DIAZABICYCLOALKANES WITH NITROGEN ATOMS IN BRIDGEHEAD POSITIONS. 16.* SYNTHESIS AND PROPERTIES OF BENZO[b]-1,4-DIAZABICYCLO[2.2.2]OCTENE AND DIBENZO[b,e]-1,4-DIAZABICYCLO[2.2.2]OCTADIENE, CONTAINING PRIMARY AROMATIC AMINO ACIDS

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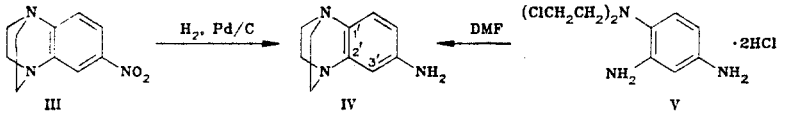
4'-Aminobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene and 4'-aminodibenzo[1',2'-b,e]-1,4-diazabicyclo[2.2.2]octadiene have been prepared by cyclization reactions of N-β-chloroethyl derivatives of 1,2,4-triaminobenzene and aminophenazine, and subsequent catalytic hydrogenation of the corresponding 4'-nitrobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene and 4-benzylaminodibenzo[1',2'-b,e]-1,4-diazabicyclo[2.2.2]-octadiene. Using the conversion of these compounds to azides as an example, we have demonstrated the feasibility of applying these primary aromatic amines for the synthesis of derivatives of these heterocycles.

We have previously synthesized benzo[b]-1,4-diazabicyclo[2.2.2]octene (I) and dibenzo[b,e]-1,4-diazabicyclo[2.2.2]octadiene (II) [3], and have also investigated their behavior under electrophilic substitution reaction conditions [1, 4]. The observed reaction principles (which were elucidated) severely restrict the utility of these compounds for the synthesis of functionalized derivatives of heterocycles I and II. For this reason it was of interest to us to examine other approaches for the preparation of derivatives via modification of the substituents in the aromatic rings. The most promising compounds in this regard seemed to be amino-substituted heterocycles, which could be easily prepared either by construction of the diazabicyclic fragment from intermediates containing the desired primary amino groups, or else by reactions of groups which have been introduced in a preliminary step into heterocyclic systems I and II. We have demonstrated both synthetic variations.

4'-Aminobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (IV) was prepared in high yield by reduction of the previously reported compound, 4'-nitrobenzo[1,2-b]-1,4-diazabicyclo[2.2.2]octene (III) [4].



III IV V

However, compound III is not readily available, so we decided to investigate the double cyclization reaction of N^1,N^1-bis(β-chloroethyl)-1,2,4-triaminobenzene dihydrochloride (V) in greater detail. We found that the conditions used for the formation of the unsubstituted compound I (refluxing hydrobromic acid [2]) were not suitable for the preparation of amine IV, since the amine is not stable in this medium. Dimethylformamide proved to be expedient solvent for the cyclization reaction of dihydrochloride V, in that it slowly decomposes upon heating to 140°C with release of a base, namely, dimethylamine. This probably facilitates gradual removal of the proton protecting group in the starting material, and neutralization of the hydrogen chloride which is evolved during the cyclization reaction. Compound IV could be easily isolated from the complex reaction mixture due to its extreme hydrophilicity. Initial introduction of base, or the use of other solvents for this cyclization reaction, dramatically reduces the yield of the desired reaction product. Based on the PMR spectrum of compound IV

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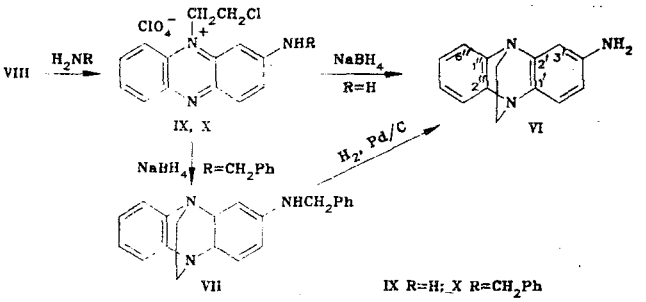
TABLE 1. PMR Spectra of Synthesized Compounds

Compound	Aromatic proton signals,** ppm (J, Hz)				CH_2 group proton signals
	3'(1)-H, d	5'(3)-H, d.d	6'(4)-H,d	3''-6''(5-8)-H	
IV	6.56 (2,5)	6,50	6,96 (7,5)	—	2,6—3,2 sym.m
VI	6,71 (2,2)	6,40 (7,2)	7,08—7,41 m		3,23 s
VII	6,62 (2,1)	6,26 (7,4)	6,99—7,38 m		3,13 s; 4,22 s ($PhCH_2$)
IX	7,18 (1,8)	7,78 (9,1)	7,91—8,59 m		4,35 t, 5,40 t
X	6,58 (2,0)		7,29—8,34 m***		4,01 t; 5,07 t; 4,51 s ($PhCH_2$)
XI	6,90 (2,5)	6,87	7,15 (9,0)	—	2,6—3,3 sym.m
XII	6,77 (2,0)	6,38 (8,0)	7,02—7,42 m		3,17 s

*In $CDCl_3$; in the case of phenazines IX and X, in DMSO-D_6.
**Proton numbering for phenazines IX and X is given in parentheses.
***The phenyl group signals fall within the same range.

(see Table 1), the diazabicyclic fragment is readily identified, with its characteristic multiplet at 2.6-3.2 ppm. The position of the amino group in the aromatic ring was verified by the presence of SSCC corresponding to 1,2,4-trisubstituted benzenes; the amino group gives rise to a broad signal at 3.5 ppm. The IR spectrum contains bands which are characteristic of substituted benzo[1,4-b]-1,4-diazabicyclo[2.2.2]octenes [4]. The NH_2 group bending vibrations for compound IV in the solid state give rise to two absorption bands, at 1649 and 1623 cm^{-1}, while in solution only one band appears, at 1629 cm^{-1}.

4'-Aminodibenzo[1',2'-b,e]-1,4-diazabicyclo[2.2.2]octadiene (VI) and 4'-benzylaminodibenzo-[1',2'-b,e]-1,4-diazabicyclo[2.2.2]octadiene (VII) were prepared using 5-(β-chloroethyl)phenazinium chloride (VIII), which has been described previously [3].



In the first stage of this reaction we utilized the well known nucleophilic substitution reactions of quaternary phenazine ammonium salts [5, 6]. The second stage in this reaction was carried out under reductive cyclization conditions, which were analogous to those used earlier for the synthesis of dibenzo[b,e]-1,4-diazabicyclo[2.2.2]octadienes [6]. Compound VI proved to be stable only in dilute hydrocarbon solutions; upon crystallization from these solutions the compound decomposes, to give a set of colored polymeric products. All attempts to stabilize the amine by conversion to a salt or by acylation only accelerated decomposition. We were also able to synthesize compound VI by debenzylation of the reliably identified compound VII. The benzyl group was removed by catalytic hydrogenation in methanol, which gave compound VI in excellent yield; the spectral characteristics of the latter were completely superimposable on the spectral characteristics of a sample of compound VI synthesized via cyclization. The substance prepared in this manner was also unstable in the crystalline state, apparently because of its susceptibility to intermolecular alkylation in the crystalline state.*

The ethylene bridge protons in compound VI appear in the PMR spectrum (Table 1) in the form of a singlet at 3.23 ppm, which is characteristic of 4'-substituted dibenzo[b,e]-1,4-diazabicyclo[2.2.2]octadienes [6]. Three groups of multiplets are observed downfield; these appear to be due to overlap of the signals for 1,2- and 1,2,4-substituted benzene rings. Be-

*A similar type of rate acceleration in the solid phase is well known for the rearrangement of methyl p-(dimethylamino)benzenesulfonate and p-(trimethylammonium)benzenesulfonate [7].

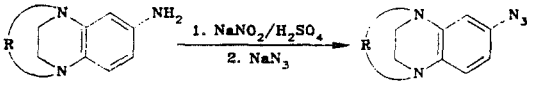
TABLE 2. IR and UV Spectra of Synthesized Compounds

Compound	IR Spectrum (KBr), cm⁻							UV spectrum (in alcohol) λ_{max} nm (log ε)
	stretching vibrations				bending vibrations			
	C—N	N=N=N	C—H	N—H	CH_2	arom. C—H	N—H	
IV	1050	—	2977, 2948, 2875	3424, 3319	1496, 822	845, 829	1649, 1623*	207 (4,14), 240 (4,07), 294 (3,34)
VI	1055	—	2947, 2882, 2845	3418, 3314	1459	889, 824, 800, 761	1625	208 (4,24), 276 (3,44), 298 (3,44)
VII	1023	—	3028, 2937, 2869	3308	1458	883, 844, 800, 739	1618	207 (4,76), 258 (4,22), 300 (3,61)
IX	1023, 1048	—	2955, 2865	3422	1483, 1412	855, 757	1647	236 (4,41), 285 (4,60), 380 (3,96), 395 (4,01), 518 (4,13)
X	—	—	3010, 2955	3448	1461	844, 762, 711	1651	212 (4,30), 237 (4,44), 296 (4,47), 380 (3,93), 400 (4,00), 538 (4,07)
XI	1047	2122	2975, 2951, 2882	—	1484, 815	845, 824	—	210 (4,21), 252 (4,16), 280 (3,50)
XII	1023	2120	3008, 2967	—	1467	890, 840, 790, 770	—	214 (4,12), 268 (3,76)

*When the spectrum was recorded for a solution in $CHCl_3$, only one band appeared, at 1629 cm^{-1}.

cause of the instability of compound VI in the crystalline state it was not possible to obtain accurate elemental analysis data for this compound; its high resolution mass spectrum confirmed the proposed elemental composition, however. Additional evidence for the structure comes from confirmation of the structure of its immediate precursor, compound VII, which is stable; its spectra exhibit all of the characteristic structural elements for dibenzo[b,e]-1,4-diazabicyclo[2.2.2]octadiene.

In order to establish the feasibility of exchanging the primary amino groups in compounds IV and VI for other substituents, we examined the diazotization reactions of these amines and subsequent workup with sodium azide. The corresponding azides were prepared in ~80% yields in this manner.



IV, VI — XI, XII

IV, XI R=C_2H_4; VI, XII R=1,2-C_6H_4

Azide XI is a stable, low-melting crystalline substance, which is sensitive to UV irradiation. In the PMR spectrum of this compound the diazabicyclic fragment appears at 2.6-3.3 ppm in the form of a symmetrical multiplet, while the aromatic protons give rise to a multiplet characteristic of a 1,2,4-trisubstituted benzene ring. The IR spectrum contains an absorption band due to the azido group at 2122 cm^{-1}.

Azide XII, just like the starting amine VI, is an unstable compound. Judging from the reduction in the intensity of the azido group absorption band at 2120 cm^{-1}, crystalline azide XII decomposes in the dark at 20°C, with a halflife of approximately 2 h. Solutions of this compound are more stable, but they are sensitive to UV irradiation. The PMR spectrum of the azide corresponds to the assigned structure, but also undergoes gradual changes, namely, the ethylene bridge signal at 3.15 ppm is converted to unresolved signals at 4.3 and 5.1 ppm, which correspond to proton signals for a $N^+CH_2CH_2X$ fragment; this is indicative of cleavage of the diazabicyclic fragment. Due to the absence of reliable elemental analysis data for azide XII, its composition was confirmed by high resolution mass spectrometry (cf. Table 4).

The mass spectra of the substituted benzo[b]- and dibenzo[b,e]-1,4-diazabicyclo[2.2.2]-octadienes prepared in this study (Table 3) contain, in addition to the peaks corresponding to the molecular ions, peaks for $(M - 28)^+$ ions, reflecting cleavage of the ethylene bridge, or in the case of azides, corresponding to cleavage of nitrogen. In the UV spectra of amines IV, VI, VII, and azides XI, XII, the absorption band at 240-300 nm is apparently associated

TABLE 3. Mass Spectra of 4'-Substituted Benzo[b]-1,4-diazabicyclo[2.2.2]octenes IV and XI and Dibenzo[b,e]-1,4-diazabicyclo[2.2.2]octadienes VI, VII, and XII

Compound	m/e values (ion peak intensity as % of maximum)
IV	176 (16), 175 (99) M^+, 174 (10), 147** (50), 146 (100), 133 (52), 119 (13), 88 (15), 74 (13), 65 (12), 60 (12)
VI	223 (12) M^+, 209 (14), 208*** (100), 207 (80), 206 (13), 193 (21), 181 (13), 180** (82), 179 (21), 152 (10), 104 (11), 113 (11), 90 (19), 77 (16), 76 (15)
VII	314 (20), 313 (100) M^+, 312 (41), 285** (34), 284 (16), 222 (33), 195 (10)
XI	202 (11), 201 (100) M^+, 173** (22), 172 (14), 146 (18), 145** (40), 144 (12), 119 (13), 118 (14), 117 (18), 63 (12), 42 (20)
XII	250 (14), 249 (91) M^+, 221** (24), 220 (100), 194 (12), 193** (76), 168 (16), 149 (13), 112 (12)

*Only peaks due to ions with intensities >10%.
**Characteristic $[M - 28]^+$ ion; cleavage of either a C_2H_4 and/or N_2 fragment.
***Cleavage of an NH group.

primarily with the substituents attached to the benzene ring, since the structural rigidity of the heterocycles practically precludes conjugation of the bridgehead nitrogen atoms with the aromatic system.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer using KBr pellets; UV spectra were obtained on a Specord UV-Vis spectrophotometer using solutions in ethanol, while PMR spectra were obtained on a Bruker HX-90 spectrometer versus HMDS as internal standard. Mass spectra were measured on an MS 8200 apparatus (Finnigan MAT). Thin layer chromatography was performed on Silufol UV-254 plates using the following systems: tert-butyl alcohol–methyl ethyl ketone–formic acid–water, 8:6:3:3 (A); chloroform–methanol, 5:1 (B).

The principal characteristics of the newly synthesized compounds are summarized in Tables 1-4.

4'-Aminobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (IV). A solution of 0.82 g (4.0 mmole) of 4'-nitrobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (prepared as in [4]) in 50 ml ethanol was mixed (agitated) under an atmosphere of hydrogen with 0.1 g of 10% palladium catalyst, which was deposited on activated charcoal. After completion of hydrogen uptake, the catalyst was removed by centrifugation and the solution was evaporated under vacuum. The residue was washed with refluxing petroleum ether (70-100°C), dried under vacuum, and recrystallized from toluene. A colorless crystalline substance, it sublimes at 170°C (0.2 mm Hg) with partial decomposition.

4'-Aminobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene Dihydrochloride (IV·2HCl). A solution of 15.0 g (46.7 mmole) of N^1,N^1-di(β-chloroethyl)-1,2,4-triaminobenzene dihydrochloride (prepared as in [8]) in 1.5 liter DMF (which had been stored over NaOH, distilled, and dried over 4A zeolites) was heated at 140°C for 4 h under an Ar atmosphere. The solution was cooled to 20°C and treated with 50 ml concentrated HCl, then evaporated under vacuum. The residue was dissolved in 100 ml water and filtered through a column containing 150 cm^3 of activated charcoal. The column was washed with an additional 270 ml of water and the combined filtrates were evaporated under vacuum. The residue, a mixture of dimethylamine hydrochloride and the trihydrochloride of compound IV, was dissolved in 250 ml of boiling ethanol, cooled to 0°C, and 150 ml ether was added. This results in the precipitation of the dihydrochloride of compound IV in the form of colorless crystals, mp 242-250°C (in a sealed tube, dec.). Base IV could be isolated by neutralization of its dihydrochloride IV·2HCl with an equivalent amount of 10% NaOH. Chloroform was added to the solution, water was removed with anhydrous $MgSO_4$, and the solution was concentrated and then washed with petroleum ether. Colorless crystals, mp 230-233°C (from toluene, in a sealed tube). The compound prepared in this manner did not reveal a mp depression when mixed with a sample of base IV prepared by reduction of the nitro derivative III; the IR spectra of the two samples were also identical.

TABLE 4. Characteristics of Synthesized Compounds

Compound	mp, °C	$R_f \cdot 10^2$ A ~ (B)	Found, %				Molecular formula	Calculated				Yield, %
			C, %	H, %	N, % (Cl, %)	M		C, %	H, %	N, % (Cl, %)	M	
IV	230—233*	26	68,3	7,32	24,0	175,1095	$C_{10}H_{13}N_3$	68,5	7,48	24,0	175,1109	90
IV·2HCl	242—250*	26	48,4	6,11	16,7 (28,7)		$C_{10}H_{13}N_3 \cdot 2HCl$	48,4	6,09	16,9 (28,6)		37**
VI	>60***	31				223,2689	$C_{14}H_{13}N_3$				223,2684	13 (A), 81 (B)
VII	165—167	(54)	80,6	6,11	13,4	313,1578	$C_{21}H_{19}N_3$	80,5	6,11	13,4	313,1579	19
IX	121—123	60	46,8	3,54	11,5 (20,0)		$C_{14}H_{13}Cl_2N_3O_4$	46,9	3,65	11,7 (19,8)		38
X	104—107	78	56,1	4,28	9,40 (15,7)		$C_{21}H_{19}Cl_2N_3O_4$	56,2	4,27	9,37 (15,8)		50
XI	45—46	(74)	59,7	5,47	34,8	201,1011	$C_{10}H_{11}N_5$	59,7	5,51	34,8	201,1014	80
XII	>80***	(75)				249,1018	$C_{14}H_{11}N_5$				249,1014	83

*In a sealed capillary.

**Base IV was isolated in the form of IV·2HCl in 95% yield.

***Unstable in the crystalline state, melts with decomposition.

2-Amino-10-(β-chloroethyl)phenazinium Perchlorate (IX). To a solution of 1.0 g (3.6 mmole) 5-(β-chloroethyl)phenazinium chloride (prepared as in [3]) in 10 ml water was added with stirring 0.8 g (4.2 mmole) ammonium persulfate, and after 10 min 5 ml of 25% ammonia solution was added. The mixture was allowed to stand for several days, after which the resulting precipitate was removed by filtration and washed with hot water until the intense red color of the filtrate disappeared. The combined filtrate was then evaporated under vacuum to 5 ml in volume, and cooled in ice. The resulting precipitate was removed by filtration and washed on the filter. The crystals which were obtained in this manner were dissolved in 5 ml methanol and ether was added to precipitate 2-amino-10-(β-chloroethyl)phenazinium chloride. The chloride was further purified by refluxing it for 0.5 h in 20 ml water with 0.4 g of activated charcoal. The solution was filtered and 5 ml of 10% lithium perchlorate in 5% perchloric acid was added to precipitate the desired perchlorate IX. Black, needle-shaped crystals.

2-Benzylamino-10-(β-chloroethyl)phenazinium Perchlorate (X). To a solution of 1.4 g (5 mmole) 5-(β-chloroethyl)phenazinium chloride in 35 ml dry acetonitrile was added with stirring 1.7 g (5.3 mmole) of chloranil; after 10 min 4 ml of benzylamine was added to the solution. After 0.5 h a precipitate appeared; it was filtered, washed with acetonitrile, and the combined filtrate was evaporated down to 5 ml in volume. Compound X was then precipitated with ether. Recrystallization from 5% perchloric acid gave dark red, needle-shaped crystals.

4'-Benzylaminodibenzo[1',2'-b,e]-1,4-diazabicyclo[2.2.2]octadiene (VII). To a suspension of 0.2 g (5.3 mmole) sodium borohydride in 20 ml dry xylene at 70°C was added with vigorous stirring a solution of 0.45 g (1.0 mmole) of perchlorate X in 2 ml dry sulfolane. The reaction mixture was refluxed for 6 h, and the precipitate was removed by filtration and washed with ether. The combined filtrate was evaporated under vacuum and 5 ml of water was then added to the oily residue. Compound VII was extracted with ether in a continuous extraction apparatus. Traces of sulfolane were removed by washing the extract with 20 ml water, and the ether extract was then dried over $MgSO_4$; the solvent was removed under vacuum and the residue was chromatographed on a column (1.5 × 90 cm) with Silasorb-600 (15 μm) silica gel using solvent system B. The column flow rate was 4 ml/min, and the retention time for compound VII was 35 min. Light yellow crystals (from hexane), it could be visualized on TLC with p-(dimethylamino)benzaldehyde or based on spot darkening after UV irradiation.

4'-Aminodibenzo[1',2'-b,e]-1,4-diazabicyclo[2.2.2]octadiene (VI). A. Prepared from perchlorate IX using the procedure described above for the synthesis of compound VII. Yellow, rapidly darkening crystals.

B. A solution of 0.06 g (0.2 mmole) compound VII in 20 ml methanol was mixed (agitated) under an atmosphere of hydrogen with 0.05 g 10% Pd/C, until the calculated amount of hydrogen had been absorbed. The catalyst was removed by filtration and the solvent was evaporated under vacuum; the resulting oily residue was crystallized from pentane. The spectral data and physical properties of the compound prepared according to these two methods A and B were identical.

4'-Azidobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (XI). A solution of 1.24 g (5.0 mmole) of dihydrochloride IV•2HCl in 5 ml concentrated H_2SO_4 was evacuated to remove HCl, and then diluted with cooling with 5 ml of water; diazotization was carried out by adding dropwise over 0.5 h 5 ml of 1 M $NaNO_2$ (5.0 mmole), while maintaining the temperature of the reaction mixture below −5°C. The mixture was stirred in the cold for 2 h, and then treated over 5 min with 5.5 ml of 1 M NaN_3 (5.5 mmole); the mixture was kept until no more nitrogen gas was evolved. The solution was then neutralized upon cooling with 15 ml of 25% ammonia, and the azide was extracted with ether (3 × 20 ml), dried over $MgSO_4$, and evaporated under vacuum; the residue was crystallized from 10 ml petroleum ether (40-70°C) by cooling to −10°C. Light yellow crystals. The compound sublimes under vacuum at 60°C (0.2 mm Hg), and is relatively stable when exposed to light, although it is sensitive to UV irradiation.

4'-Azidodibenzo[1',2'-b,e]-1,4-diazabicyclo[2.2.2]octadiene (XII). This was prepared in a manner analogous to that described above, starting with compound VI. Light yellow crystals, they darken rapidly (from pentane). The compound is relatively stable in solution in the absence of acids, but is sensitive to UV irradiation.

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THE SIMPLEST PHENYLNITRONES AND THEIR CONVERSION INTO ISOXAZOLIDINE DERIVATIVES

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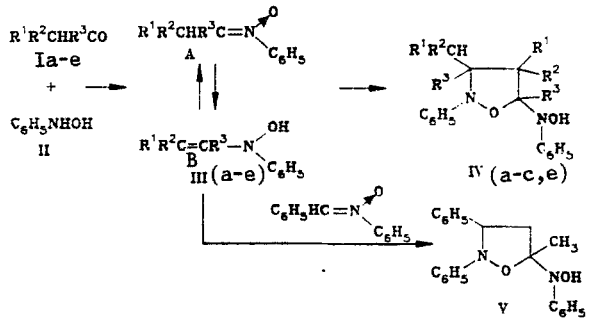
Reactions of N-phenylhydroxylamine with the simplest alkanals leads initially to the formation of N-phenylnitrones, dimerization of which gives 5-substituted isoxazolidine. Taking the reactions of N-phenylnitrones, benzaldehyde, and acetone as an example, the possibility of a crossover reaction has been established.

The possibility of using nitrones in 1,3-bipolar cycloaddition reactions has attracted some attention [1]. However, N-alkylnitrones of aliphatic enolizable aldehydes and ketones have only recently been characterized [2, 3] and reliable information on the corresponding N-phenyl nitrones is lacking. N-arylnitrones have been discovered only for carbonyl components with not more than one hydrogen atom at the α-position or with sterically displaced N-arylhydroxylamines [3].

The product of the reaction of acetone with N-phenylhydroxylamine was first isolated by Bamberger and Rudolf [4] but its dimer structure, 2-phenyl-3,3,5-trimethyl-5-(N-phenylhydroxylamino)isoxazolidine (IVe), was not established until sixty years later [5]. Recent work [2, 3] shows that the formation of similar dimers is a general feature of the reaction of the majority of N-arylhydroxylamines and their alkyl analogs with aldehydes and ketones.

Dimerization is regarded as the mechanism of the 1,3-bipolar cycloaddition of the corresponding nitrones IIIA to their enamine tautomers IIIB [6]. The applicability of this conversion to derivatives of N-phenylhydroxylamine leads one to expect the formation of the corresponding nitrones in this reaction also.



I, III, IV a $R^1=R^2=R^3=H$; b $R^1=CH_3$, $R^2=R^3=H$; c $R^1=C_2H_5$, $R^2=R^3=H$; d $R^1=R^2=CH_3$, $R^3=H$; e $R^1=R^2=H$, $R^3=CH_3$

It is found that the aldonitrones IIIAa-d are obtained practically instantaneously and quantitatively on mixing the reagents with $CDCl_3$, although the reaction with acetone is reversible in the presence of water-abstracting media or acidic catalysts.

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