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REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH AMINES

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The literature contains highly contradictory data on products of the reaction of 2H-azirines with aromatic and cyclic amines, and there are no data at all on the reaction of azirine I with aliphatic amines. As a result of heating of 2-phenylazirine with aniline and its derivatives, six types of compounds were obtained: benzanilide, pyrazine, phenacylaniline, indole, pyrrole, and an enediamine [1]. The reaction of 5-aminoisoxazoles with aniline and its analogs gives N,N-diarylureas and substituted pyrazine-2,5-dicarboxamides, products of the reaction of amines with the intermediate 2H-azirine [2, 3]. As a result of 1,3-dipolar cycloaddition of substituted aziridines to 2-phenyl-2H-azirine, diazabicyclohexanes are formed [4].

We investigated the reactions of 2,2-dimethyl-3-phenylazirine (I) with ammonia, methylamine, aziridine, pyrrolidine, and piperidine. As a result of the reaction of azirine I with ammonia and methylamine, adducts (III and IV) of the reacting substances in 2:1 and 1:1 ratios, respectively, were isolated. The vibrational spectra of the obtained compounds contained bands of NH_2-group vibrations (3300 and 3380 cm^{-1}); the spectrum of compound III also contained a band of NH-group stretching vibrations (3250 cm^{-1}); and the spectrum of compound IV contained a band of the C=N bond (1650 cm^{-1}). To determine the structure, we investigated the ^1H and ^{13}C NMR spectra of the obtained compounds (the spectral data are given in the experimental part). In the proton NMR spectrum of adduct III, we observed a broadened NH-group singlet and also the presence of two groups of phenyl protons. In the region of 176 ppm, its ^{13}C NMR spectrum contained a singlet which could be assigned only to resonance of the carbon atom of the C=N group (in the IR spectrum, the band of C=N bond stretching vibrations apparently overlapped the band of aromatic-ring vibrations). The presence of nonequivalent resonance signals of the four C-CH_3 groups in the ^1H and ^{13}C NMR spectra of compound III indicates the involvement of two molecules of azirine I in the reaction with ammonia (as confirmed by the data of elemental analysis) and also indicates the cyclic structure of the obtained compound III.

The ^{13}C NMR spectrum of compound IV contained only one carbon-atom C=N singlet (see the experimental part), and it should therefore have an acyclic structure. This was also confirmed by the equivalence of the CH_3 groups in the ^1H and ^{13}C NMR spectra. Mass-spectrometric analysis of IV showed the presence of M^+ 176 corresponding to the empirical formula of IV. Thus, on the basis of spectral and analytical data, we can consider that 2-amino-3,3,6,6-tetramethyl-2,5-diphenyl-2,3,5,6-tetrahydropyrazine (III) was formed in the reaction of azirine I with ammonia and that N-(2-amino-2-methyl-1-phenylpropylidene)methylamine (IV) was formed in the case of the similar reaction with methylamine.

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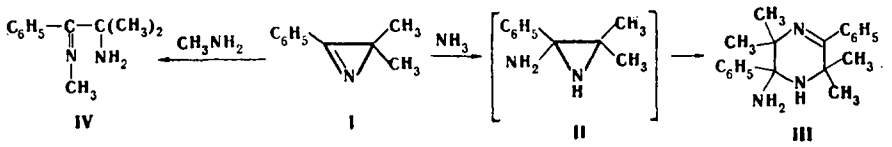
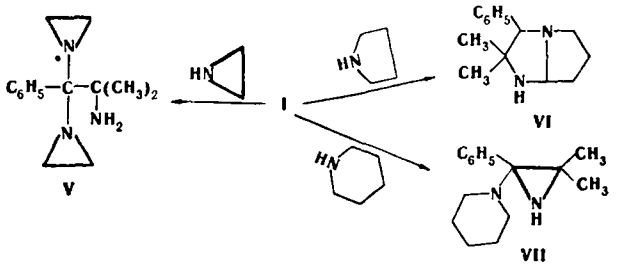


The formation of azomethine IV is in agreement with the results of [5]; tetrahydropyrazine III was probably formed as a result of addition of a second molecule of azirine I to the intermediate aziridine II, tending to undergo isomerization to the ylide structure.

As a result of reaction of azirine I with cyclic amines, three different types of compounds were obtained:



The vibrational spectrum of compound V contained two bands of stretching vibrations of the NH_2 group (3320 and 3390 cm^{-1}) and also of the CH_2 group of the aziridine ring (3075 cm^{-1}). Its ^1H NMR spectrum contained a broadened singlet of the NH_2 group and a singlet of CH_2 protons of the aziridine ring with relative intensity of 8H, something which makes it possible to assume the presence of a structure with two aziridine rings. This conclusion is favored by the equivalence of the CH_3 groups in the NMR spectra. From all the analytical data, we can consider that 2-amino-2-methyl-3,3-diaziridino-3-phenylpropane (V) was formed in the reaction of azirine I with aziridine. Similar compounds were isolated during treatment of alkali-metal ethyleneamides with geminal halides [6].

The ^1H NMR spectrum of compound VI contained absorption signals of two CH groups, each with relative intensity of 1H. One CH group had no vicinal protons, and the other was next to the CH_2 group. The nonequivalence of the CH_3 groups in the NMR spectra indicates the cyclic structure of compound VI. Its IR spectrum contained an absorption band of the NH group (3250 cm^{-1}), but there was no absorption of the C=N bond. On the basis of the above-presented data, we can assume that the reaction of azirine I with pyrrolidine gave 3,3-dimethyl-2-phenyl-1,4-diaza[3.3.0]bicyclooctane (VI). Mass-spectrometric analysis showed the presence of M^+ 216 corresponding to the empirical formula of VI.

Substituted 2-aminoaziridine VII was isolated only in the reaction of azirine with piperidine. Nonequivalence of the methyl groups was observed in the NMR spectra of adduct VII, something wich indicates its cyclic structure. The proton NMR spectrum also contained a singlet of the NH group, the presence of which was confirmed by the data of the IR spectra (3280 cm^{-1}).

The variety of the structure of the obtained compounds was probably due to the tendency of the addition products to undergo isomerization with the formation of ylide systems [7] and their subsequent rearrangement in relation to the amine enzyme.

EXPERIMENTAL

The IR spectra were obtained with a UR-20 spectrometer in Nujol and in the form of pure liquids. The mass spectra were recorded with an MS-905 spectrometer (70 eV). The ^1H NMR spectra were obtained with a Perkin-Elmer R-12A spectrometer (60 MHz) for 5% solutions with TMS as the internal standard. The ^{13}C NMR spectra were recorded with a Bruker WH-90 spectrometer. The chemical shifts were measured with respect to TMS. The physicochemical characteristics of compounds III-VII are given in Table 1.

TABLE 1. Physicochemical Characteristics of Compounds III-VII

Compound	bp, °C (pressure, mm)	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
III	77 (0,001)	78,6	8,4	13,4	$C_{20}H_{26}N_2$	78,3	8,2	13,2	72
IV	40 (0,001)	74,7	8,8	15,6	$C_{11}H_{16}N_2$	75,0	9,1	15,9	50
V	67 (0,005)	72,5	8,9	17,8	$C_{14}H_{21}N_3$	72,8	9,1	18,2	66
VI	67 (0,005)	77,5	9,0	12,8	$C_{14}H_{20}N_2$	77,7	9,2	13,0	47
VII	64 (0,003)	78,0	9,4	12,1	$C_{15}H_{22}N_2$	78,3	9,6	12,2	48

2-Amino-3,3,6,6-tetramethyl-2,5-diphenyl-2,3,5,6-tetrahydropyrazine (III). Ammonia (5 g) (0.3 mole) was added to a solution of 4.74 g (0.03 mole) of azirine I [8] in 30 ml of methyl alcohol. The whole was stirred for 1 h 30 min at room temperature, the alcohol was distilled off, and the residue was recrystallized from petroleum ether. Yield, 3.5 g (73%). Mp 101°C. Proton NMR spectrum ^1H ($CDCl_3$), δ: 1.00, 1.07, 1.25, 1.54 (singlet, C–CH_3), 1.78 (singlet, NH_2), 1.97 (singlet, NH), 7.18 (5H, multiplet, C_6H_5), 7.63 (5H, multiplet, C_6H_5). Carbon-13 NMR spectrum ^{13}C ($CDCl_3$), δ: 26.27, 27.44, 28.81, 29.85 (C–CH_3), 55.78 (quaternary C), 70.40 (quaternary C), 97.63 (C–NH_2), 127.59, 128.83, 129.02, 129.28, 130.52 (phenyl C), 134.52 (C_α), 145.40 (C_α), 176.14 (C=N).

Compound IV was obtained similarly.

N-(2-Amino-2-methyl-1-phenylpropylidene)methylamine (IV). Proton NMR spectrum ^1H ($CDCl_3$), δ: 1.23 (singlet, C–CH_3), 1.74 (singlet, NH_2), 2.87 (singlet, N–CH_3), 6.96 (2H, multiplet, H_o), 7.34 (3H, multiplet, H_m and H_p). Carbon-13 NMR spectrum ^{13}C ($CHCl_3$), δ: 27.07 (C–CH_3), 38.35 (N–CH_3), 54.06 (C–N). 125.06 (C_o), 125.61 (C_p), 126.31 (C_m), 135.23 (C_α), 153.26 (C=N).

2-Amino-2-methyl-3,3-diaziridino-3-phenylpropane (V). Azirine I (4.74 g) (0.03 mole) and 1.29 g (0.03 mole) of aziridine were held at 70°C in an ampul for 10 h and then distilled. Yield, 2.5 g (66%). Proton NMR spectrum ^1H ($CDCl_3$), δ: 1.23 (6H, singlet, C–CH_3), 1.38 (2H, singlet, NH_2), 1.74 (8H, singlet, CH_2), 7.14 (3H, multiplet, H_m and H_p), 7.65 (2H, multiplet, H_o). Carbon-13 NMR spectrum ^{13}C ($CHCl_3$), δ: 21.19 (CH_2), 27.56 (CH_3), 58.73 (C–NH_2), 78.85 (benzyl C), 126.21 (C_p), 126.45 (C_o), 128.30 (C_m), 138.42 (C_α).

Compounds VI and VII were obtained similarly. The individuality of compounds III-VII was confirmed by thin-layer chromatography.

3,3-Dimethyl-2-phenyl-1,4-diaza[3.3.0]bicyclooctane (VI). Proton NMR spectrum ^1H ($CDCl_3$), δ: 0.80 and 1.23 (3H and 3H, singlet, C–CH_3), 1.49 (1H, singlet, NH), 1.8 (4H, multiplet, 6.7-CH_2), 2.56 and 2.83 (2H, multiplet, 8-CH_2), 3.36 (1H, singlet, 2-CH), 4.63 (1H, triplet, 5-CH), 7.29 (5H, multiplet, C_6H_5). Carbon-13 NMR spectrum ^{13}C ($CDCl_3$), δ: 21.23 and 26.34 (quarter,* C–CH_3), 24.21 (triplet, 6-CH_2), 32.88 (triplet, 7-CH_2), 53.54 (triplet, 8-CH_2), 64.21 (singlet, quaternary C), 77.08 (doublet, 2-CH), 80.20 (doublet, 5-CH), 126.09 (doublet, C_p), 126.87 (doublet, C_o), 127.06 (doublet, C_m), 140.14 (C_α).

2-Piperidino-2-phenylaziridine (VII). Proton NMR spectrum ^1H ($CDCl_3$), δ: 0.92 and 1.21 (3H and 3H, singlet, C–CH_3), 1.52 (6H, multiplet, δ- and γ-CH_2), 2.32 (4H, multiplet, α-CH_2), 2.48 (1H, singlet, NH), 7.36 (5H, multiplet, C_6H_5). Carbon-13 NMR spectrum ^{13}C ($CHCl_3$), δ: 18.78 and 22.65 (C–CH_3), 23.12 (γ-CH_2), 24.88 (β-CH_2), 42.44 (quaternary C), 48.93 (α-CH_2), 66.64 (quaternary C), 125.96 (C_o), 127.93 (C_m), 133.20 (C_α).

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