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PREPARATION AND PROPERTIES OF AZINIUM SALTS OF

THE 2-PYRAZOLINE SERIES

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Azinium salts containing pyrazoline fragments have been obtained by the reaction of 2-pyrazolines with aromatic and heteroaromatic aldehydes, acetylacetone, and acetoacetic ester in the presence of  $H_2SnCl_6$  and  $HBF_4$ . Reactions of nucleophilic addition to the multiple bonds and also some cycloaddition reactions among the arylidene derivative have been studied. From the azinium salts of a series of  $\beta$ -dicarbonyl compounds have been obtained previously unknown enamino carbonyl compounds of the 2-pyrazoline series.

Up to the present time, the synthesis of only a few representatives of azinium salts of the 2-pyrazoline series [1] and their hydrolysis [2, 3] and reduction [4] has been described. On studying the possibility of activating the C=N bond in 2-pyrazolines to the attack of nucleophilic agents, we turned to a more detailed study of the properties of this class of compounds. In addition to the fact that this system consists of a model of a pyrazoline ring activated at the  $N_{(1)}$  atom, it contains two C=N groups the reactivities of which may differ sharply. As the object of investigation we selected two types of azinium salts: the benzylidene salts (Ia-g, Table 1), which permitted us to study the reactivities of the azinium systems themselves, and the condensation products of salts of 2-pyrazolines with  $\beta$ -dicarbonyl compounds — acetoacetic ester and acetylacetone (IV and V in Table 1) — which enables us to study mutual influence in a system of conjugated bonds. In addition to the preparation of hexachlorostannates by known methods [1, 2], we obtained the tetrafluoroborates in a two-phase system.

In the PMR spectra of the benzylidene derivative (I) obtained, the signals of all the protons of the pyrazoline ring were shifted downfield in comparison with the free 2-pyrazolines. Thus, the signal of the 5-H proton was shifted into the 6.2-ppm region as compared with 4.5 ppm, and the signals of the 4-H protons into the 3.8-4.5 ppm region as compared with 2.8-3.2 ppm for the free pyrazoline. The IR spectra of the salts (I) each contained two different bands of the vibrations of the C=N and C=N<sup>+</sup> bonds, in the 1600-cm<sup>-1</sup> regions, regions, respectively.



I, III a  $R^1 = R^2 = R^3 = CH_3$ ,  $R^4 = Ph$ ,  $X = \frac{1}{2} SnCl_6^{2-}$ ; b  $R^1 = R^2 = Ph$ ,  $R^4 = C_6H_3(OCH_3)_2$ -2.3, X=BF<sub>4</sub><sup>-</sup>; c  $R^1 = CH_3$ ,  $R^2 = R^4 = Ph$ , X=BF<sub>4</sub><sup>-</sup>

M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 101-105, January, 1984. Original article submitted August 2, 1983 TABLE 1. Constants and Yields of the Compounds Synthesized

			, I						
Com-	6) °	Found	d, %	elinea formula	Calcula	ted,	R spectrum,	PMR spectrum, 5, ppm	'pı
punod	ر du	υ	н	Empirical rounda	υ	н	cm <sup>-1</sup>		% %
Ia	223 <sup>b</sup>	ι.	u	C26H34Cl6N4Sn			1620, 1655	1.84 (6H, s, 5-CH <sub>3</sub> ); 2,50 (3H, s, 3-CH <sub>3</sub> ); 3,36 (2H, s, 4-H); 7,61-8,76 $\begin{bmatrix} 7 \\ 6H \\ 6H \end{bmatrix}$	74
Ib Ic	221 <sup>C</sup> 226 <sup>C</sup>	62,8 60,3	5,2 4,9	C <sub>24</sub> H <sub>23</sub> BF4N <sub>2</sub> O <sub>2</sub> C <sub>17</sub> H <sub>17</sub> BF4N <sub>2</sub>	62,8 60,6	5,0 5,1	1600, 1650 1620, 1650	$\begin{array}{c} \begin{array}{c} \begin{array}{c} 0 \\ 2,80 \end{array} (3H, s, 3.CH_3); 3,80 \\ 1H, d, d, 4-H); 4,20 \\ 1H, d, d, 4-H); 6,25 \\ 1H, \frac{8}{10} \end{array} \\ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	82
IVa	184c	37,0	5,4	C <sub>24</sub> H <sub>42</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>4</sub> Sn	36,8	5,4 4,5	1635, 1670, 1750	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} 1.51 \\ 1.51 \\ 1.51 \\ 1.51 \\ 1.52 $	87
IVb	130°C	42,8	4,2	C <sub>30</sub> H <sub>38</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>4</sub> Sn			1630, 1670,	(1H, m, 4-H); 4,20 (2H, m, OEI) 1,28 (3H, m, OEI); 2,58 (3H, s, CH <sub>3</sub> C=N+); 2,89 (1H, s, $\alpha$ -H); 3,49 (1H, 12, $\alpha$ -H); 3,31 (1H, m 4-H); 3,89 (1H, m, 4-H); 4,20 (2H, m, OEI); 6,36 (1H, 12, $\alpha$ -H); 3,31 (1H, m 4-H); 3,89 (1H, m, 4-H); 4,20 (2H, m, OEI); 6,36 (1H, 12, $\alpha$ -H); 3,31 (1H, 2H); 3,39 (1H, 2H)	95
IVc	164°	43,8	5,3	$C_{32}H_{42}Cl_6N_4O_4Sn$	43,8	4,8	1625, 1665, 1750	m, b-H); $(,54 \ (5H, m, Ph); 8,52 \ (1H, t, 3-H)$ 1,1 (3H, m, OEt); 2,39 (3H, s, 3-CH <sub>3</sub> ); 2,49 (3H, s, CH <sub>3</sub> C=N <sup>+</sup> ); 2,89 (1H, 8 s, $\alpha$ -H); 3,56 (1H, s, $\alpha$ -H); 3,20 (1H, m, 4+H); 3,82 (1H, m, 4-H); 4,19 (2H, 8 m, OEt), $\alpha$ so (1H, s, $\alpha$ -H); 3,70 (1H, m, DL); 2,99 (2H, 8)	89
Va	173 <sup>c</sup>	39,9	5,6	C <sub>28</sub> H <sub>46</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>2</sub> Sn	40,1	5,9	1600, 1660	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c}$	75
4V P	188 <sup>c</sup>	44,8	4,9	C <sub>32</sub> H <sub>42</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>2</sub> Sn	44,8	4,9	1605, 1655	$\begin{array}{c} 3.06  (2.1,111, OEU); \ 5.094  (111, 41, 62-11) \\ 1,21  (3H, m, OEU); \ 2.09  (3H, d, CH_{a}C=C); \ 2.59  (1H, m, 4-H); \ 2.58  (3H, s) \\ CH_{a}C=N^{+}); \ 3.20  (1H, m, 4-H); \ 3.78  (2H, m, OEL); \ 6.04  (1H, t, 3-H); \ 6.36  800 \\ (1H, 1, 2H); \ 5.70  (1H, 1, 2H); \ 6.36  800 \\ (1H, 1, 2H); \ 5.70  (1H, 1, 2H); \ 5.70  (2H, 1, 2H); \ 5.70  (2H, 1, 2H); \ 5.70  800 \\ (2H, 1, 2H); \ 5.70  (2H, 1, 2H); \ ($	85
Vc	197 <sup>c</sup>	46,5	5,3	C <sub>34</sub> H <sub>46</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>2</sub> Sn	46,7	5,3	1600, 1655	$(114, m, 5-H); 5,38, (1H, 3d, \alpha-H); 7,40, (3H, m, PH)$ 1,08, (3H, m, OEb); 1,91, (3H, d, CH3C=C); 2,10, (3H, s, 3-CH3); 2,48, (3H, s, CH3C=N); 3,00, (2H, m, 4-H); 3,41, (2H, m, OEb); 6,52, (1H, m, 5-H); 7,00, (2H, m, 4-H); 3,41, (2H, m, OEb); 6,52, (1H, m, 5-H); 7,00, (2H, m, 4-H); 3,41, (2H, m, OEb); 6,52, (1H, m, 5-H); 7,00, (2H, m, 4-H); 3,41, (2H, m, OEb); 6,52, (1H, m, 5-H); 7,00, (2H, m, 4-H); 3,41, (2H, m, OEb); 6,52, (1H, m, 5-H); 7,00, (2H, m, 4-H); 3,41, (2H, m, OEb); 6,52, (1H, m, 5-H); 7,00, (2H, m, 4-H); 7,00, (2H, m,	62
١٧	115	70,5	7,3	$C_{16}H_{15}N_2\bar{O}_2$	70,6	7,4	1640, 1685	$7,39$ (bH, m, Pn); 7,09 (1H, d, $\alpha$ -H) 1,16 (3H, t, OE1); 2,03 (3H, s, 3-CH3); 2,64 (3H, s, CH3C=N+); 2,62 (1H, m, 0-1); 3,21 (1H, m, 4-H); 4,62 (1H, s, $\alpha$ -H); 5,12 (1H, m, 5-H); 7,22 (5H, 10-1); 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	82
ΝI	86	74,7	8,1	C <sub>15</sub> H <sub>18</sub> N <sub>2</sub> O	74,4	7,4	1620, 1720	$ \begin{bmatrix} m, FH \\ 2.07 & (3H, s, CH_3); 2, 12 & (3H, s, CH_3); 2, 18 & (3H, s, CH_3); 2, 74 & (1H, m, 4-H); \\ 3,21 & (1H, m, 4-H); 5,57 & (1H, m, 5-H); 5,64 & (1H, s, \alpha-H); 7, 14 & (5H, m, Ph) \end{bmatrix} $	30
a Reci insolu	cystallize ible in or	ed fro ganic	m met solv	hanol-acetone (	1:2).	b Ac	cording to	[9], mp 225°C. <sup>c</sup> With decomposition. <sup>d</sup> Compound	

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The reduction of the salt (Ib) with lithium tetrahydroaluminate formed the corresponding alkylpyrazolidine, which was isolated in the form of the phenylthiocarbamoyl derivative (II), i.e., both multiple nitrogen-carbon bonds took part in reaction with the hydride ion, as in the known case of alkylidene salts [4].

The reactions of hydroxyl and cyanide ions with the azinium salts proved to be more selective. The addition of the CN<sup>-</sup> ion took place at the exocyclic multiple bond and led with a yield of 40% to the corresponding cyano derivatives (IIIa-c). In addition to this, a process of the hydrolysis with the formation of l-unsubstituted 2-pyrazolines was observed.

We have obtained for the first time previously unknown condensation products of salts of 2-pyrazolines with  $\beta$ -dicarbonyl compounds, (IV) and (V), and studied some of their properties. The IR spectra of the salts (IV) showed the bands of vibrations of the C=N and C=N<sup>+</sup> bonds at 1670 and 1623 cm<sup>-1</sup>, respectively, and also a band at 1745 cm<sup>-1</sup> corresponding to the frequency of vibrations of the carbonyl group.

In the PMR spectra, the signals of the protons of a pyrazoline ring quaternized at the  $N(_1)$  atom and of an acetoacetic ester residue were observed — at 1.2 and 4.2 ppm (CH<sub>3</sub>CH<sub>2</sub>O group, J = 7 Hz) — and the signals of the protons of the CH<sub>2</sub> group appeared in the spectrum in the form of two singlets at 2.9 and 3.5 ppm. Thus, these salts may be regarded as products of the condensation of the pyrazoline ring with the carbonyl group of the acetoacetic ester; the ester group had remained unchanged.

In contrast to this, in the reaction with acetylacetone both carbonyl groups took part: One of them entered into a condensation reaction with the pyrazoline base, and the other was converted under the reaction conditions into the enol ether (V).



IV, V, VI, VII a  $R^1 = R^2 = R^3 = CH_3$ ; b  $R^2 = Ph$ ; c  $R^1 = CH_3$ ,  $R^2 = Ph$ 

The IR spectra of the salts (V) showed the bands of the vibrations of imine groups at 1600 and 1655 cm<sup>-1</sup>, and there was no band corresponding to the vibrations of a carbonyl group. In the PMR spectrum, in addition to the signals of the protons of the pyrazoline ring of two methyl groups from the acetylacetone residue, a one-proton weak-field signal was observed in the 6.5-7.7 ppm region and also the signals of an ethyl group at 1.1 and 3.5 ppm.

As might have been expected, the action of pyridine on compounds (IV) and (V) formed the enamino carbonyl compounds (VI) and (VII), respectively. While for salt (IV) the reaction took place as a simple deprotonation, in the case of compound (V) the reaction apparently began with the addition of a molecule of pyridine giving the intermediate salt (VIII), the hydrolysis of which led to the formation of the enamino ketone (VII). We have not succeeded in obtaining these compounds directly from 2-pyrazolines and  $\beta$ -dicarbonyl compounds by the methods known for enamino ketones [5].

The action of triethyloxonium tetrafluoroborate on the enamino ketones (VII) gave the initial salts (V)  $(X = BF_4)$ , which serves as an additional proof of the formation of enol ethers in the reaction of pyrazolines with acetylacetone.

The IR spectra of compounds (VI) and (VII) contained the bands of the vibrations of the C=N bonds at 1640 and 1620 cm<sup>-1</sup> and the absorption bands of conjugated carbonyl groups at 1685 and 1720 cm<sup>-1</sup>, respectively. In the PMR spectra, the vinyl proton appeared in the form of a singlet at 5.64 ppm (compound (VII)) and at 4.62 ppm (compound (VI)). In the UV spectra, one intense absorption maximum was observed for the whole conjugated  $\pi$ -system at 307 nm. The enamino carbonyl compounds of the dialkylamine series have absorption maxima in the UV spectra

at 280 nm [6], which indicates a high degree of cross-conjugation in the system of enamino carbonyl compounds of the 2-pyrazoline series in which the C=N bond of the pyrazoline ring takes part.

This can apparently be explained by the fact that compounds (VI) and (VII) exhibit inertness in cycloaddition reactions. In actual fact, in studying the reactions of the compounds that we have obtained we turned to analogies in the series of enamino ketones obtained from secondary amines and  $\beta$ -dicarbonyl compounds. For them are known, for example, annelation reactions with methylene sulfone [7] and with acetylenedicarboxylic ester [8], leading in high yields to six- and seven-membered rings, respectively. The formation of the expected compounds was not observed in our case. Thus, an enamino ester (VI) was isolated quantitatively from its reaction mixture with acetylenedicarboxylic ester after it had been boiled for 20 h in monoglyme.

Hence, the replacement of the dialkylamino group in the molecule of enamino ketone by a pyrazoline residue substantially decreases the reactivity of the compound in cycloaddition reactions. At the same time, the reactivities of the C=N bonds in azinium salts of the pyrazoline series in relation to nucleophilic agents are different, in spite of the existence of cross-conjugation in the molecule.

## EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument in paraffin oil, PMR spectra on Varian T-60 and Tesla BS-497 instruments with working frequencies of 60 and 100 MHz, respectively (internal standard - TMS), and UV spectra on a Pye Unicam SP 8000 instrument in methanol. The individuality of the compounds obtained was checked by TLC on Silufol and neutral alumina of activity grade II.

Preparation of the Hexachlorostannates (I), (IV), and (V). With stirring, 0.07 mole of the appropriate carbonyl compound was added to a solution of 0.05 mole of the appropriate free 2-pyrazoline and 0.03 mole of SnCl. in 100 ml of absolute ethanol saturated with HCl. The mixture was stirred for 1 h, and the resulting precipitate was filtered off and washed with absolute methanol and with dry ether. It was recrystallized from a mixture of methanol and acetone. The constants and yields of the compounds obtained are given in Table 1.

Preparation of the Tetrafluoroborates (Ia-c). With ice cooling, a solution of 0.1 mole of 50% HBF4 and then, in portions, with stirring, a solution of 0.025 mole of the appropriate carbonyl compound in methylene chloride were added to a solution of 0.025 mole of the appropriate free pyrazoline in methylene chloride. The mixture was stirred for 1 h, and the precipitate was filtered off and washed with chloroform. It was recrystallized from methanol or from methanol with acetone (see Table 1).

 $\frac{1-(2,3-\text{Dimethoxybenzy1})-3,5-\text{dipheny1-2-phenylcarbamoylpyrazolidine (II).}$  In portions, with stirring, a solution of 0.27 g (7 mmole) of lithium tetrahydroaluminate in ether was added to a suspension of 1 g (2.2 mole) of 1-(2,3-dimethoxybenzylidene)-3,5-dipheny1-2-pyrazolinium tetrafluoroborate in 30 ml of absolute ether. The mixture was boiled for 1 h and was decomposed with water. The precipitate of inorganic salts was filtered off and washed with ether, the mother solution being collected in a vessel containing 0.3 g (2.2 mmole) of phenyl isothiocyanate. The resulting solution was evaporated to half volume and boiled for 1 h. The crystals that deposited were filtered off and recrystallized from ethanol. Yield 0.8 g (75%), mp 132°C. Found: C 70.1, H 5.9%. C<sub>31</sub>H<sub>31</sub>N<sub>3</sub>O<sub>2</sub>S. Calculated: C 70.1, H 6.1%.

<u>1-(α-Cyanobenzy1)-3,5,5-trimethy1-2-pyrazoline (IIIa)</u>. A solution of 2.27 g (0.035 mole) of potassium cyanide in 15 ml of water was treated with 2 g (0.03 mole) of the salt (Ia), and 50 ml of ether was added. The reaction mixture was shaken until the pyrazolinium salt had dissolved completely. The ethereal extract was separated off, the aqueous layer was extracted with ether (3 × 20 ml), the ethereal extracts were combined and dried with sodium sulfate, and the solvent was evaporated off. The residue was recrystallized from a mixture of hexane and ethyl acetate. Yield 0.6 g (41%), mp 106°C. IR spectrum, cm<sup>-1</sup>: 1630, 2230. <sup>13</sup>C NMR spectrum, ppm (CC1<sub>4</sub>): 16.4; 22.6; 25.9; 51.2; 52.3; 66.5; 127-135; 152.6; 118.7. Found: C 74.0, H 7.8%. C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>. Calculated: C 74.0, H 7.5%.

 $\frac{1-(\alpha-\text{Cyanobenzy1})-3-\text{methyl}-5-\text{phenyl}-2-\text{pyrazoline (IIIb)}.}{\text{This was obtained similarly from the salt (Ib). Yield 42%, mp 97°C. IR spectrum, cm<sup>-1</sup>: 1670, 2240. Mass spectrum (m/z, % on the maximum ion peaks): 275 (48.4), 235 (100.0), 220 (26.6), 218 (46.1), 193 (27.3), 192 (38.3), 159 (74.2), 116 (66.4), 91 (36.7).}$ 

 $\frac{1-(\alpha-\text{Cyano-2,3-dimethoxybenzyl})-3,5-\text{diphenyl-2-pyrazoline (IIIc).}}{\text{from the salt (Ic). Yield 35\%, mp 187°C. IR spectrum, cm<sup>-1</sup>: 1675, 2280.} Mass spectrum: 397 (10.0), 222 (21.2), 221 (100.0), 176 (23.2), 116 (24.7), 115 (57.6), 104 (44.4), 103 (77.5), 91 (67.2), 77 (36.2).}$ 

1-(1-Ethoxycarbonylprop-1-en-2-yl)-3-methyl-5-phenyl-2-pyrazoline (VI). A solution of 3 g (3.5 mmole) of the salt (IVa) in 15 ml of absolute pyridine was left to stand for 2 h. Then the pyridine was evaporated off and the residual mass was treated with 10 ml of water and extracted with chloroform (3 × 10 ml). The extract was dried with sodium sulfate, the solvent was evaporated off, and the residue was recrystallized from hexane. The constants and yield of the substance are given in Table 1.

<u>3-Methyl-l-(4-oxopent-2-en-2-yl)-5-phenyl-2-pyrazoline (VII)</u>. This was obtained similarly from salt (Vc) (see Table).

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## FUNCTIONALIZED DERIVATIVES OF DIBENZO[c,j]DIPYRAZOLO-

[3,4-f:3',4'-m][1,2,5,8,9,12]HEXAAZACYCLOTETRADECINATE

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A number of derivatives of dibenzo[c,j]dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecinate with peripheral nitro, amino, and acetylamino groups have been synthesized.

Functionalized derivatives of macroheterocyclic compounds are of interest in connection with the broad possibilities of obtaining from them "picket fence" [1, 2], capped [3, 4], cyclophane (binuclear) homo- and heterobinuclear [5, 6], and other superstructures [7-9], and also spin-labeled [10], oligo peptide [11], and polymeric [12] derivatives and systems covalently bound to the surface of a solid [13] or to an organic polymer [14].

In order to obtain such structures from tetraazatetradecine systems condensed with hetarene rings, we have performed the synthesis of diamino derivatives of substituted dibenzodipyrazolohexaazacyclotetradecinates (the first model system). Out of the various possible methods of synthesizing the diamino derivatives we chose the method of selectively reducing nitro groups in the corresponding dinitro derivatives in order to obtain aminonitro compounds, which are of independent interest and also permit the comparison of a number of physicochemical characteristics to be performed.

The diazotization of 2-bromo-5-nitroaniline (I) followed by azo coupling with 5-amino-3methyl-1-propylpyrazole (II) led to the isolation of the azo compound (III), the template selfcyclization of which [15] yielded new macrocyclic compounds — derivatives of dibenzo[c,j]dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12]hexaazocyclotetradecinate (IV-VI):

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