acetal [5] was dissolved in 30-40 ml of concentration HCl at 20°C. The precipitate formed was filtered off and recrystallized from alcohol.

1-Alkyl(aryl)-5-phenylimidazolin-2-ones (II). Ten mmole of N-alkyl(aryl)carbamoyl-α-aminoacetophenone [6] was dissolved in 30-40 ml of concentration HCl at 20°C. The precipitate formed was filtered off and recrystallized from alcohol.

1-(4-Chlorophenyl)-4,5-dimethoxyimidazolidin-2-one (III). To a solution of 2 mmole of compound Ic in 50 ml of absolute methanol was added dropwise a solution of 2.5 mmole of nitrosyl chloride in 10 ml of absolute methanol at –10 to –15°C. The solution was kept at this temperature for 3-4 h, after which the mixture was left to stand at 20°C for 2 days. The solvent was evaporated under vacuum, and 70-80 ml of water was added to the residual oil. The aqueous layer was extracted with benzene (3 × 30 ml). The extract was dried over magnesium sulphate, the benzene was evaporated, and the residual oil without further purification was crystallized out by freezing (–40 to –60°C). Yield, 60%; mp, 93-96°C. IR spectrum (KBr): 1090 (C–O–C), 1690 (C=O), 3450 cm^{-1} (NH). Found, %: C 52.2; H 5.3; N 10.9. $C_{11}H_{13}ClN_2O_3$. Calculated, %: C 51.5; H 5.1; N 10.9.

1-Alkyl(aryl)-4-oximino-5-alkoxy-5-phenylimidazolidin-2-ones (VP). A. To a solution of 10 mmole of compound II in 30 ml of methanol (or ethanol) was added dropwise a solution of 20 mmole of nitrosyl chloride in 15-20 ml of methanol (or ethanol) at a temperature of –10 to –15°C. The reaction mass was maintained for 1-2 h (chromatographic monitoring by TLC), the solvent was then evaporated under vacuum, and the residue was recrystallized to give compounds V.

B. A solution of 10 mmole of compound VIIa in methanol was boiled for 30 min, the solvent was evaporated, and the residue was recrystallized from benzene to give compound Va.

1-Aryl-4-nitroso-5-phenylimidazolin-2-ones (VII). To a solution of 10 mmole of compound IIb in 30 ml of diethyl ether was added a solution of 20 mmole of nitrosyl chloride in 30 ml of ether at –10 to –15°C. The reaction mass was maintained for 30 min, the solvent was evaporated under vacuum, and the residue was recrystallized from diethyl ether. Yield, 77%; mp, 125-127°C. Found, %: C 67.7; H 4.0; N 15.9. $C_{15}H_{11}N_3O_2$. Calculated, %: C 67.9; H 4.2; N 15.8. Compound VIIb was obtained in a similar manner from compound IId. Yield, 70%; mp, 131°C. Found, %: C 60.8; H 3.2; Cl 12.1; N 14.3. $C_{15}H_{10}ClN_3O_2$. Calculated, %: C 60.1; H 3.4; Cl 11.8; N 14.0.

1-Aryl-5-phenyl-5-hydroxyhydantoin (VIII). To a suspension of 2 mmole of compound IIb in 30 ml of dry ether was added dropwise a solution of 5 mmole of nitrosyl chloride in 10 ml of dry ether. The mixture was kept at a temperature of –10 to –15°C for 2 h, and it was then increased to 20°C and the reaction mass was left overnight. The solvent was evaporated and the residual reaction product, having first been washed with dry hexane, was recrystallized from benzene. Yield, 60%; mp, 180°C. IR spectrum (CCl_4): 3590 (OH); (KBr): 1700, 1780 (C=O), 3450 cm^{-1} (NH). Found, %: C 67.2; H 4.6; N 10.0. $C_{15}H_{12}N_2O_3$. Calculated, %: C 67.2; H 4.5; N 10.4.

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MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO COMPOUNDS.

9.* 2-DIAZO-2-CYANOACETAMIDES

A. T. Lebedev, P. A. Sharbatyan, A. G. Kazaryan,
V. A. Bakulev, Yu. M. Shafran, and V. S. Petrosyan

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An analysis of the electron impact mass-spectra of 2-diazo-2-cyanoacetamides and the 4-cyano-5-hydroxy-1,2,3-triazoles isomeric to them, showed that the molecular ions of these compounds do not isomerize one into another. The diazo compounds decompose, undergoing a Wolff rearrangement. To study the fragmentation of the diazoamides, one can use the crystalline adducts of these diazo compounds with triphenylphosphine, and to study the fragmentation of the triazoles, their salts with aliphatic amines.

It was shown previously [2] that diazoketones with a heteroatomic grouping in the carbon chain eliminate a molecule of nitrogen and cyclize to form heterocyclic compounds. This takes place in solution by the action of an acid as well as in the gas phase by the action of electron impact. Such an analogy allowed a prediction to be made on the basis of mass-spectral data of the direction and approximate yield of the cyclic product when the reaction was carried out in solution [1, 2].

The question of th linear or cyclic form of diazo compounds containing C=O, C=S, or C=NH groups in position α to the diazo group has already been investigated in papers by Wolff [3, 4] and Dimroth [5]. At the present time, it is reliably known that diazoketones and diazoesters exist exclusively in the linear form [6]: the alternative, 1,2,3-oxadiazole form is unstable and is easily opened as a result of an electrocyclic reaction to the more stable linear form [7]. Diazothioketones exist exclusively in the form of thiadiazoles and attempts to obtain these compounds in the linear form have not, so far, led to success [6]. Diazoamides occupy an intermediate position and can exist in the linear form as well as in the cyclic, triazole form, which can, under certain conditions, change back and forth [6, 8, 9]. These structural features of diazo compounds are determined unambiguously by the increase in the electronegativity of the heteroatoms in the order S < N < O.

Comparing the stability of the molecular ions (M^+) of the linear diazo compounds and their isomeric heterocyclic systems, one can suppose that M^+ of the cyclic isomers should be rather stable (aromatic system) and decompose along a specific path characteristic for such ring. At the same time, M^+ of the linear, diazo compounds are significantly less stable, as a rule, and in the spectra of many of them, the M^+ peak is not observed at all [1, 2, 9].

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*See [1] for No. 8 in the series.

M. V. Lomonosov Moscow State University, Moscow 117234. The Scientific Research Institute of Organic Intermediates and Dyes, Moscow 103787. S. M. Kirov Urals Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1343-1349, October, 1986. Original article submitted March 25, 1985.

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