$OCH_2\underline{CH_3}$); 2.10 (3H, s, β-CH_3); 2.32 (3H, s, α-CH_3); 4.04 (2H, q, OCH_2); 6.85-7.50 (6H, br. m, arom.); (III) – 1.26 (3H, t, $OCH_2\underline{CH_3}$); 2.38 (3H, s, CH_3); 4.18 (2H, q, OCH_2); 7.34 (1H, d.d, 5-H); 7.98 (1H, d, 4-H); 8.13 (1H, d, 6-H); (IV) – 2.18 (6H, s, β-CH_3); 2.42 (6H, s, α-CH_3); 7.10-8.00 (6H, br. m, arom.); (V) – nonprotonated ring: 2.07 (3H, s, β-CH_3); 2.27 (3H, s, α-CH_3); 7.60-8.00 (br. m, arom.); protonated ring: 2.61 (3H, s, β-CH_3); 2.81 (3H, s, α-CH_3); 7.60-8.00 (2H, br. m, 4- and 5-H); 8.10 (1H, d, 6-H); (VIa) – 2.38 (3H, s, CH_3); 6.80 (1H, s, β-H); 7.00-7.50 (13H, br. m, arom.); (VIb) – 2.14 (3H, s, β-CH_3); 2.32 (3H, s, α-CH_3); 7.00-7.45 (3H, br. m, arom.); (VIc) – 2.12 (3H, s, β-CH_3); 2.18 (3H, s, α-CH_3); 6.80-7.50 (16H, br. m, arom.); (VII) – 2.15 (3H, s, β-CH_3); 2.20 (3H, s, α-CH_3); 6.80-7.50 (15H, br. m, arom.); (VIIIa) – 2.48 (3H, s, CH_3); 7.00-7.55 (11H, br. m, β-H + 2-C_6H_5); 7.68 (1H, d.d, 5-H); 8.05 (1H, d, 4-H); 8.42 (1H, d, 6-H); (VIIIb) – 2.33 (3H, s, β-CH_3); 2.44 (3H, s, α-CH_3); 7.00-7.50 (10H, br. m, arom.); 7.62 (1H, d.d, 5-H); 8.00 (1H, d, 4-H); 8.36 (1H, d, 6-H).

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5-HYDRAZINO-2-PYRAZOLINES

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1-Acyl-5-hydrazino-2-pyrazolines have been obtained by reaction of the appropriate hydrazines with aliphatic 1,3-diketones, 1-acyl-5-hydroxy-2-pyrazolines, and 1-acyl-5-methylene-2-pyrazolines. The latter were synthesized by acylating 3,4,4,5-tetramethyl-4H-pyrazole with carboxylic anhydrides. The structures of the products were established by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

We have recently shown in a few instances [1, 2] that the condensation products of hydrazines with 1,3-diketones in a ratio of 2:1 are the 1-acyl-5-hydrazino-2-pyrazolines (I) rather than the bisacylhydrazones, as previously believed [3, 4]. It was then found that (I) can be synthesized also by reacting hydrazines with 1-acyl-5-hydroxy-2-pyrazolines (IV).

We here report the results of a study of the synthesis of this new group of compounds. Their possible preparation from the hydrazines (III) and 2,4-pentanedione and its 3-methylated homologs (II), or the corresponding compounds (IV), has been examined. In addition,

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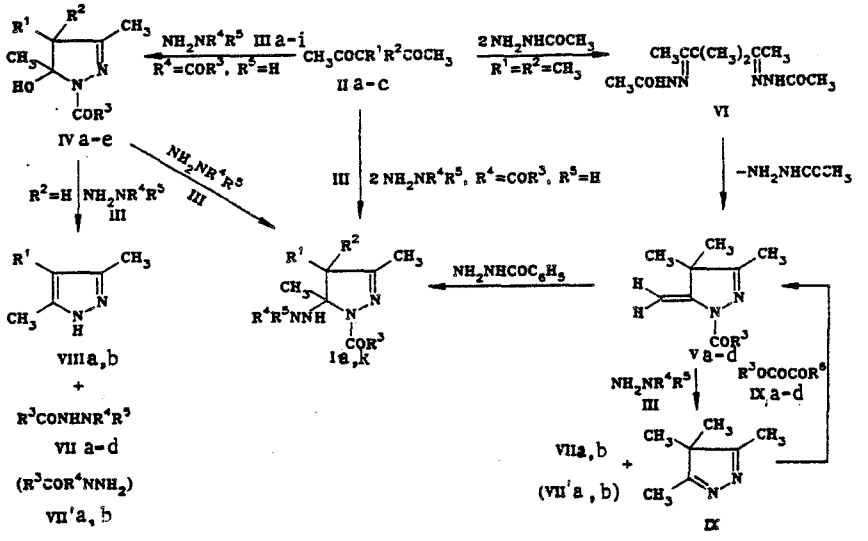
in the case of 3,3-dimethyl-2,4-pentanediones a further possibility has been investigated, namely addition of substituted hydrazines to the double bond in 1-acyl-5-methylene-2-pyrazolines (V). The ability of the latter to undergo addition reactions would be expected by analogy with 1-alkyl(or aryl)-5-methylene-3,4,4-trimethyl-2-pyrazolines, which react readily with water, phenylhydrazine [5], and hydroxylamine [6]. 1-Acyl-5-methylene-3,4,4-trimethyl-2-pyrazolines (Va-d) have been obtained for the first time by the reaction between the carboxylic anhydrides (X) and 3,4,4,5-tetramethyl-4H-pyrazole (IX) in near-quantitative yields. Of these compounds (Va-d), only the benzoyl derivative (Vd) is known, obtained by a different route [3].

It was found that aliphatic and aromatic acid hydrazides (IIIa-d) react with β-diketones to give addition products with the pyrazoline structure (Ia-c, g, h, k). The scope of this reaction is, however, limited. For instance, the reaction between formylhydrazine (IIIa) and 3-methyl-2,4-pentanedione (IIb), even under mild conditions (without heating or acid catalysis), gave 1,2-diformylhydrazine (VIIa) and 3,4,5-trimethylpyrazole (VIIIb) only. These compounds may be formed by transacylation between the intermediate 1-acyl-5-hydroxy-2-pyrazoline (IV) and the starting hydrazine (IIIa). This undesired transacylation was observed to a greater or lesser extent in virtually all the condensations, becoming predominant under severe conditions, for example on prolonged heating. The formation of the products (VIIa-c) and (VIIIa, b) was shown by PMR spectroscopy and TLC in comparison with authentic specimens. In only one of these condensations, namely that of acetylhydrazine (IIIb) with 3,3-dimethyl-2,4-pentanedione (IIc), was the product the bishydrazone (VI) rather than the corresponding 5-hydrazido-2-pyrazone (Ii).

The other route, (reaction of 1-acyl-5-hydroxy-2-pyrazolines (IV) with hydrazines), also in many instances led to the formation of (I) in satisfactory yields, but here also undesirable reactions also occurred. For example, reaction of asym-dimethylhydrazine (IIIe) with 1-(4-bromobenzoyl)-5-hydroxy-3,5-dimethyl-2-pyrazoline (IVc) gave 3,5-dimethylpyrazole (VIIIa) and 4-bromobenzodimethylhydrazide (VIId), i.e., in this case also, transacylation predominated. Even on boiling 1-benzoyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (IVe) with asym-dimethylhydrazine (IIIe) for many hours, scarcely any (I) was formed..



I a $R^1=R^2=R^3=R^5=H$, $R^4=CHO$; b $R^1=R^2=R^5=H$, $R^3=C_2H_5$, $R^4=COC_2H_5$; c $R^1=R^2=R^5=H$, $R^3=C_6H_5$, $R^4=COC_6H_5$; d $R^1=R^2=H$, $R^3=C_6H_5$, $R^4=R^5=CH_3$; e $R^1=R^2=H$, $R^3=R^5=C_6H_5$, $R^4=CH_3$; f $R^1=R^2=H$, $R^3=4\text{-}CH_3C_6H_4$, $R^4=R^5=CH_3$; g $R^1=R^5=H$, $R^2=R^3=CH_3$, $R^4=COCH_3$; h $R^1=R^5=H$, $R^2=CH_3$, $R^3=C_6H_5$, $R^4=COC_6H_5$; i $R^1=R^2=R^3=CH_3$, $R^4=COCH_3$, $R^5=H$; j $R^1=R^2=R^3=CH_3$, $R^4=COC_6H_5$, $R^5=H$; k $R^1=R^2=CH_3$, $R^3=C_6H_5$, $R^5=H$; II a $R^1=R^2=H$; b $R^1=H$, $R^2=CH_3$; c $R^1=R^2=CH_3$; III a $R^4=COH$, $R^5=H$; b $R^4=COCH_3$, $R^5=H$; c $R^4=COC_2H_5$, $R^5=H$; d $R^4=COC_6H_5$, $R^5=H$; e $R^4=R^5=CH_3$; f $R^4=CH_3$, $R^5=C_6H_5$; g $R^4=CH_3$, $R^5=H$; h $R^4=CH(CH_3)_2$, $R^5=H$; i $R^4=C_6H_5$, $R^5=H$; IV a $R^1=R^2=H$, $R^3=C_6H_5$; b $R^1=R^2=H$, $R^3=4\text{-}CH_3C_6H_4$; c $R^1=R^2=H$, $R^3=4\text{-}BrC_6H_4$; d $R^1=R^2=R^3=CH_3$; e $R^1=R^2=CH_3$, $R^3=C_6H_5$; V a $R^3=H$; b $R^3=CH_3$; c $R^3=CF_3$; d $R^3=C_6H_5$; VII a $R^3=R^5=H$, $R^4=COH$; b $R^3=CH_3$, $R^4=COCH_3$, $R^5=H$; c $R^3=C_6H_5$, $R^4=COC_6H_5$, $R^5=H$; d $R^3=4\text{-}BrC_6H_4CO$, $R^4=R^5=CH_3$; VII' a $R^3=H$, $R^4=CH_3$; b $R^3=R^4=CH_3$; VIII a $R^1=H$; b $R^1=CH_3$; X a $R^3=H$, $R^6=CH_3$; b $R^3=R^6=CH_3$; c $R^3=R^6=CF_3$; d $R^3=R^6=C_6H_5$

Of the monosubstituted hydrazines, only hydrazides can be used for the preparation of (I). Reaction of 1-benzoyl-5-hydroxy-3,5-dimethyl-2-pyrazoline (IVa) with monoalkyl- or arylhydrazines (isopropylhydrazine or phenylhydrazine) gave quantitative yields of the 1-alkyl-(or aryl)-3,5-dimethylpyrazole and benzohydrazide (IIId). When the reaction was carried out in the sensor of a PMR spectrometer, we failed to observe the formation of any intermediate products.

Neither was it possible to obtain the 5-hydrazino-2-pyrazoline (Id) by reaction of benzohydrazide (IIId) with acetylacetone monomethylhydrazone, since in this case transhydrazination occurred with the formation of 1-benzoyl-5-hydroxy-3,5,-dimethyl-2-pyrazoline (IVa) with 5-hydrazido-2-pyrazoline (Ic) as an impurity.

The addition of hydrazines to 1-acyl-5-methylene-3,4,4-trimethyl-2-pyrazolines (Va-d) is more restricted in its applications than the two preceding methods. These compounds (Va-d) show little tendency to undergo such reactions with a wide variety of hydrazines (IIIa, b, d, g-i). However, under severe conditions (heating, acid catalysis), 3,4,4,5-tetramethyl-4H-pyrazole (IX) and the corresponding hydrazides (VII) are obtained, or with methylhydrazine and (Va, b), the compounds (VII'a, b), the formation of these compounds being confirmed by comparison of the spectral and other physicochemical properties with those of authentic samples [7-9]. An exception is provided by the reaction of benzohydrazide with (Va, d), which gives (Ij) and (Ik) respectively.

Proof of the structures of the 5-hydrazino-2-pyrazolines (I) obtained was obtained from the magnetic nonequivalence of the signals for the methyl groups in the 3- and 5-positions of the ring, and the doubling of the NH signals and of the same substituents in the 4-position (Ia-f, i-k) in the PMR spectra (Table 1). In addition, in some instances the NH signals were coupled (J = 2.5-5.5 Hz). None of this would be possible with bishydrazones or other straight-chain structures. Noteworthy also is the high dependence of the NH signals on temperature, concentration, and solvent. In the proposed [3] bishydrazone structure for (Ik) and some of its analogs, the nonequivalence of the signals for all these groups is due to strong intramolecular hydrogen bonding involving one of the NH groups, and this must be the reason for the low sensitivity of the NH signals to external factors.

In the ^{13}C NMR spectra of (I), a signal for sp^3 hybridized carbon at $C_{(5)}$ is seen at 79-88 ppm. All the other signals are also in agreement with the cyclic structure (Table 2).

We draw attention to a characteristic feature of the PMR spectra of 2,4-pentadiones and 3-methyl-2,4-pentanediones (Ia-h), namely the additional spin coupling of the 4-H protons with one of the methyl groups (J = 1.0 Hz). The position of the signal for this methyl group is not constant with respect to the signal for the other, and therefore their chemical shifts cannot be used for reliable assignment. A similar interaction is seen also in the starting 1-acyl-5-hydroxy-3,5-dimethyl-2-pyrazolines (IVa-c). In order to establish which of the two methyl groups is involved in this interaction, we compared the spectral data for (I) and (IV) with those for 1-formyl-3,5,5-trimethyl-2-pyrazoline (XI, Tables 1 and 2), which are susceptible of only one interpretation. This comparison showed that the methyl group involved in the interaction was that at the C=N bond, i.e., in the 3-position. It is noteworthy that in the carbon spectra of the same compounds the following relationship is observed: a quartet signal for the 5-CH_3 carbon (but not 3-CH_3) coupled by a remote constant (J = 4.6 Hz) with the 4-H protons. These effects served as the basis for the assignment of the methyl group signals, from which it was found that the signals for the 3-CH_3 group in the PMR spectra more often occur at lower field with respect to 5-CH_3, whereas in the carbon spectra the reverse is the case.

The mass spectra of the compounds examined in [3] (Ik, ℓ, etc.), in the opinion of the author, confirm their linear structure. However, a closer examination of these spectra and our own mass spectral studies suggest otherwise. In the gas phase, compounds (Ia-i) (Table 4) exist largely or wholly in the cyclic form of the pyrazoline molecular ion. Although, as in [3], in most instances [apart for (Ie, g)] the molecular ions were not found in the mass spectra, the nature of the fragment ions enable a breakdown pathway to be proposed.

The principal fragment ions in the mass spectra of all the compounds were acylpyrazoline ions F_1, which break down (in the acetyl derivatives) further with the elimination of a molecule of ketene (ion F_3), then with decomposition of the heterocycle (ion F_8). Such fragmentation is characteristic of α-substituted cyclic amines [10], and in particular of pyrazolines [11]. In addition, when R^5 = H or CH_3, additional strong peaks are observed for the

TABLE 1. Properties of Products

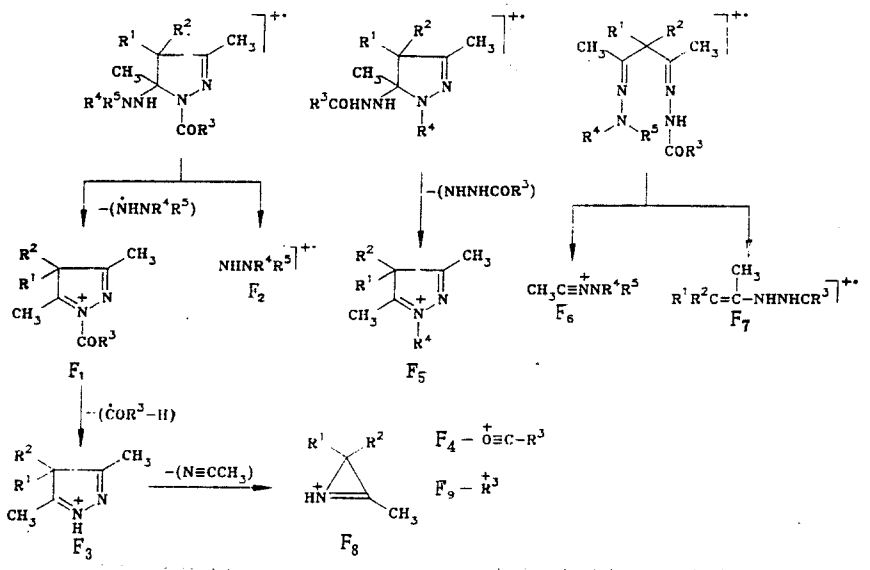
Compound	T_{mp}, °C (solvent for recrystallization)	Solvent	PMR spectra, ppm					Yield, % (method)
			3H, 3-CH_3	3H, s, 5-CH_3	R^4 (J, Hz)	NH (J, Hz)	other signals	
Ia*	131—132 (ethanol)	DMF-D_7	1,85t	1,55	2,82 and 2,98 (2H, 18,5, H)	5,50 (1H, br.s); 8,50 (1H, br.s)	7,92 and 7,96 (2H, br.s, 2-HCO)	40 (A)
Ib**	66—67 (benzene)	$CDCl_3$	1,86 t	1,59	2,50 and 3,28 (2H, 19,0, H)	5,00 and 5,39 (1H, br.s); 7,21 and 8,80 (1H, br.s)	0,9—1,1 (3H, m, CH_3CH_2); 2,09 and 2,54 (2H, q, J=7,5 Hz, CH_2CH_3)	40 (A)
Ie	128 (ethanol)	$CDCl_3$	2,02t	1,98	2,67 and 3,23 (2H, 18,0, H)	4,85 (1H, br.s)	3,15 (3H, s, CH_3N); 6,7—7,8 (10H, m, arom.)	64 (B)
If	83—85 (hexane)	$CDCl_3$	1,92 t	1,63	2,51 and 3,31 (2H, 18,0, H)	4,08 (1H, br.s)	2,28 (3H, s, CH_3, arom.) 2,32 (6H, s, CH_3N); 7,12 and 7,65 (4H, d, J=9,0 Hz, arom.)	80 (B)
Ig*	129—130 (benzene)	Py-D_5	1,71, 1,76 t	1,37 and 1,57	0,94 and 0,96 (3H, d, 7,5, CH_3); 3,11 and 3,30 (1H, q, 7,5, H)	6,05 (d, 3,0) and 6,11 (1H, br.s); 8,89 (br.s) and 9,68 (1H, d, 3,0)	1,89 and 2,07 (3H, s CH_3CO); 2,11 and 2,16 (3H, s, CH_3CO)	33 (A)
			1,88 d cis	1,56	1,23 (d, 7,0, CH_3); 3,14 (q, 7,0, H)	5,17 and 8,80 (d, 3,0)		
Ih***	123 (ethanol)	$CDCl_3$	1,92 d trans	1,75	1,31 (d, 7,0, CH_3); 2,97 (q, 7,0, H)	5,01 and 8,95 (d, 3,0)	7,3—8,0 (10H, m, arom.)	7 (A)
Ii**	109—110 (benzene)	Py-D_5	1,80s and 1,85s	1,15and 1,54	0,88; 0,91; 1,05; 1,11 (6H, s, CH_3)	5,10 and 6,08 (1H, br.s); 8,81 9,40 (1H, br.s)	1,98 and 2,05 (3H, s, CH_3CO); 2,18 and 2,23 (3H, s, CH_3CO)	36 (B)
Ij	128 (benzene)	DMSO-D_6	1,86s	1,36	0,90 and 1,05 (6H, s, CH_3)	5,73 (1H, d, 4,0); 9,59 (1H, d, 4,0)	1,96 (3H, s, CH_3CO); 7,3—7,7 (5H, m, arom.)	96 (C)
XI	—	CCl_4	1,95 (t, J=1,0Hz)	1,48	2,76 (2H, q, 1,0, H)	—	8,50 (1H, s, CHO)	—

*Spectrum obtained at 120°C.
**Mixture of Z and E-conformers.
***cis:trans = 2:1.

TABLE 2. ^{13}C NMR spectra of (I) and (XI), ppm

Compound	Solvent	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	C=O	3-CH_3, q*	5-CH_3, q*	Other signals
Ia**	DMF-D_7	157,2	46,8t***	79,7	159,4; 161,0; 175,5	14,6	20,8; 21,0**	—
Ie	$CDCl_3$	155,6	45,7t***	84,0	164,7	16,1	24,5**	40,8 (CH_3) 114—153 (C arom.)
Ii**	$CDCl_3$	162,4; 162,9	52,3; 52,5 s	86,2	168,3; 169,1; 170,6; 171,0	12,7—22,7 (ten CH_3 signals)		
Ij	$CDCl_3$	162,7	52,4 s	86,4	165,6; 170,9	12,1; 16,0; 18,3; 22,6 (CH_3)		126—133 (C arom.)
XI	$CDCl_3$	158,3	53,6 t**	62,7	160,7	15,6	25,7**	—

*J_{CH} = 129-130 Hz.
**E,Z-isomers.
***J_{CH} = 134-135 Hz.
**J_{CCH} = 4-6 Hz.

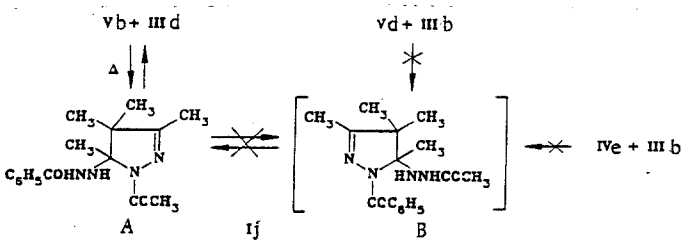


rearranged ions F_2, indicating that the molecular ion in the gas phase undergoes conversion from (I) to (V). When this occurs, thanks to the lower ionization energy of the resulting hydrazines the positive charge is localized at the hydrazine moiety, and the intensity of the peaks for the pseudomolecular ions is no greater than 0.1-0.4% of the total ion current. However, in hardly any of the mass spectra of these compounds [except for (VI)] were fragments (F_6 and F_7) of the open form of the molecular ion found, and although these ions are present in the mass spectra of (Ia, g, h), their intensities are no greater than 1.1%. Hence, the mass spectrometric behavior of these compounds shows that both in the gas phase and in solution they possess the cyclic pyrazoline structure.

Comparison of the spectral properties of (VI) (see Experimental) with those of 5-hydrazino-2-pyrazolines (I) shows conclusively that this compound is the bishydrazone. The isomeric 1-acetyl-5-acethydrazido-3,4,4,5-tetramethyl-2-pyrazoline (Ii) was obtained by reacting acetylhydrazine with 1-acetyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (IVd).

In fact, comparison of the mass spectrometric behavior of the isomeric compounds (Ii) and (VI) shows that in the mass spectra of the latter strong peaks for ions F_6 and F_7 are present, these being largely absent from the spectra of (Ii). This leads to the conclusion that in the gas phase (VI) has predominantly the linear bishydrazone structure, but the simultaneous presence of ions F_1 and F_2 in the mass spectra shows that the molecular ion of (VI) partially cyclizes to structure (Ii). We have failed to observe the exchange (VI) $\rightleftarrows$ (Ii) in an extensive range of solvents, on heating or on prolonged storage. Heat and acid catalysis results in quantitative conversion of (VI) and (I) into acethydrazide (IIIb), and into 1-acetyl-5-methylene-3,4,4,-trimethyl-2-pyrazoline (Vb). Consequently, here also the cyclic structure is preferred to the linear structure. In the remaining cases, however, as already stated, only the 5-hydrazino-2-pyrazolines (I) were obtained.

The product of the addition of benzhydrazide (IIId) to 1-acetyl-5-methylene-3,4,4-trimethyl-2-pyrazoline (Vb) is of interest in respect of its potential ability to undergo ring–ring tautomerism [2]:



However, in CD_3OD or DMSO-D_6, or in nonpolar solvents, even in the presence of CF_3COOH, no tendency to undergo the transition A $\rightleftarrows$ B was observed. Proof of the existence of (Ij) in

TABLE 3. Physicochemical Constants of 1-Acyl-5-methylene-3,4,4-trimethyl-2-pyrazolines (Va-d)

Compound*	T_{mp}, °C	R_f	PMR spectrum in CCl_4, ppm			
			3H, s, 3-CH_3	3H, s, 4-CH_3	2H, 5-CH_2	other signals
Va	Oil	0,64	1,87	1,15	4,45 s, 5,77 s	8,71 (1H, s, HCO)
Vb	67—69	0,67	1,89	1,15	4,35s ; 5,81 s	2,18 (3H, s., CH_3CO)
Vc	Oil		2,05	1,32	4,75 d, 5,99 d (J=2,0 Hz)	—
Vd	114**		1,88	1,20	4,51 s, 6,05 s	7,2—7,7 (5H, m, arom.)

*(Va) was eluted from a mixture of acetone and benzene (1:4), and (Vc) from benzene).
**According to [3], mp 111-113°C.

TABLE 4. Intensities of Characteristic Ions in the Mass Spectra of (I) and (VI) ($\%\Sigma_{39}$)

Compound	W_M	F_1	F_2	F_3	F_4	F_6	F_7	F_8	F_9
Ia	—	22,2	0,3	27,0	—	1,1	0,3	13,1	—
Ic	—	16,5	0,9	—	38,1	—	—	—	15,3
Id	—	5,1	22,7	—	25,5	—	—	0,7	11,0
Ie	0,04	2,8	30,4	—	25,3	—	—	—	10,8
If	—	7,5	23,3	—	29,3	—	—	—	10,0
Ig	0,01	17,1	0,2	21,7	10,2	0,6	—	4,6	—
Ih	—	18,3	1,1	—	27,6	—	—	—	17,8
Ii	—	2,7	0,8	27,5	10,0	0,7	—	0,8	—
Ij	—	1,8	0,7	—	5,0	—	—	—	7,9
Ik	—	4,1	0,7	—	39,6	—	—	—	15,8
Il	—	6,9**	0,9	—	16,4	—	—	—	18,0***
Im	—	11,9	0,9	—	35,5	—	—	—	19,2
VI	—	4,2	5,7	22,9	9,3	6,1	3,8	2,8	—

*(Il) — 1-benzoyl-5-(4-chlorobenzoylhydrazino)-3,4,4,5-tetramethyl-2-pyrazoline and its tautomer [2]; (Im) — 1-benzoyl-5-benzoylhydrazino-3-methyl-5-ethyl-2-pyrazoline and its tautomer [2].
**Ion F_5 also present (16.7).
***Chlorine-containing ion F_4.

form A is its partial reversible dissociation into benzhydrazide (IIId) and 5-methylene-2-pyrazoline (Vb) in solution on heating, or in the presence of catalytic amounts of acid.

The mass spectra of the "asymmetrical" compounds (Ij) and (Il), as in the case of compounds (Ia-m), contained ions of type F_1. In addition, ions F_5 are present, and in the case of (Il), ions F_2 both with and without a chlorine atom. This indicates the presence in the gas phase of both cyclic tautomeric forms of the molecular ion, but at the same time in the mass spectra of these compounds the ions F_6 and F_7 were absent. Hence, the presence of both forms is not due to tautomeric interconversion in the gas phase, but to the independent evaporation of each tautomeric form from the solid state.

Form B of (Ij) could not be obtained by reacting acetylhydrazine with 1-benzoyl-5-hydroxy-(methylene)-2-pyrazolines (IVe, Vd). Hence, the factors dictating the preferential existence of one or the other of the possible 5-hydrazino-2-pyrazoline forms A—B will require further study.

1-Benzoyl-5-benzoylhydrazino-3,4,5-trimethyl-2-pyrazoline (Ih) is, to judge from its PMR spectra (Table 1), a mixture of cis- and trans-isomers, differing in the mutual disposition of the substituents in the 4- and 5-positions. In contrast, the acetyl compound (Ig) is a single geometric isomer, and the splitting of the signals in its spectrum is due to Z,E isomerism arising from restricted rotation in the acetamide grouping in the exocyclic hydrazide moiety, as confirmed by the reversible coalescence of the signals when the signals were recorded at different temperatures in Py-D_5. Z,E isomerism has also been observed in other derivatives (Ia, b, g, i) with aliphatic hydrazide substituents in the 5-position.

This is in accordance with the properties of 1,2-disubstituted hydrazides of formic, acetic, and other acids [7, 8].

Hence, the 1-acyl-5-hydrazino-2-pyrazolines (I) may be regarded as a readily-accessible group of compounds. The information obtained on their synthesis extends the preparative possibilities for the reactions of hydrazines with β-dicarbonyl compounds, which have hitherto been used in heterocyclic syntheses for the preparation of pyrazoles [12] and 5-hydroxy-2-pyrazolines [13].

EXPERIMENTAL

^1H and ^{13}C NMR spectra (100 MHz and 20.41 MHz, respectively) were obtained on a Tesla BS-497 instrument, internal standard HMDS. Mass spectra were recorded on an MAT-212 mass spectrometer, ionizing electron energy 70 eV, ionization chamber temperature 120-150°C. The purities of the products were checked by TLC on Silufol UV-254 plates. 1-Formyl-3,5,5-trimethyl-2-pyrazoline (XI) was obtained as described in [14], 3,4,4,5-tetramethyl-4H-pyrazole as in [9], 1-isopropyl- and 1-phenyl-3,5,-dimethylpyrazole as in [15], and the hydrazides (VII) as in [7, 8].

1-Acyl-5-methylene-3,4,4-trimethyl-2-pyrazolines (V). To a solution of 0.15 mole of the anhydride (Xa-d) in 30 ml of ether at 20°C was added a solution of 12.4 g (0.1 mole) of 3,4,4,5-tetramethyl-4H-pyrazole (IX). After keeping for one day, the volatile components were removed under reduced pressure. Compounds (Va, c) were spectrally pure products, and were used without further purification. Compounds (Vb, d) were further recrystallized from pentane. Data for (V) are given in Table 3. Compounds (IVa-c, d) were obtained as described in [3, 13].

1-Acetyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (IVd). A mixture of 8.3 g (0.05 mole) of 1-acetyl-5-methylene-3,4,4,-trimethyl-2-pyrazoline (Vb) and 40 ml of water with the addition of CF_3COOH was boiled, extracted with ether, and dried over sodium sulfate. The solvent was distilled off, and the product was used without further purification. Yield 8.9 g (96%). Oil, R_f 0.33 (benzene–acetone, 4:1). PMR spectrum ($CDCl_3$): 0.85, 1.02 (6H, s, two 4-CH_3); 1.51 (3H, s, 5-CH_3); 1.83 (3H, s, 3-CH_3); 2.12 (3H, s, CH_3CO); 4.65 ppm (1H, br. s, OH).

5-Hydrazino-2-pyrazolines (I). A. A mixture of 0.05 mole of the 1,3-diketone (II) with double the amount of the hydrazide (III) in absolute ethanol was kept for one day, the solvent removed under reduced pressure, and the residue recrystallized. In the isolation of (Ih), the residue was first dissolved in the minimum amount of ether, and precipitated therefrom in the cold.

Compounds (Ic, k) were obtained as described in [3, 4]. Their spectral data were given in [1].

B. A mixture of 0.05 mole of the appropriate 1-acyl-5-hydroxy-2-pyrazoline (IV) with the equivalent amount of the hydrazine (II) was boiled [(Ic) in alcohol for 5 h, (Ie) in benzene with a drop of CF_3COOH for 4 h, (If) in benzene for 3 h, (Ii) in chloroform with addition of CF_3COOH for 20 h], and after cooling the mixture was filtered, the filtrate evaporated, and the residue recrystallized. When isolating (Ii), the residue was first dissolved in ether, and precipitated therefrom in the cold. (Ic) was obtained by this method in 34% yield. The preparation of (Id) has been described [1].

C. A mixture of 0.05 mole of 1-acetyl(or benzoyl)-5-methylene-3,4,4-trimethyl-2-pyrazoline (Vb, d) with an equimolar amount of benzohydrazide (IId) was kept for one day in chloroform, and the solvent was then removed under reduced pressure.

Compound (Ik) was obtained using this method in 87% yield.

Bis(acetylhydrazono)-3,3-dimethyl-2,4-pentanedione (VI). A mixture of 4.0 g (0.03 mole) of dimethylacetylacetone (IIIc) and 4.5 g (0.06 mole) of acetylhydrazine (IIIb) was boiled for 3 h in ethanol, evaporated, and the residue recrystallized from ethanol. Yield 39 g (54%), mp 191°C. PMR spectrum ($CDCl_3$): 1.25 (6H, s, 2-CH_3); 1.66 (6H, s, CH_3CN); 2.21 (6H, s, CH_3CO); 8.83 ppm (2H, br. s, NH). ^{13}C NMR spectrum ($CDCl_3$): 12.0, 20.4, 23.3 (CH_3); 50.4 (α-C); 153.5 (C=N); 173.8 ppm (C=O).

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FORMATION OF IMIDAZOLIDINE DERIVATIVES FROM DIMETHYL (2,2-DIMETHYLHYDRAZINO)SUCCINATE IN REACTIONS WITH ALLYL AND PHENYL ISOTHIOCYANATES*

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The reaction of (2,2-dimethylhydrazino)succinic acid ester with allyl and phenyl isothiocyanates leads to esters of 1-substituted (3-dimethylamino-5-oxo-2-thioxo-4-imidazolidinyl)acetic acids, which in protic solvents undergo a slight degree of elimination of dimethylamine to give esters of 1-substituted (5-oxo-2-thioxoimidazolidin-4-ylidene)acetic acids. The structure of methyl (1-allyl-5-oxo-2-thioxoimidazolidin-4-ylidene)acetate was proved by x-ray diffraction analysis.

Within the framework of a systematic study of the reactivities of hydrazino carboxylic acids [1, 2] we have investigated the reaction of dimethyl (2,2-dimethylhydrazino)succinate (I) with allyl and phenyl isothiocyanates. In the reaction of allyl isothiocyanate with ester I at high temperatures in ethanol we obtained two products in the form of a light-yellow oily liquid and a small amount of yellow crystals. The corresponding thiosemicarbazides are usually formed in the reaction of trisubstituted hydrazines with isothiocyanates [3]. However, an analysis of the spectra of the compounds obtained showed that neither of them is

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