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CONDENSED IMIDAZO-1,2,4-AZINES.

19.* SYNTHESIS OF 4-IMINO DERIVATIVES OF 2-METHYL-7,8-DIPHENYL-5H-IMIDAZO[1,2-b]-1,2,4-TRIAZEPINE

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A number of new 4-imino-substituted 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepines were synthesized by replacing the S atom in 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepine-4-thione by the action of nitrogen-containing nucleophiles. It is shown that the imine form is characteristic for the synthesized compounds.

To study the reactivities of 4-oxo and 4-thioxo derivatives of imidazo[1,2-b]-1,2,4-triazepine (ITA) [2] we carried out nucleophilic substitution reactions with primary and secondary amines, hydroxylamine, hydrazine hydrate, p-bromobenzoic acid hydrazide, aminoacetic acid, and 1,2-diamino-4,5-diphenylimidazole.

The starting components were isolated in the reaction with 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepin-4-one [2] in various solvents (alcohols, acetic acid, DMF), while refluxing imidazotriazepin-4-one with hydroxylamine hydrochloride in isopropyl alcohol led to destruction of the triazepine ring, the principal product of which was 1,2-diamino-4,5-diphenylimidazole. A negative result was also obtained in carrying out the synthesis by the method in [3] with use of triethylamine and phosphorus oxychloride. In this connection we used another representative of ITA — 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepine-4-thione (I) — as the starting substrate.

Thione I reacts with monoethanolamine, aniline, morpholine, hydroxylamine, hydrazine hydrate, or p-bromobenzoic acid hydrazide in the case of refluxing in alcohols. Substitution with aminoacetic acid and 1,2-diamino-4,5-diphenylimidazole was observed only when the process was carried out in refluxing DMF (see top of following page).

The $\nu_{C=S}$ absorption band at 1145 cm^{-1} that is specific for the IR spectrum of starting thione I [2] is absent in the IR spectra of substitution products II-IX. The ν_{NH} absorption at 3045-3220 cm^{-1}, which is also observed in the spectrum of the starting imidazotriazepine-4-thione I, is characteristic for the IR spectra of II-IV and VI-VIII. This similarity shows that the compounds under consideration, like substituted imidazo[1,2-b]-1,2,4-triazepin-4-

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*See [1] for communication 18.

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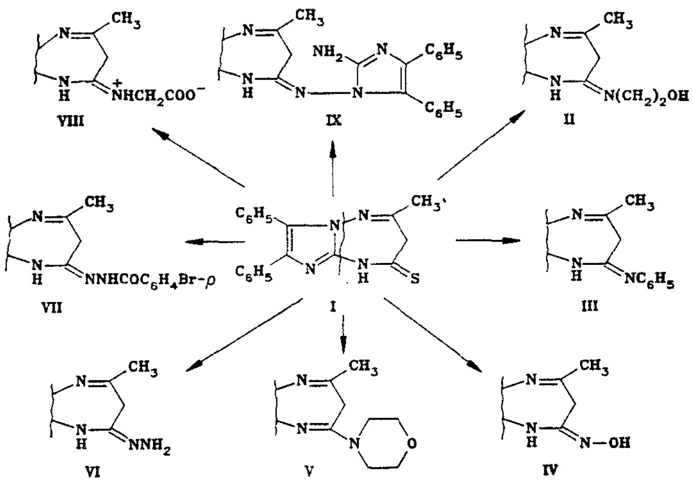

ones [2], exist in the imine form. In addition to the band noted above, the absorption of an alcohol hydroxy group (ν_{OH} 3455 cm^{-1}, δ_{OH} 1335 cm^{-1}) and a C—O bond (ν_{C-O} 1075 cm^{-1}) is observed in the spectrum of β-hydroxymethylamino-substituted ITA II.

In addition to the absorption of a hydroxy group (ν_{OH} 3410 cm^{-1}, δ_{OH} 1335 cm^{-1}), the spectrum of IV contains bands that are characteristic for oximes [4] ($\nu_{C=N}$ 1680 cm^{-1}, ν_{N-O} 920 cm^{-1}).

The broad band at 2800-3400 cm^{-1} in the IR spectrum of hydrazine VI corresponds to the absorption of a hydrazine group. In the case of hydrazide VII, a $\nu_{C=O}$ band at 1640 cm^{-1} is observed in addition to this band.

The structure of amino acid VIII deserves individual discussion. Two characteristic bands — a strong band at 1550-1610 cm^{-1} and a medium band at 1400 cm^{-1} — which correspond to asymmetrical and symmetrical vibrations of the bonds in the carboxylate ion, are observed in its IR spectrum. In addition, there is a band at 2360 cm^{-1}, which corresponds to the absorption of an NH^+ group.

In the mass spectrum of VIII a molecular-ion peak (M^+) at 373* appears only at a sample-vaporization temperature of 320°C; this indirectly indicates its betaine structure, thereby confirming the IR spectroscopic data. The high-resolution mass spectrum (HRMS) obtained gives the indicated empirical composition of the VIII molecule (experimentally determined value 373.1540 vis-à-vis 373.1539 calculated for $C_{21}H_{19}N_5O_2$). The observed (in the first step of the fragmentation of M^+) splitting out of H_2O (355; experimentally determined value 355.1475 vis-à-vis 355.1433 calculated for $C_{21}H_{17}N_5O$) and COOH (328; experimentally determined value 328.1521 vis-à-vis 328.1562 calculated for $C_{20}H_{18}N_5$) particles, together with the $[M - CH_2COO]^+$ ion peak (315; experimentally determined value 315.1474 vis-à-vis 315.1484 calculated for $C_{19}H_{17}N_5$) of the 4-imino-2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepine structure [2], proves the presence of a carboxy group in the investigated molecule. The direct elimination from M^+ of an $HNCH_2COO$ particle (300; HRMS: experimentally determined value 300.1381 vis-à-vis 300.1375 calculated for $C_{19}H_{16}N_4O$), together with the ion at 315, confirms the betaine structure of the compound. The direct splitting out of CH_2COO and $HNCH_2COO$ particles from M^+ was confirmed by the mass spectra of metastable ions (the DADI technique).

The subsequent trend of the fragmentation is typical for triazepine structures and is accompanied by the ejection of a CH_3CN particle (ring contraction) [5-7] from $[M - COOH, -H]^+$ (286; experimentally determined value 286.1236 vis-à-vis 286.1218 calculated for $C_{18}H_{14}N_4$) and $[M - HNCH_2COO]^+$ ions (259; experimentally determined value 259.1078 vis-à-vis 259.1109 calculated for $C_{17}H_{13}N_3$). Thus the set of IR and mass-spectral data not only proves the existence of two-ring system VIII in the form of a dipolar ion but also confirms its imine structure.

The mass spectrum of IX is characterized by a maximally intense M^+ peak at 548 (HRMS: experimentally determined value 548.2412 vis-à-vis 548.2378 calculated for $C_{34}H_{28}N_8$). The initial acts in the fragmentation of M^+ involve cleavage of the $=N-N-$ bond in the hydrazone

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*The numbers that characterize the ions are the m/z values.

TABLE 1. Characteristics of II-IX

Compound	mp, °C*	IR spectrum, NH, cm^{-1}		Found, %			Empirical formula	Calc., %			Yield, %
		ν	δ	C	H	N		C	H	N	
II	264—266	3065	1495	70,0	5,8	19,7	$C_{21}H_{21}N_5O$	70,2	5,9	19,5	70
III	292—293	3085	1505	77,0	5,5	18,0	$C_{25}H_{21}N_5$	76,7	5,4	17,9	65
IV	276—278	3120	1490	69,1	5,1	21,3	$C_{19}H_{17}N_5O$	68,9	5,2	21,1	49
V	274—275	—	—	71,4	6,1	18,0	$C_{23}H_{23}N_5O$	71,7	6,0	18,2	57
VI	217—219	3080	1490	69,0	5,4	25,7	$C_{19}H_{18}N_6$	69,1	5,5	25,4	50
VII	248—250	3050	1490	60,5	4,1	16,6	$C_{26}H_{21}BrN_6O$	60,8	4,1	16,4	62
VIII	318—320	—	—	67,4	5,2	18,4	$C_{21}H_{19}N_5O_2$	67,6	5,1	18,7	45
IX	287—289	3090	1510	74,2	5,0	20,3	$C_{34}H_{28}N_8$	74,4	5,1	20,4	50

*The compounds were recrystallized: II-VII from aqueous DMF, and VIII and IX from DMF.

fragment joining the two heterorings in the IX molecule (HRMS: experimentally determined value 234.1033 vis-à-vis 234.1031 calculated for $C_{15}H_{12}N_3$, and experimentally determined value 314.1411 vis-à-vis 314.1406 calculated for $C_{19}H_{16}N_5$); this was proved by the spectra of the metastable ions [8]. Cleavage of the =N—N— bond is accompanied by migration of hydrogen atoms and the formation of pseudomolecular ions at 235 and 315 of the 2-amino-4,5-diphenylimidazole and 4-imino-2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepine structures, respectively.

The character of the fragmentation of the latter corresponds to the fragmentation scheme described in [2]; this proves the presence of an imidazotriazepine two-ring system in the investigated IX.

The direct elimination from M^+ of NH (HRMS: experimentally determined value 533.2377 vis-à-vis 533.2328 calculated for $C_{34}H_{27}N_7$) and NH_2CN (HRMS: experimentally determined value 506.2181 vis-à-vis 506.2218 calculated for $C_{33}H_{26}N_6$) particles indicates the presence of an H_2NCN grouping in IX; this, together with the ions at 234 and 235, confirms the participation in the formation of the investigated compound of the 1-amino group of the diaminoimidazole residue (the direct elimination of NH from M^+ is probably due to the "ortho effect").

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The mass spectra were obtained with a Varian MAT-311A spectrometer with direct introduction of the samples into the ion source under standard recording conditions [9]. The high-resolution mass spectra (HRMS) were obtained under the same conditions with M/ΔM = 10,000 and PFK as the standard.

The analytical characteristics of II-IX are presented in Table 1.

4-Substituted 2-Methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepines II-VII. A 10-mmole sample of the corresponding amino derivative (in the case of hydroxylamine hydrochloride the latter was first neutralized with 50% $NaHCO_3$ solution) was added to a suspension of 10 mmole of imidazotriazepine-4-thione I in 50 ml of isopropyl alcohol, and the reaction mixture was refluxed for 5 h. It was then cooled, and the precipitate was removed by filtration, washed with isopropyl alcohol, and dried.

Compounds VIII and IX were synthesized by refluxing the starting components in DMF (6 h).

Mass spectrum* of VIII (sample-vaporization temperature 320°C), m/z (%): 373 (21), 355 (24), 328 (11), 327 (31), 315 (10), 301 (16), 300 (60), 299 (41), 287 (10), 286 (37), 285 (11), 272 (11), 271 (19), 259 (13), 258 (16), 246 (12), 235 (22), 234 (15), 218 (11), 193 (33), 190 (22), 178 (20), 167 (93), 165 (64), 129 (21), 122 (32), 104 (98), 103 (85), 89 (30), 77 (100), 76 (38).

Mass spectrum of IX (sample-vaporization temperature 220°C), m/z (%): 549 (35), 548 (100), 533 (16), 532 (14), 508 (15), 507 (40), 506 (34), 492 (22), 491 (35), 332 (21), 315 (14), 314 (12), 274 (34), 273 (14), 259 (12), 246 (11), 235 (19), 234 (16), 193 (29), 178 (16), 165 (17), 129 (10), 126 (18), 104 (36), 103 (46), 91 (21), 77 (29), 76 (12).

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*The ion peaks with intensities ≥10% of the maximum peak in the spectra are presented.

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HYDROXY-, ALKOXY-, AMINOMETHYLATION OF NH-OXAZIRIDINES*

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3,3-Dimethyloxaziridine reacts with chloral and acetaldehyde to give crystalline N-(α-hydroxyalkyl)oxaziridines; the reaction with acetaldehyde is reversible. The N-aminomethylation of NH-oxaziridines is not realized, evidently because of the tendency of oxaziridines to iminate nucleophiles. The weakly nucleophilic chloromethylphthalimide and chloromethyl methyl ether give imidomethyl- and methoxymethyloxaziridines. 3,3-Dimethyldiaziridine reacts with excess chloromethyl methyl ether to give the N-monomethoxymethyl derivative. It is shown that α-hydroxyalkyloxaziridines and methoxymethyl-substituted oxaziridine and dizaridine do not enter into the aminomethylation of compounds with a labile hydrogen.

The products of the reaction of secondary amines with carbonyl compounds — aminocarbinols — and alkoxymethylamines are active α-aminoalkylating reagents. However, their reactivities decrease markedly when a nitrogen atom is included in the strained three-membered ring. Thus, aziridines and diaziridines react with carbonyl compounds to give stable aminocarbinols [3-5], which do not give symmetrical aminals with excess starting amine [4, 6], while alkoxymethylamines are formed in the presence of alcohol [4, 7]. Stable adducts with chloral are used for the isolation and identification of aziridines [3, 8] and diaziridines [5].

In the present research the reaction of NH-oxaziridines with aldehydes was studied for the first time. It is shown that 3,3-dimethyloxaziridine (I) reacts with chloral or chloral hydrate to give adduct II in the form of one diastereomer† (according to PMR), which is a stable crystalline compound that does not react with excess starting oxaziridine. In contrast to chloral, acetaldehyde reacts with oxaziridine I reversibly. The formation of oxaziridinocarbonyl III in the form of a mixture of diastereomers IIIa and IIIb is observed from the PMR

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*Communication 54 of the series "Asymmetric Nitrogen" (see [1] for communication 53); communication 35 of the series "Geminal Systems" (see [2] for communications 34).

†Here and subsequently, the absolute configurations of the diastereomeric oxaziridines are shown conventionally.

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