REACTIVITIES OF ISOMERIC (1-DIMETHYLAMINOVINYL)PYRIDINES.

REACTION WITH SULFENE

L. N. Koikov, P. B. Terent'ev, I. P. Gloriozov, V. N. Torocheshnikov, V. N. Baidin, and Yu. G. Bundel' UDC 547.821.2'333.2'379.5.07: 540.14.5:543.422'51

It is shown by means of quantum-chemical calculations (MINDO/3) and data from the <sup>13</sup>C NMR and photoelectron (PE) spectra that a weak interaction between the enamine fragment and the heteroring, which deviates from its plane, exists in pyridyl enamines. The reaction of (1-dimethylaminovinyl)pyridines with sulfene leads to mixtures of 3-dimethylamino-3-pyridylthietane 1,1-dioxide (80%) and the corresponding methylsulfonyl ketone, the yield of which decreases as the acceptor character of the aromatic ring increases ( $\alpha$ -Py <  $\gamma$ -Py <  $\beta$ -Py < Ph). The structures of the enamines and the products of their reaction with sulfene were proved by IR, UV, and PMR spectroscopy, mass spectrometry, and the results of elementary analysis.

We have previously shown that lower aryleneamines that contain a benzene or electronsurplus thiophene ring react with sulfene to give mixtures of a [2+2] cycloadduct and the product of substitutive addition of sulfene to the  $C_{(2)}$  atom of the enamine fragment [1]. However, the direction of the reaction of sulfene with hetaryleneamines that contain an electron-deficient aromatic substituent has remained unclear. In this connection we synthesized isomeric  $\alpha$ -,  $\gamma$ -, and  $\beta$ -(1-dimethylaminovinyl)pyridines (Ia-c) and studied their reaction with sulfene. In order to make a more detailed study of such reactions we compared the spectral properties and some quantum-chemical parameters (calculated by the MINDO/3 method) of these compounds with the analogous data for 1-dimethylamino-1-phenylethylene (Id).

This comparison is also of interest in that it makes it possible to evaluate the degree of transmission of electronic effects in nonplanar conjugated systems, since the planarity of the pseudodiene system in such aryleneamines is disrupted due to deviation of the aromatic ring from the plane of the dialkylaminovinyl groups [2]. If this interaction is sufficiently strong, one might expect suppression of the enamine properties and a reaction of the [2+4]-cycloaddition type with sulfene (similar to the reactions of 1-substituted vinylpyridines with dienophiles [3, 4]).



Our quantum-chemical calculations\* of pyridyl enamines (Table 1) show that even under the assumption of a planar conformation of the entire molecule (geometry B), which ensures the best conjugation, the maximum coefficients of the AO are localized on the enamine fragment.

<sup>\*</sup>Made by the MINDO/3 method with a BESM-6 computer with the aid of a complex of VIKING programs [5].

M. V. Lomonosov Moscow State University, Moscow 117234. Scientific-Research Institute of Chemistry, A. A. Zhdanov Leningrad State University, Leningrad 199164. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 643-650, May, 1983. Original article submitted July 9, 1982.

| -u         | Compound <sup>a</sup> |    | (In      | qantha   | НОМО           |                           |                    |
|------------|-----------------------|----|----------|----------|----------------|---------------------------|--------------------|
| Con<br>Pou | Compound              |    | 42       | oruio    | C <sub>2</sub> | [ <i>c</i> <sub>1</sub> ] | c <sub>ortho</sub> |
|            | c ortho               | Ab | -0,1700  | 0,0600   | 0,5504         | 0,2502                    | 0,0245             |
|            |                       | В  | -0,1835  | -0,0578  | 0,5632         | 0,2443                    | 0,1446             |
| la         | NMe2<br>N C           | Α  | -0,1617  | -0,1538  | 0,5518         | 0,2582                    | 0,0166             |
|            |                       | В  | -0,1646  | -0,1823  | 0,5665         | 0,2653                    | 0,1936             |
| Ιb         | NMe <sub>2</sub>      | A  | -0,1766  | -0,0671  | 0,5553         | 0,2557                    | 0,0248             |
|            |                       | В  | -0,1794  | -0,0686  | 0,5661         | 0,2578                    | 0,1146             |
|            | NMe <sub>2</sub><br>с | А  | -0,1849  | - 0.0657 | 0.5630         | 0.2603                    | 0.0187             |
|            | N. L                  | В  | -0,1951  | 0,0661   | 0,5819         | 0,2659                    | 0,1215             |
| lc         | NMe2                  |    |          |          |                |                           |                    |
|            |                       | A  | -0,1926  | 0,0708   | 0,5674         | 0,2575                    | 0,0130             |
| Īđ         | NMe2                  | В  | - 0,2042 | 0,1267   | 0,5865         | 0,2609                    | 0,1327             |
|            |                       | A  | -0,1894  | 0,0029   | 0,5599         | 0,2591                    | 0,0308             |
|            | NMe2                  | В  | -0,1900  | 0,0033   | 0,5805         | 0,2632                    | 0,1305             |
|            |                       | 1  |          |          | ļ              |                           |                    |

## TABLE 1. Quantum-Chemical Parameters of Ia-d

TABLE 1 (continued)

| -1<br>Id |        |                  | LUMO             | P                  | E                 |           |  |
|----------|--------|------------------|------------------|--------------------|-------------------|-----------|--|
| Con      |        | C2               | c <sub>1</sub>   | c <sub>ortho</sub> | <sup>ь</sup> номо | LUMO      |  |
| Ĭe       | A<br>B | 0,2103<br>0,3904 | 0,1307<br>0,2765 | 0,1135<br>0,1780   | 7,96<br>7,87      | 0,60 0,72 |  |
| 197      | A      | 0,1466           | 0,0893           | 0,0552             | 7.98              | 0,60      |  |
|          | B      | 0,4025           | 0,2820           | 0,1779             | 7,90              | 0,78      |  |
| IЬ       | A      | 0,1920           | 0,1142           | 0,1605             | -7,95             | 0,62      |  |
|          | B      | 0,3922           | 0,2764           | 0,3066             | -7,92             | 0,76      |  |
| T.       | A      | 0,1716           | 0,1071           | 0,1947             | 7,91              | 0,70      |  |
|          | B      | 0,3661           | 0,2709           | 0,4297             | 7,70              | 0,86      |  |
| IC.      | A      | 0,1692           | 0,1067           | 0,1645             | 7,90              | 0,67      |  |
|          | B      | 0,3565           | 0,2642           | 0,4424             | 7,86              | 0,85      |  |
| Id       | A      | 0,1784           | 0,1113           | 0,1575             | - 7,91            | 0,69      |  |
|          | B      | 0,3859           | 0,2826           | 0,3123             | - 7,84            | 0,86      |  |

<sup>a</sup>Standard geometry: C=C 1.34 Å, C-C= 1.47 Å, =C-H 1.1 Å,  $\angle C-C=C = \angle C=C-N 117^{\circ}$ , C-N 1.46 Å, C-Carom 1.39 Å, C-Narom 1.37 Å, and C-Harom 1.087 Å. <sup>b</sup>Geometry A is the equilibrium geometry of Id: the dimethylaminovinyl grouping is virtually planar, and the angle of rotation of the aromatic ring is 55 deg. In geometry B the aromatic ring, the multiple bond, and the amino nitrogen atom lie in the same plane. <sup>c</sup>Less favorable conformation.

This "isolated character" of the dimethylamino group is retained even in the case of the most strongly acceptor  $\alpha$ -pyridine ring in Ia (compare with Id).

The strong polarization of the pseudodiene system, which makes the occurrence of [2+4]cycloaddition reactions unlikely, is a consequence of this. At the same time, the calculations made for the nonplanar conformations of Ia-d, which more accurately reflect the actual distribution of the electron densities (Table 1, geometry A), constitute evidence for

|               | •               |  |  |  |  |          |
|---------------|-----------------|--|--|--|--|----------|
| Com-<br>pound | bp, °C<br>(mm)  | IR<br>spec-<br>trum,<br>cm <sup>-1</sup> | UV spec-<br>trum,<br>$\lambda_{\max}$ , nm<br>(log $\varepsilon$ ) | PMR spectrum, δ, ppm (J, Hz)   | Mass spectrum, m/z<br>(relative intensity,<br>%) <sup>a</sup>  | Yield, 껴 |
| Ja            | 92—94<br>(18)   | 1620                                     | 218 (3,98),<br>242 (3,78),<br>275 (3,53)                           | 8,56–8,30 ( <sup>III</sup> , $\alpha$ -11); 7,70–6,80<br>(III, $\gamma$ -H+ $\beta$ -H+ $\beta$ '-H); 4,50,4,10<br>(s, =CH <sub>2</sub> ); 2,60 [s, N(CH <sub>3</sub> ) <sub>2</sub> ] | 148 (43), 147 (25),<br>133 (32), 106 (48),<br>105 (88), 104 (100),<br>79 (40), 78 (60), 77             | 20       |
| lb            | 107—109<br>(20) | 1605                                     | 214 (4,27),<br>275 (3,51)  | 8,55 [dd, (4, 2), $\alpha$ -H]; 7,28 [dd,<br>(4, 2), $\beta$ -H]; 4,25, 4,13 <sup>5</sup> (s,<br>=CH <sub>2</sub> ); 2,60 [s, N(CH <sub>3</sub> ) <sub>2</sub> ]                       | (13)<br>148 (40), 147 (100),<br>132 (26), 106 (20),<br>104 (19), 92 (30), 79<br>(16), 78 (19), 77 (14) | 66       |
| Ic            | 100—103<br>(16) | 1605                                     | 214 (4,37).<br>268 (3,52)  | $\begin{array}{llllllllllllllllllllllllllllllllllll$   | 148 (29), 147 (100),<br>132 (20), 106 (12),<br>104 (20), 92 (42), 79<br>(8), 78 (18), 77 (20)          | 35       |

TABLE 2. Properties of (1-Dimethylaminoviny1)pyridines (Ia-c)

<sup>a</sup>The molecular-ion peak and the eight most intense ion peaks are presented. <sup>b</sup>The signal is broadened due to trans coupling with the dimethylamino group ( ${}^{5}J_{trans} < 0.5$  Hz).

the existence of a certain interaction [the charge on the  $C_{(2)}$  atom increases regularly as the electron-deficient character of the aromatic ring decreases]. The experimental data also indicate the existence of such a weak interaction.

The UV spectra (Table 2) of pyridyl enamines Ia-c, the synthesis of which is discussed below, are very similar to the spectrum of phenyl-substituted Id. The band corresponding to the  $\pi \rightarrow \pi^*$  transition of the entire conjugated system is located between the absorption at 270 nm (local excitation of the aromatic ring) and 220 nm (transitions with participation of the higher-lying orbitals) and cannot serve to characterize it.\* At the same time, data from photoelectron (PE) spectroscopy indicate the existence of interaction of the dimethylaminovinyl grouping and the aromatic ring even in the nonplanar conformation of the molecule. Thus, when the phenyl group in Id is replaced by a  $\gamma$ -pyridyl group (Ib), the first ionization potential increases from 7.69 eV to 8.02 eV, while the transition from  $\alpha$ -dimethylaminostyrene Id to  $\alpha$ -diethylaminostyrene (an increase in the electron-donor character of the dialkylamino group) gives rise to a decrease in the first ionization potential to only 7.51 eV.

The <sup>13</sup>C NMR spectra of the pyridyl enamines prove to be unexpectedly informative (Table 3). On the one hand, the "isolated character" of the aromatic ring is confirmed by the fact that the introduction of a 1-dimethylaminovinyl group has only a slight effect on the chemical shifts of the carbon atoms of the pyridine ring that are not bonded directly to it (the deviations from the chemical shifts of the corresponding pyridine carbon atoms do not exceed 1.2 ppm). As compared with pyridine, the signal of the quaternary carbon atom is shifted 12 ppm to weak field for Ib, c and 8 ppm to weak field for Ia (Table 3). A similar "ortho effect" is observed for acetylpyridines (the weak-field shifts of the signal of the quaternary carbon atom with respect to pyridine are 7.7 and 6.3 ppm for the  $\gamma$  and  $\beta$  isomers, as compared with 3.2 ppm for the  $\alpha$  isomer) [6]. On the other hand, the signal of the C(2) atom is shifted to weak field as the acceptor character of the pyridine ring increases, which is in agreement with the calculated data (see Table 1) and confirms the existence of a certain amount of "drawing off" of the surplus electron density of the enamine fragment due to interaction with the aromatic ring (even though it is markedly weakened!).

Compounds Ia-c were obtained from the corresponding acetylpyridines and dimethylamine in the presence of TiCl<sub>4</sub>. We found that the use of the standard method [7] leads to an azeotropic mixture of the enamine and the starting ketone, while the use of a 5-10% excess of dimethylamine and a 1-2% excess of TiCl<sub>4</sub> (as compared with the stoichiometric amounts) makes it possible to obtain the pure enamine, although in somewhat lower yield (Table 2).

<sup>\*</sup>We assigned the transitions on the basis of calculations by the CNDO/S method for various conformations of Id, which has the following spectrum:  $\lambda_{max}(\log \epsilon)$ : 220 (4.32) and 268 nm (3.51).

| Com-<br>pound | Pyridy1  | C <sub>(1)</sub> | C <sub>(2)</sub> a | Cα                         | C <sub>β</sub>             | Cγ     | C <sub>X</sub>   | N (CH <sub>3</sub> ) <sub>2</sub> |
|---------------|--|------------------|--------------------|----------------------------|----------------------------|--------|------------------|-----------------------------------|
| I a<br>Ib     | $\begin{array}{l} \alpha\text{-}C_5H_4N\\ \gamma\text{-}C_5H_4N \end{array}$ | 158,15<br>156,10 | .92,89<br>.92,04   | 149,55<br>151,40<br>150,34 | 122,48<br>122,72<br>121,53 | 138,88 | 158,15<br>143,22 | 40,23<br>41,46                    |
| lc            | $\beta\text{-}C_5H_4N$   | 155,13           | 91,26              | 149,84<br>149,67           | 123,09                     | 135,01 | 135,89           | 41,56                             |

TABLE 3. <sup>13</sup>C NMR Spectra of (1-Dimethylaminovinyl)pyridines (Ia-c)

\*For Id, C(2) is 89.90 ppm.

The individuality of Ia-c is confirmed by analysis by gas-liquid chromatography (GLC), and their structure is confirmed by data from IR and UV spectroscopy and mass spectrometry as well as from PMR and <sup>13</sup>C NMR spectroscopy (Tables 2 and 3). The presence of a double bond is indicated by bands in the IR spectrum (1605-1620 cm<sup>-1</sup>) and signals of olefin protons at 4.0-4.5 ppm in the PMR spectra. Rather intense peaks of molecular ions and  $M^+ - 1$  ions are observed in the mass spectra of all of the pyridyl enamines; the peaks of the latter ions are the maximum peaks in the spectra of the  $\gamma$ - and  $\beta$ -pyridyl-substituted compounds. At the same time, the  $M^+ - 44$  ion peak has the maximum intensity in the spectrum of  $\alpha$ -pyridyl-substituted enamine Ia; this is associated with the effect of the nitrogen atom of the pyridine ring, which is adjacent to the dimethylaminovinyl group, on which the positive charge in the molecular ion is most likely localized.

In complete agreement with the conclusions based on the results of quantum-chemical calculations and data from the PE and <sup>19</sup>C NMR spectra, the reaction of pyridyl enamines Ia-c (as well as Id [1]) with sulfene leads to mixtures of [2+2] cycloadducts IIa-d and the corresponding ketones IIIa-d, the yields and constants of which are presented in Table 4.



The structures of the substances obtained were confirmed by spectral studies, and their compositions were confirmed by the results of elementary analysis (Table 4). Bands in the IR spectra at 1320-1325 ( $\nu_{as}$ ) and 1135-1170 cm<sup>-1</sup> ( $\nu_{s}$ ) indicate the presence of a sulfo group in II and IIIa-c. The presence of a heteroaromatic ring is evident from the UV spectra (absorption at 254-284 nm) and from the character of the PMR spectra at 7.35-9.20 ppm.

Molecular-ion peaks are observed in the mass spectra of compounds with cyclic (II) and linear (III) structures; however, their intensities are low in the spectra of thietane 1,1dioxides II, and this serves as an indirect confirmation of the presence of a four-membered ring in these compounds. The principal process of fragmentation of the molecular ions of these compounds is retro [2+2] fragmentation with the ejection of sulfene rather than ethylene, and as would be observed in the case of the regioisomeric cycloadduct with a structure of the "head-to-head" type (B).



The PMR spectra of adducts IIa-c also constitute evidence for A-type addition of sulfene to the pyridyl enamines (see Table 4). Rearrangement processes that involve hydrogen transfer and were previously studied by us in the case of aromatic derivatives [1] are also characteristic for the mass spectra of IIa-c; in the case of pyridyl-substituted cycloadduct IIa they cause a significant decrease in the intensity of the molecular ion. TABLE 4. Properties of Dioxides IIa-c and Methylsulfonyl Ketones IIIa-c

| Yield,   | %<br>/0          | 81  | 78  | 80   | 0,2  | 3,5   | 4,5   |
|--|------------------|---|---|--|--|---|---|
| Mass spectrum, $m/z$ (relative intensity, $q_0$ ) <sup>b</sup> |                  | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$   | $ \begin{array}{rrrr} M^+ & 226 & (30), & 149 & (41), \\ 148 & (83), & 147 & (100), & 133 \\ (40), & 120 & (25), & 104 & (45), \\ 92 & (67), & 78 & (26) \\ \end{array} $ | $ \begin{array}{rrrrr} M^+ & 226 & (26), & 161 & (65), \\ 149 & (53), & 148 & (85), & 147 \\ (100), & 133 & (58), & 120 & (33), \\ 104 & (33), & 92 & (54) \end{array} $                   | M+ 199 (76), 184 (30),<br>121 (12), 120 (21), 106<br>(21), 79 (100), 78 (79) | M <sup>+</sup> 199 (8), 106 (100),<br>79 (21), 78 (79)  | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  |
| Calc., %   | C H              | 24,6  | 24,6  | 24,6   |  | 48,2 4,6  | 48,2 4,6  |
| Empirical<br>formula   |                  | C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S .<br>. 2HCl   | C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S ·<br>· 2HCl   | C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S ·<br>• 2HCl  | C <sub>8</sub> H <sub>9</sub> NO <sub>3</sub> S                              | C <sub>8</sub> H <sub>9</sub> NO <sub>3</sub> S   | C <sub>6</sub> H <sub>9</sub> NO <sub>3</sub> S   |
| Found, 🌮   | СН               | 24,4d   | 24,6d   | 24,5d  |  | 48,0 4,8  | 48,5 4,7  |
| PMR spectrum, 6,<br>ppm (J, Hz)                                |                  | $\begin{array}{c} 8.64  (m, \ \alpha \cdot H); \ 7,90  (m, \ \gamma \cdot H); \ 7,58  (m, \ \beta' \cdot H); \ 7,36  (m, \ \beta' \cdot H); \ 7,36  (m, \ \beta' \cdot H); \ 4,82, \ 4,40  (m, \ CH_2); \ 2,12  [s, N(CH_3)_2] \end{array}$ |   | $ \begin{array}{c} 8,40-8,16 \ (m,\alpha-H+\alpha'H);\\ 7,65 \ [dd. \ (8,\ 2),\ \gamma-H];\\ 7,35 \ [dd. \ (8,\ 4,\ 5),\ B-H];\\ 4,60 \ (s,\ CH_2);\ 2,10 \ [s,\\ N(CH_3)_2] \end{array} $ | ł  | 8,85 [m, 2 (α-H)]; 7,73<br>[dd, (5, 2), 2 (β-H)]; 4,60<br>(s, CH <sub>2</sub> ); 3,30 (s, CH <sub>3</sub> ) | $\begin{array}{c} 9.20 \ (m,  \alpha' - H); \ 8,80 \ [dd, \ (2, \ 4, \ 5), \ \alpha - H]; \ 8,25 \ (m, \ Y - H); \ Y - H]; \ R - H]; \ R$ |
| UV spec-<br>trum, $\lambda_{max}$ ,                            | nm (10g E)       | 254 (3,80),<br>258 (3,81)   | 259 (3,64)  | 255 (3,50),<br>260 (3,51)  | $\begin{array}{ccc} 236 & (3,41), \\ 271 & (3,16) \end{array}$               | 224 (3,83),<br>284 (3,20)   | 234 (3.71),<br>268 (3.31),<br>330 (2.90)  |
| IR spectrum  | cm <sup>-1</sup> | 1320, 1170,<br>1155, 1135   | 1325, 1170,<br>1160, 1145   | 1320, 1170,<br>1155  | 1750, 1715   | 1710, 1320,<br>1135   | 1700, 1320,<br>1140   |
| , K  |                  | 0,2C <sup>C</sup>   | 0,23  | 0,19   | 0,62 <b>c</b>  | 0,35  | 0,28  |
| mn <sup>a</sup> °C   | o du             | 140   | 188<br>(dec.)   | 138139   | 107-108  | 117—118   | 7879  |
| Com-   | punod            | 8<br>1<br>1<br>8  | qII   | IIc  | IIIa   | qIII  | IIIc  |

<sup>a</sup>From methanol. <sup>b</sup>The ions with peak intensities >1% are presented. <sup>c</sup>In a hexane-acetone system (3:7). <sup>d</sup>Analysis for chlorine was performed for the corresponding hydrochlorides by a "wet" method [1].

The dissociative ionization of the sulfonyl ketones of the pyridine series (IIIa-c) is also extremely interesting, since in this case also anomalies are observed for the  $\alpha$ -pyridylcontaining compound. Whereas the PyCO<sup>+</sup> ion peak (m/z 106) is the most intense peak for the mass spectra of the ketones that contain  $\gamma$ - and  $\beta$ -pyridine rings, rearrangement processes involving the ejection of sulfene are observed in the mass spectrum of IIIa.



This is evidently explained by the fact that due to pushing apart of the electron clouds of the CO and SO<sub>2</sub> groups in sulfonyl ketones IIIb, c in the gas phase, they exist primarily in the anti conformation, which makes rearrangement impossible. At the same time, the closeness of the nitrogen atom and the SO<sub>2</sub> group in the  $\alpha$ -pyridyl-containing compound destabilizes the anti conformation and leads to the development of a certain amount of the syn form, the characteristic fragmentation of which is also observed in the mass spectrum of IIIa.



anti - (CO and SO2) syn-

This assumption is confirmed by the fact that two absorption bands of a carbonyl group at 1750 and 1715 cm<sup>-1</sup> with an intensity ratio of 1:3 are observed in the IR spectrum of this compound (solution in CHCl<sub>3</sub>), while only one band at 1700-1710 cm<sup>-1</sup> is observed in the IR spectra of ketones IIIb, c. Although it is not legitimate to apply the data on the ratios of the conformers obtained for solutions to the gas phase, the very fact of recording a second conformer by means of mass spectrometry is noteworthy.

Except for the least electron-deficient IIIc, rearrangement of the sulfo group to a sulfinyl ester, which is very characteristic for sulfones [8], is not observed in the mass spectra of ketones III. This is probably associated with the short lifetime of the molecular ion and the competitive loss by it of a PyCO<sup>+</sup> fragment (see the scheme presented above). However, this rearrangement can be recorded in the case of elimination of the least stable  $\beta$ -PyCO<sup>+</sup> ion from the molecular ion, and only a methanesulfinic acid ester is formed as a result.

The virtually identical yields of thietane 1,1-dioxides in the IIa-d series (see Table 4) confirm the conclusion that the bond between the aromatic ring in Ia-d and the enamine fragment is relatively weak. At the same time, the presence of this bond is confirmed by the decrease in the yields of the electrophilic addition products in the order IIId > IIIc > IIIb > IIIa,\* which correlates with the decrease in the nucleophilicity of the  $C(_2)$  atom (Tables 1 and 2) due to an increase in the acceptor character of the aromatic substituent.

Thus, on the basis of the results of model quantum-chemical calculations and physicochemical studies, one can predict the reactivities of rather complex and uninvestigated vinylheteroaromatic systems that contain several reaction centers. This, in turn, opens up routes to the purposeful synthesis of cyclic or linear structures of the II and III type from readily accessible enamines of the pyridine series.

## EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl<sub>4</sub> (Ia-c),  $d_6$ -acetone (IIa-c), and CDCl<sub>3</sub> (IIIb,c) were recorded with a T-60 spectrometer with tetramethylsilane as the internal

\*We have previously shown that II and III are formed independently [1, 2]. The yields of IId and IIId are 86 and 13%, respectively.

standard. The <sup>13</sup>C NMR spectra of 60% solutions of the compounds in cyclohexane were obtained with a CFT-80 spectrometer with the solvent as the internal standard. The mass spectra of IIa-c and IIIa-c were recorded with an MAT-212 spectrometer (80 eV).\* The chromatographic mass-spectrometric analysis of Ia-c was carried out with an MAT-111 spectrometer (80 eV) with a 1.5 m by 3 mm steel column filled with 3% OV-1 on Chromaton N-Super with temperature programming from 100 to 200°C at 8°C/min. The UV spectra of solutions of the compounds in absolute heptane (Ia-c) or 96% ethanol (IIa-c, IIIa-c) were recorded with a Cary-219 spectrophotometer. The IR spectra of films (Ia-c), mineral oil suspensions (IIa-c), films from CHCl<sub>3</sub> (IIIb, c), or a solution in CHCl<sub>3</sub> were recorded with a UR-20 spectrometer.

Analytical chromatography was carried out on Silufol plates impregnated with a solution of Rhodamine 6Zh in a heptane-acetone system (1:1).

(1-Dimethylaminovinyl)pyridines (Ia-c). A solution of 11.6 g (0.06 mole) of TiCl<sub>4</sub> in 100 ml of benzene was added with stirring to a cooled (to -15°C) solution of 0.1 mole of the corresponding acetylpyridine in 300 ml of dry benzene and 18 g (0.4 mole) of a solution of dimethylamine in 100 ml of absolute ether at such a rate that the temperature did not rise above -5°C. The reaction mixture was then allowed to stand overnight, after which the precipitate was removed by filtration and washed with dry benzene. The filtrate was evaporated in vacuo, and the residue was distilled. All of the operations were carried out in a stream of dry argon. The pyridyl enamines readily underwent self-condensation (Ia could be stored in a refrigerator for only a few days).

Reaction of (1-Dimethylaminoviny1)pyridines with Sulfene. A flame-dried and dry nitrogen-purged flask was charged with 13.5 mmole of enamine Ia-c, 28.5 mmole of absolute triethylamine, and 30 ml of absolute  $CH_2Cl_2$ , the mixture was cooled with ice, and a solution of 22.1 mmole of methanesulfonyl chloride in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring. The solution was stirred for 1 h with ice cooling and for 2 h at room temperature, after which it was allowed to stand overnight. The triethylamine hydrochloride was washed with two 10-ml portions of cold water (IIa-c and IIIa-c are moderately soluble in water!), and the organic layer was evaporated and washed with hexane to remove the nonpolar impurities. The residue was recrystallized three times from methanol to give the bulk of cycloadducts III. The hexane solutions and the mother liquor after recrystallization were combined and evaporated, and the residue was separated with a column filled with L  $100/160 \mu$  silica gel in a petroleum ether (40-70°C)-acetone system (5:1) [in the case of thin layer chromatography (TLC) on Silufol the ketone was developed as a violet spot in visible light, while the cycloadduct was developed as a whitish spot]. In the case of Ia the mixed fraction containing IIa and IIIa was separated preparatively on Silufol UV-254 plates in a petroleum ether (40-70°C)-acetone system (3:7), whereas in the case of enamine Ib the mixture of IIb and IIIb was applied to a volumn filled with activity II Al<sub>2</sub>O<sub>3</sub>, and the cycloadduct was eluted with petroleum ether  $(40-70^{\circ}C)$ -ethyl acetate (1:4), and ketone IIIb was eluted with warm methanol. The yields and properties of II and III are presented in Table 4.

The addition of an ether solution of hydrogen chloride to solutions of bases IIa-c led to the production of the corresponding dihydrochlorides, which, according to PMR data, exist in the form of monoprotonated dimethylammonium salts in aqueous solutions.

## LITERATURE CITED

1. L. N. Koikov, P. B. Terent'ev, and N. S. Kulikov, Zh. Org. Khim., <u>17</u>, 1087 (1981).

2. L. N. Koikov, Master's Dissertation, Moscow State University, Moscow (1981).

3. P. B. Terent'ev, V. G. Kartsev, I. K. Yakushenko, L. N. Prostakova, A. N. Kost, and

I. P. Gloriozov, Khim. Geterotsikl. Soedin., No. 5, 639 (1979).

4. P. B. Terent'ev, V. G. Kartsev, A. V. Gorelov, I. P. Gloriozov, Yu. V. Gulevich, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 9, 1248 (1980).

5. Yu. A. Ustynyuk (editor), Quantum-Chemical Methods for the Calculation of Molecules [in Russian], Khimiya, Moscow (1980).

- 6. M. Goh, S. Yoshio, and S. Miyoko, Chem. Pharm. Bull., 20, 429 (1972).
- R. Carlson, R. Phan-Tan-Luu, D. Mathieu, F. S. Ahouande, A. Babadjamian, and J. Metzger, Acta Chem. Scand., <u>B32</u>, 335 (1978).
- 8. R. A. Khmel'nitskii and Yu. A. Efremov, Usp. Khim., 46, 83 (1977).

\*We thank N. S. Kulikov for recording the mass spectra.