The band of an associated group is shifted to 3000-3200 cm^{-1} and is overlapped by absorption of the stretching vibrations of the C–H bonds.

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NEW METHOD FOR THE PREPARATION OF CONDENSED IMIDAZOLONES

Yu. M. Yutilov and I. A. Svertilova

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Condensed imidazolones were obtained by the action of diethyl pyrocarbonate on aromatic o-diamines.

Condensed imidazolones (I) are obtained mainly by reaction of aromatic diamines with urea [1], phosgene [2], carbonyldiimidazole [3], or diethylcarbamoyl chloride [4]. The first method is the simplest and most widely used, but requires the use of excess urea, which sometimes hinders the isolation and purification of the imidazolones. In this respect, our method [5] for the synthesis of I by the action of aromatic o-diamines (II) with diethyl pyrocarbonate (DEPC) is more convenient. We used this method (method A) to obtain benzimidazolones (Ia,b), imidazo[4,5-b]-2-pyridones (Ic-g), and imidazo[4,5-c]-2-pyridones (IIh-q). The reaction of DEPC with diamines commences in the cold, but heating to 150-180°C is required to complete the process. The evolution of carbon dioxide and alcohol vapors that accompanies the reaction can be used to monitor the completeness of the conversion of diamines II. Practically pure imidazolones I containing a small amount of DEPC, which is removed by vacuum distillation or washed out with petroleum ether, are obtained at the end of the reaction. (See scheme on following page.)

In contrast to urea [4], DEPC reacts with N,N'-dimethyl-o-phenylenediamine (IIb). The described reaction probably proceeds in two steps. Initially one of the amino groups of diamine II reacts with the reagent, which can be considered to be the anhydride of carbonic acid monoester. The urethane derivative formed in this way is subsequently cyclized to imidazolone I as a result of intramolecular reaction of the carbethoxy group with the second

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Institute of Physical-Organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1277-1280, September, 1976. Original article submitted October 28, 1975.

TABLE 1. Condensed Imidazolones I

Compound I	Reaction conditions				mp, °C	Literature mp, °C	Crystallization solvent	Empirical formula	Found, %		Calc., %		Yield, %	
	method A		method B											
	temp., °C	time, h	temp., °C	time, h					C	H	C	H	method A	method B
a	200—210	0,25			308	308[6]	Ethanol	$C_7H_6N_2O$	—	—	—	—	95	—
b	160—170	0,5	—	—	107	107[6]	Hexane	$C_9H_{10}N_2O$	—	—	—	—	95	—
c	150—160	1	170—180	1,5	274	271—274[7]	Water	$C_6H_5N_3O$	—	—	—	—	90	90[a]
d	150—155	0,5	160—180	2	200—201	200—201[8]	Benzene	$C_7H_7N_3O$	—	—	—	—	85	85
e	170—175	0,5	170—180	1—2	235—236	234—235[9]	Ethanol	$C_7H_7N_3O$	—	—	—	—	83	87
f	165—170	1	160—170	3	234—235	—	Ethanol	$C_{12}H_9N_3O$	68,1	4,2	68,2	4,3	99	99
g	175—180	0,5	185—190	2	175—176	—	Ethanol	$C_{13}H_{11}N_3O$	69,1	4,7	69,3	4,9	99	99
h	150—160	1	185—190	3	315—316	305—306[10]	Water	$C_6H_5N_3O$	—	—	—	—	93	90[r]
i	170—175	0,5	175—180	3	271—272	—	Benzene	$C_7H_7N_3O$	56,6	4,7	56,4	4,7	90	85
j	170—175	0,5	170—180	1	259—260	—	Ethanol	$C_7H_7N_3O$	56,1	4,6	56,4	4,7	99	75
k	175—180	0,5	165—170	0,5	250—251	—	Water	$C_{12}H_9N_3O$	68,2	4,3	68,2	4,3	90	77
l	170—175	0,5	170—175	3	192—193	—	THF	$C_8H_9N_3O$	59,0	5,7	58,9	5,6	80	63
m	180—185	0,5	170—175	1	206—207	—	Ethanol—water	$C_{13}H_{11}N_3O$	69,2	4,7	69,3	4,9	93	80
n	170—175	0,25	160—165	2	342	—		$C_6H_4ClN_3O$	42.3	2,5	42,5	2,4	99	82
o	165—170	0,25	165—170	2	267—268	—	Ethanol	$C_7H_6ClN_3O$	45,8	3,5	45,8	3,3	99	90
p	150—180	2	175—185	3	>400	—	DMF	$C_6H_4N_4O_3$	39,8	2,5	40,0	2,2	80	72
q	175—180	1	180—185	2	239—240	—	Pyridine—ether	$C_7H_6N_4O_3$	43,5	3,3	43,3	3,1	87	70

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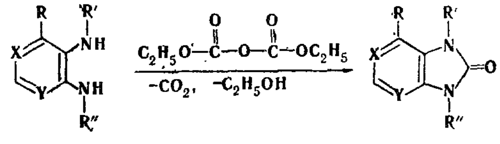
a) The yield of benzimidazolone Ib obtained from diamine IIc and urea was not indicated in [7].
b) Obtained in 86% yield by heating N-(2-amino-3-pyridyl)methylurethane [8].
c) In 15% yield according to the data in [9].
d) Obtained [10] in 70% yield by fusing diamine IIh with urea (at 165° for 1 h).
e) Purified by reprecipitation from weakly alkaline solution by the addition of hydrochloric acid. Found: Cl 20.7%. Calculated: Cl 20.9%.
f) Found: Cl 19.5%. Calculated: Cl 19.3%.



II a-q   I a-q

I, II a X=Y=CH, R=R′=R″=H; b X=Y=CH, R=H, R′=R″=CH_3; c X=CH, Y=N, R=R′=R″=H; d X=CH, Y=N, R=R″=H, R′=CH_3; e X=CH, Y=N, R=R′=H, R″=CH_3, f X=CH, Y=N, R=R′=H, R″=C_6H_5; g X=CH, Y=N, R=R′=H, R″=$CH_2C_6H_5$; h X=N, Y=CH, R=R′=R″=H; i X=N, Y=CH, R=R′=H; R″=CH_3; j X=N, Y=CH, R=R″=H, R′=CH_3; k X=N, Y=CH, R=R′=H, R″=C_6H_5; l X=N, Y=CH, R=R″=H, R′=C_2H_5; m X=N, Y=CH, R=R′=H, R″=$CH_2C_6H_5$; n X=N, Y=CH, R=Cl, R′=R″=H; o X=N, Y=CH, R=Cl, R′=H, R″=CH_3; p X=N, Y=C−NO_2, R=R′=R″=H; q X=N, Y=C−NO_2, R=R′=H, R″=CH_3

amino group of the diamine. It is known [8] that N-(2-amino-3-pyridyl)urethane is converted to imidazolone Ic under similar conditions.

For comparison, imidazolones Ic-q were also obtained by fusion of diamines IIc-q with urea (method B).

EXPERIMENTAL

o-Diaminopyridines (IId,e,h-k,m,n,p). These compounds were obtained by the methods in [11] (IId,e,i,j), [12] (IIh), [13] (IIk), [14] (IIm,n), and [15] (IIp).

2,3-Diaminopyridine (IIc). A 5.6-g (0.04 mole) sample of 3-nitro-2-aminopyridine [16] was added in portions at 75-80° to a solution of 18 g (0.075 mole) of $Na_2S \cdot 9H_2O$ in 80 ml of water, after which the mixture was evaporated to one-third its original volume, and the residual solution was cooled. The resulting precipitate was removed by filtration to give 3.7 g (85%) of needles with mp 118-119° (from benzene) (mp 118.5-119.5° [7]).

3-Nitro-2-phenylaminopyridine. A mixture of 3.2 g (0.02 mole) of 3-nitro-2-chloropyridine [17] and 1.9 g (0.02 mole) of aniline was heated at 120-125° for 1 h, after which it was cooled and dissolved in 10 ml of water, and the solution was neutralized with ammonia. The precipitate was removed by filtration and washed with water to give 4.3 g (99%) of orange needles with mp 70-71° (from alcohol). Found: C 61.6; H 3.9%. $C_{11}H_9N_3O_2$. Calculated: C 61.4; H 4.2%.

3-Amino-2-phenylaminopyridine (IIf). A 4-g (0.071 g-atom) of iron carbonyl and 0.6 ml of concentrated HCl were added in portions with stirring to a refluxing solution of 2.5 g (11.6 mmole) of 3-nitro-2-phenylaminopyridine in a mixture of 15 ml of alcohol and 10 ml of water, and the mixture was refluxed for another 3 h. The hot mixture was filtered, and the solid material was washed on the filter with hot alcohol and water. The filtrate was evaporated to one-fourth its original volume, and the residual solution was made alkaline with 20% NaOH solution. The resulting precipitate was removed by filtration, washed with a small amount of cold water, and dissolved in 10% HCl solution. The solution was refluxed with charcoal and filtered, and the filtrate was neutralized with 20% NaOH solution to give 3.7 g (99%) of a product with mp 140-141° (mp 141° [18]).

3-Nitro-2-benzylaminopyridine. An 8.6-g (80 mmole) sample of benzylamine was added to a solution of 5.7 g (36 mmole) of 3-nitro-2-chloropyridine in 60 ml of benzene, and the mixture was refluxed for 1 h. It was then cooled, and the precipitated benzylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness, and the residue was recrystallized from alcohol to give 8.17 g (99%) of yellow prisms with mp 71-72° (from alcohol). Found: N 18.5%. $C_{12}H_{11}N_3O_2$. Calculated: N 18.3%.

3-Amino-2-benzylaminopyridine (IIg). A 5.6-g (0.1 g-atom) sample of iron carbonyl was added in portions with vigorous stirring to a refluxing solution of 5.7 g (25 mmole) of 3-nitro-2-benzylaminopyridine in 50 ml of acetic acid and 15 ml of water, and the mixture was stirred and refluxed for another 2 h. The hot mixture was filtered, and the solid material was washed on the filter with hot 75% acetic acid solution. The filtrate was evaporated almost to dryness, and the residue was made strongly alkaline with concentrated alkali solution. The diamine was extracted with hot benzene. Workup gave 3.5 g (70%) of prisms with mp 90° (from n-hexane) (mp 87-90° [19]).

4-Nitro-3-ethylaminopyridine N-Oxide. A 5.6-g (124 mmole) sample of ethylamine was added dropwise to a cooled (to 12°) solution of 5.5 g (25 mmole) of 3-bromo-4-nitropyridine N-oxide [20] in 45 ml of dioxane, and the mixture was allowed to stand at room temperature for 1 h. It was then evaporated to dryness, and the residue was washed with 5 ml of water and crystallized from alcohol to give 3.3 g (72%) of golden prisms with mp 153-154°. Found: C 45.7; H 4.6; N 23.1%. $C_7H_9N_3O_3$. Calculated: C 45.9; H 4.9; N 22.9%.

4-Amino-3-ethylaminopyridine (IIl). This compound was obtained by reduction of 4-nitro-3-ethylaminopyridine [6.0 g (33 mmole)] with iron [21 g (0.37 g-atom)], as in the preparation of amine IIf. Workup gave colorless prisms, with mp 126-127° (from benzene), in 90% yield. Found: C 61.5; H 8.3; N 30.5%. $C_7H_{11}N_3$. Calculated: C 61.3; H 8.1; N 30.6%.

2-Chloro-3-amino-4-methylaminopyridine (IIo). A solution of 33.9 g (0.15 mole) of $SnCl_2 \cdot 2H_2O$ in 40 ml of concentrated HCl was added dropwise at 85-90° to a solution of 6.12 g (0.04 mole) of 3-nitro-4-methylaminopyridine [14] in 35 ml of concentrated HCl, and the mixture was refluxed for 1.5 h. It was then cooled and made alkaline with 40% NaOH, and the resulting precipitate was removed by filtration, squeezed thoroughly on the filter, and washed several times with hot chloroform–benzene (1:1). The extract was dried with sodium sulfate, the solvents were removed by distillation, and the residue was crystallized from benzene to give 3.5 g (55%) of colorless needles with mp 165°. Found: C 45.4; H 4.9; Cl 22.3%. $C_6H_8ClN_3$. Calculated: C 45.7; H 5.1; Cl 22.5%.

3,5-Dinitro-4-methylaminopyridine. This compound was obtained by nitration of 3-nitro-4-methylaminopyridine as in the preparation of 3,5-dinitro-4-aminopyridine [15]. Workup gave yellow rhombic plates, with mp 101-102° (from alcohol), in 77% yield. Found: C 36.4; H 3.0; N 28.1%. $C_6H_6N_4O_4$. Calculated: C 36.4; H 3.0; N 28.3%.

5-Nitro-3-amino-4-methylaminopyridine (IIq). This compound was obtained by reduction of 3,5-dinitro-4-methylaminopyridine with ammonium sulfide, as in the preparation of 5-nitro-3,4-diaminopyridine [15]. Workup gave orange prisms, with mp 153° (from benzene), in 66% yield. Found: C 42.7; H 4.7; N 33.1%. $C_6H_8N_4O_2$. Calculated: C 42.9; H 4.8; N 33.3%.

Condensed Imidazolones (Ia-q, Table 1). A) A mixture of 20 mmole of o-diamines IIa-q and 21-25 mmole of diethyl pyrocarbonate, prepared by cooling with ice water, was allowed to stand at room temperature until carbon dioxide evolution ceased. It was then heated on an oil bath, during which alcohol vapors were evolved and excess reagent was removed by distillation. The cooled solid mass was pulverized and crystallized from a suitable solvent.

B) A mixture of 0.1 mole of diamine IIc-q and 0.2-0.3 mole of urea was heated, after which it was cooled and washed with 20-30 ml of water.

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α-OXIDES IN REACTIONS WITH NH ACIDS OF THE HETEROCYCLIC SERIES. III.* ALKYLATION OF 3,5-DICHLORO-1,2,4-TRIAZOLE WITH α-EPOXIDES

T. P. Kofman, I. V. Vasil'eva,
and M. S. Pevzner

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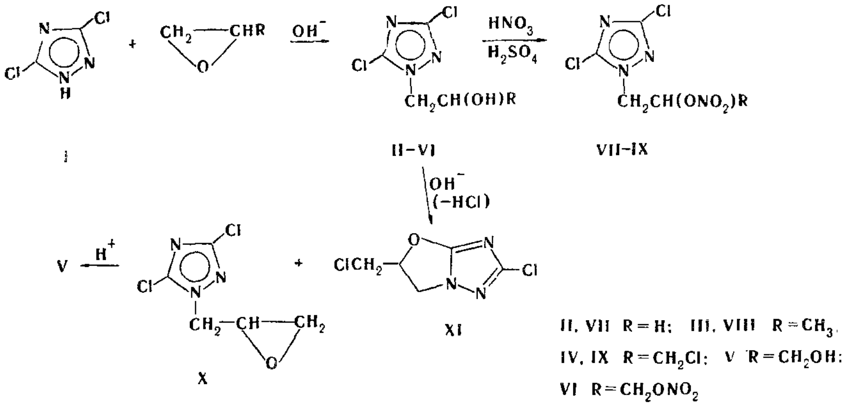
A number of 1-(2-hydroxyalkyl)-3,5-dichloro-1,2,4-triazoles and their derivatives were obtained by reaction of 3,5-dichloro-1,2,4-triazole with α-oxides in proton-donor media in the presence of bases.

The alkylation of 3,5-dichloro-1,2,4-triazole (I) with α-epoxides leads to 1-(2-hydroxyalkyl)-3,5-dichloro-1,2,4-triazoles (II-VI) (Table 1). Compounds V and VI were isolated in pure form; alcohols II and IV were identified by nitration to nitrate derivatives VII-IX (Table 2).



The formation of secondary alcohols in the reaction of unsymmetrical α-epoxides with triazole I was confirmed by the PMR spectra of II-IX. The stability of the signal of the methylene group bonded to the triazole ring in the case of primary alcohol II and alcohols III and VI, the nonequivalence of the methylene groups in the spectrum of diol V, and the shift to weak field of the signal of the methylidyne proton on passing from alcohols III and IV to nitrates VIII and IX are due to the 1-(2-hydroxyalkyl)-3,5-dichloro-1,2,4-triazole structure for III-VI.

In contrast to the more acidic 3,5-dinitro-1,2,4-triazoles (pK_a-0.66 [3]) and 3-nitro-5-bromo-1,2,4-triazole (pK_a 3.05 [2]), 3,5-dichloro-1,2,4-triazole (pK_a 5.22 [4]) does not react with α-epoxides at room temperature in the absence of bases in either aprotic (ether, acetone, and dioxane) or proton-donor media (water and alcohols). The acidity of this substrate is probably insufficient for realization of a process catalyzed by the NH acid itself.

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*See [1] for communication II.

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