recorded with a Perkin–Elmer R 12A spectrometer with tetramethylsilane as the internal standard. The ^{13}C NMR spectra of 30% solutions of the compounds in $CDCl_3$ were obtained with a Bruker WH-90 spectrometer (22.63 MHz). The accuracy in the measurements of the ^{13}C chemical shifts was ±0.1 ppm.

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REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH HYDRAZINE AND ITS DERIVATIVES

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UDC 547.717'873:543.422.25

The corresponding α-amino ketone hydrazones were obtained by reaction of 2,2-dimethyl-3-phenylazirine with hydrazine, N,N-dimethylhydrazine, methylhydrazine, and semicarbazide. It was established that unsymmetrical azines are formed in the reaction of 2-amino-2-methyl-1-phenyl-1-propanone hydrazone with aliphatic and cyclic ketones. The corresponding tetrahydro-1,2,4-triazines were obtained in the case of the analogous reaction with aliphatic and aromatic aldehydes.

2,3-Diaryl-2H-azirine-2-carboxamide reacts with hydrazine hydrate and phenylhydrazine to give 1,2,4-triazin-6-one derivatives [1, 2]. In addition to the latter, an addition product – trans-3-hydrazinoaziridine-2-carboxamide – is formed in <10% yield. The principal product of the reaction of 3-aryl-2H-azirine-2-carboxylate with hydrazine was rubazonic acid [2]. Singh and Ulmann [3] have shown that hydrazine reacts with phenyl 2-phenyl-2H-azirin-3-yl ketone to give 4-amino-3,5-diphenylpyrazole.

In the light of the above, we decided to investigate the possibility of the preparation of hydrazinoaziridines from 2,2-dimethyl-3-phenylazirine (I).

Compounds with the formula $C_{10}H_{13}N_2RR'$ (where R and R' are substituents of the hydrazine fragment) were obtained by reaction of azirine I with hydrazine, N,N-dimethylhydrazine, methylhydrazine, and semicarbazide. The band of a C=N bond is observed in the IR spectra of these compounds (Table 1).

A singlet, which can be assigned only to the resonance of the carbon atom of the C=N bond, is noted in their ^{13}C NMR spectra at 155-170 ppm (Table 2). Consequently, the indicated compounds can have only a noncyclic structure. The presence in the PMR spectrum of the product of azirine I with hydrazine of two broad singlets of the NH_2 groups, of which one (δ 1.3 ppm) is attached to an sp^3 carbon atom and the other (δ 4.8 ppm) is attached to a C=N bond, provides evidence in favor of this conclusion. The equivalence of the CH_3 groups in both the ^1H NMR spectra (Table 3) and the ^{13}C NMR spectra also confirms the noncyclic structures of the products.

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TABLE 1. IR and UV Spectra of Hydrazones II-V

Compound	$\nu_{C=N}$, cm-1	λ_{max}, nm (lg ε)
II	1600	211 (14 200), 278 (2200)
III	1630	208 (10 000), 280 (1100)
IV	1625	210 (10 000), 278 (1800)
V	*	207 (11 900), 230 (6400)

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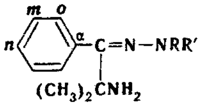
*Shoulder at 1655 cm^{-1}, and $\nu_{C=N}$ and $\nu_{C=O}$ bands at 1670 cm^{-1}.

TABLE 2. ^{13}C Chemical Shifts (20% solutions in $CDCl_3$)



Compound	R	R′	CH_3	—C—	C=N	C_α	C_o	C_m	C_n	C_R	$C_{R'}$
I	—	—	25,0	33.9	177,8	126,9	129,4	130,1	133,3	—	—
II	H	H	29,8	54,9	158,9	134,3	129,1	129,7	128,9	—	—
III	CH_3	CH_3	30,1	55,6	169,0	137,9	128,0	128,4	128,4	47,8	47,8
IV	CH_3	H	29,8	54,8	155,9	134,8	129,1	129,7	128,9	38,3	—
V	$CONH_2$	H	29,4	55,6	157,5*	132,4	128,6	129,9	129,9	158,5*	—

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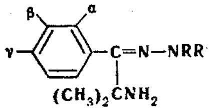
*This assignment is ambiguous.

TABLE 3. Parameters of the ^1H NMR Spectra of



Compound	R	R′	Solvent	Chemical shifts, δ, ppm					
				CH_3	NH_2	H_α	H_β and H_γ	R	R′
Azirine I	—	—	CCl_4	1,35	—	7,72	7,4	—	—
II	H	H	CCl_4	1,16	1,3	7,09	7,4	4,8	4,8
III	CH_3	CH_3	CCl_4	1,19	1,3	7,12	7,2	2,29	2,29
IV	CH_3	H	CCl_4	1,17	1,4	7,07	7,4	2,77	4,2
			d_6-DMSO	1,14	2,6	7,13	7,4	2,70	4,5*
V	$CONH_2$	H	d_6-DMSO	1,16	2,6	7,10	7,5	6,4	7,0

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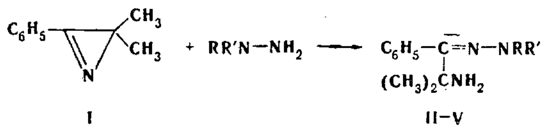
*$^3J_{HNCH}$ = 4.4 Hz.

Thus on the basis of the spectra data it can be assumed that the products of the reaction of azirine I with hydrazine and its derivatives are α-amino ketone hydrazones II-V rather than the corresponding hydrazinoaziridines.



I

II-V

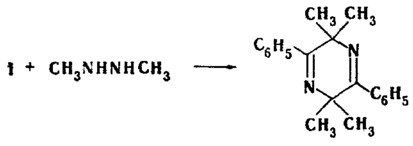
II R=R′=H; III R=R′=CH_3; IV R=CH_3, R′=H; V R=$CONH_2$, R′=H

The formation of related compounds as intermediates was assumed in the reaction of 2H-azirine with salts of amines and hydrazines [3, 4].

Additional data that confirm the II-V structures were obtained from an analysis of the UV spectra (Table 1), in which a short-wave absorption band similar in position to the absorption band of ketone dialkylhydrazones [5] but with an intensity that exceeds the intensity of the latter by a factor of five is observed. The intensity of the absorption band decreases as the number of substituents attached to the amine nitrogen atom increases because of steric hindrance, which interferes with the optimal orientation of the p and π orbitals [5, 6].

Dihydropyrazine VI was obtained in the reaction of sym-dimethylhydrazine with azirine I.

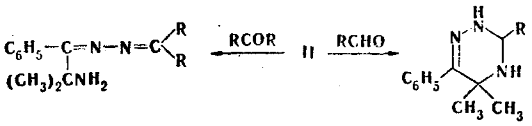
Products of addition of hydrazines to azirine I, which are inclined to undergo isomerization to azomethine ylide structures [2], are evidently formed initially; their subsequent transformations are determined by the structure of the hydrazine fragment



VI

The α-amino ketone hydrazones obtained are interesting starting compounds for the synthesis of a number of nitrogen-containing compounds [7]. At this stage in the research we investigated the reactivity of II with respect to the C=O bond. Compounds of the general formula $C_{10}H_{13}N_3R''$ (where R'' = alkylidene; the empirical formula was confirmed by mass spectrometry) are formed in the reaction of hydrazone II with acetone, cyclohexanone, acetaldehyde, and aromatic aldehydes. The band of a C=N bond is observed in the IR spectra of the products. The IR and ^{1}H and ^{13}C NMR spectroscopic data indicate that unsymmetrical azines VII and VIII are formed in the reaction of hydrazone II with ketones. Two singlets corresponding to the two carbon atoms of the C=N bonds are observed at weak field in the ^{13}C NMR spectra of the products of the reaction of hydrazone II with acetone and cyclohexanone. The singlet at 4.8 ppm, which corresponds to a hydrazone amino group and is present in the spectrum of hydrazone II, vanished in the ^{1}H NMR spectra of VII and VIII. It may therefore be assumed that the reaction of hydrazone II with ketones takes place at the hydrazone group. The electronic spectra of VII and VIII contain an intense short-wave absorption band (∿ 210 nm), the position of which coincides with the position observed for hydrazone II; however, its intensity is 1.5-2 times the intensity of the latter. The increase in the intensity of the absorption band at 210 nm attests to realization of a significant conjugation effect in nonsymmetrical azines, as previously noted in [6].

However, the reaction products in the case of aliphatic and aromatic aldehydes were substituted tetrahydro-1,2,4-triazines IX and X.



VII, VIII

IX, X

VII, IX R=CH_3; VIII R—R=—$(CH_2)_5$—; X R=p-ClC_6H_4

The singlet of a carbon atom of only one C=N band is observed in the ^{13}C NMR spectra of IX and X.

Two one-proton singlets of NH protons are present in the ^{1}H NMR spectra. Consequently, both NH_2 groups of hydrazone II are simultaneously involved in the reaction with the aldehyde. This is possible only in the case of a cyclic structure for IX and X. It should be noted that the tetrahydro-1,2,4-triazine structure is also confirmed by the nonequivalence of the resonance signals of the CH_3 groups in the ^{1}H and ^{13}C NMR spectra.

EXPERIMENTAL

The melting points of the products were determined with a Boetius microheating stage.

TABLE 4. α-Amino Ketone Hydrazones II-V

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
II	67—68	67,2	8,7	23,7	$C_{10}H_{15}N_3$	67,8	8,5	24,1	79
III	66—67	70,7	9,5	20,0	$C_{12}H_{19}N_3$	70,3	9,5	20,5	72
IV	23—24	68,8	8,7	21,4	$C_{11}H_{17}N_3$	69,2	8,9	21,9	48
V	115—116	59,7	6,9	24,9	$C_{11}H_{16}N_4O$	60,1	7,3	25,4	53

The UV spectra of $5 \cdot 10^{-5}$ M solutions of the compounds in hexane at a layer thickness of 1 cm were obtained with a Specord spectrophotometer. The IR spectra of Nujol and hexachlorobutadiene suspensions of the compounds were recorded with a UR-20 spectrometer. The ^1H NMR spectra of 5% solutions of the compounds were obtained with a Perkin–Elmer R-12A spectrometer with tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectra were obtained with a Brukker WH-90 spectrometer (22.63 MHz); the chemical shifts were measured relative to (TMS).

The physicochemical characteristics of II-V are presented in Table 4.

2-Amino-2-methyl-1-phenyl-1-propanone Hydrazone (II). A 2-g (0.06 mole) sample of anhydrous hydrazine was added dropwise to a solution of 10 g (0.06 mole) of azirine I [8] in 50 ml of methanol at such a rate that the temperature did not rise above 22°C, after which the mixture was stirred at 22°C for 1.5 h. The methanol was then removed by distillation, and the residue was recrystallized from petroleum ether to give 9.5 g (79%) of II.

Hydrazones III-V (Table 4) were similarly obtained.

2,2,5,5-Tetramethyl-3,6-diphenyl-2,5-dihydropyrazine (VI). This compound, with mp 107-108°C, was obtained by the method presented above. IR spectrum: 1625 cm⁻¹ (C=N). ^1H NMR spectrum: δ 1.25 and 1.45 [s, $C(CH_3)_2$]; 7.4 ppm (m, C_6H_5). Found, %: C 82.3; H 7.3; N 9.5. $C_{20}H_{22}N_2$. Calculated, %: C 82.7; H 7.6; N 9.7.

2-Amino-2-methyl-1-phenyl-1-propanone Isopropylidenehydrazone (VII). A mixture of 4.4 g (0.03 mole) of hydrazone II, 1.4 g (0.03 mole) of acetone, and 20 ml of methanol was heated at 80°C for 10 h, after which the alcohol was removed by distillation, and the residue was recrystallized from ethanol to give 3 g (59%) of a product with mp 44-45°C. IR spectrum: 1645 cm⁻¹ (C=N). UV spectrum, λ_{max} (log ε): 212 (21800) and 278 nm (2400). ^1H NMR spectrum (CCl_4): δ 1.40 [s, 6H, $C(CH_3)_2$], 1.83 and 1.92 [s, 3H and 3H, $=(CH_3)_2$], 2.0 (s, 2H, NH_2), 7.10 (m, 2H, H_{ortho}), and 7.4 ppm (m, 3H, H_{meta} and H_{para}). ^{13}C NMR spectrum ($CDCl_3$): δ 18.9 and 25.2 [q*, $=C(CH_3)_2$], 29.7 [q, $C(CH_3)_2$], 55.5 (s, $-\underset{|}{C}-$), 136.7 (s, C_α), 127.5 (d, C_{ortho}), 128.4 (d, C_{meta}), 128.1 (d, C_{para}), and 168.7 and 158.0 ppm (s, C=N). Found, %: C 70.9; H 8.9; N 20.0. $C_{12}H_{19}N_3$. Calculated, %: C 70.3: H 9.3: N 20.4.

2-Amino-2-methyl-1-phenyl-1-propanone Cyclohexylidenehydrazone (VIII). This compound was obtained in 53% yield and had mp 51-52°C. IR spectrum: 1640 cm⁻¹ (C=N). UV spectrum, λ_{max} (log ε): 211 (22000) and 278 nm (1800). ^1H NMR spectrum (CCl_4): δ 1.30 [s, 6H, $C(CH_3)_2$], 1.5 (m, 8H, β- and γ-CH_2, NH_2), 2.0-2.3 (m, 4H, α-CH_2), 6.96 (m, 2H, H_{ortho}), and 7.3 ppm (m, 3H, H_{meta} and H_{para}). ^{13}C NMR spectrum ($CDCl_3$): δ 29.8 [q, $C(CH_3)_2$], 28.9 and 27.5 (t, α-CH_2), 26.2 and 26.5 (t, β-CH_2), 35.7 (t, γ-CH_2), 55.5 (s, $-\overset{|}{\underset{|}{C}}-$), 136.7 (s, C_α), 127.8 (d, C_{ortho}), 128.4 (d, C_{meta}), 128.1 (d, C_{para}), and 163.1 and 169.1 ppm (s, C=N). Found, %: C 75.2; H 9.2; N 16.4. $C_{16}H_{23}N_3$. Calculated, %: C 74.8; H 8.9; N 16.3.

3,5,5-Trimethyl-6-phenyl-2,3,4,5-tetrahydro-1,2,4-triazine (IX). This compound was obtained in 42% yield and had mp 84-85°C. IR spectrum: 1680 cm⁻¹ (C=N). UV spectrum λ_{max} (log ε): 211 (12400) and 265 nm (6300). ^1H NMR spectrum (CCl_4): δ 1.20 (d, 3H, J = 5.5 Hz, CH_3), 1.23 and 1.47 [s, 3H and 3H, $C(CH_3)_2$], 2.2 (s, 1H, NH), 4.08 (q, 1H, J = 5.5 Hz, CH), 7.4 (m, 5H, C_6H_5), and 8.1 ppm (s, 1H, NH). ^{13}C NMR spectrum ($CDCl_3$): δ 28.0 and 30.2 [q,

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*The multiplicity in off-resonance experiments is indicated.

$C(CH_3)_2$], 20.6 (q, $CHCH_3$), 52.8 (s, $-\overset{|}{\underset{|}{C}}-$), 59.6 (d, CH), 135.8 (s, C_α), 128.4 (d, C_{ortho}), 128.8 (d, C_{meta}), 128.0 (d, C_{para}), and 154.1 ppm (s, C=N). Found, %: C 71.4; H 8.2; N 20.3. $C_{12}H_{17}N_3$. Calculated, %: C 71.0) H 8.4; N 20.7.

5,5-Dimethyl-6-phenyl-3-(p-chlorophenyl)-2,3,4,5-tetrahydro-1,2,4-triazine (X). This compound was obtained in 70% yield and had mp 94-95°C. IR spectrum: 1670 cm^{-1} (C=N). UV spectrum, λ_{max} (log ε): 217 (20200) and 271 nm (8200). ^1H NMR spectrum (CCl_4): δ 1.21 and 1.48 [s, 3H and 3H, $C(CH_3)_2$], 1.9 (s, 1H, NH), 4.87 (s, 1H, CH), 6.3 (s, 1H, NH), and 7.3 ppm (s, 5H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$): δ 30.2 and 28.0 [q, $C(CH_3)_2$], 54.3 (s, $-\overset{|}{\underset{|}{C}}-$), 66.1 (d, CH), 154.6 (s, C=N), 139.0, 138.4, 135.0 (s), 128.0, 128.2, 128.8, 128.9, and 129.5 ppm (d, C_{arom}). Found, %: C 68.0; H 5.9; N 14.5. $C_{17}H_{18}ClN_3$. Calculated, %: C 68.1; H 6.0; N 14.0.

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PYRROLES FROM KETOXIMES AND ACETYLENE

II.* EXHAUSTIVE HYDROGENATION OF 4,5,6,7-TETRAHYDROINDOLE AND ITS N-VINYL DERIVATIVE

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UDC 547.75:542.941.7

The hydrogenation of 4,5,6,7-tetrahydroindole and 1-vinyl-4,5,6,7-tetrahydroindole (with H_2 at 150°C and 50-100 atm) in ethanol gives 1-ethyloctahydroindole in 89 and 96% yields, respectively. The hydrogenation of 4,5,6,7-tetrahydroindole in n-butanol is also accompanied by alkylation, and its hydrogenation in tetrahydrofuran proceeds with the primary formation (69%) of nitrogen-unsubstituted octahydroindole; the principal side product (21%) is 1-butyloctahydroindole.

4,5,6,7-Tetrahydroindole (I) and 1-vinyltetrahydroindole (II), which are now readily obtainable from cyclohexanone oxime and acetylene [1], may become a source of octahydroindole and 1-ethyloctahydroindole (III), which are becoming increasingly more difficult to obtain.

The catalytic hydrogenation of II over Raney Ni in ethanol at 50-80°C under hydrogen pressure (40-60 atm) proceeds selectively [2] to give 1-ethyltetrahydroindole (IV) in 90% yield. Continuing our research in this area, we found that when the reaction temperature is

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*See [1] for communication I.

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