# TAUTOMERISM OF AZINE DERIVATIVES.

# 11.* $^{14}$N-NMR AND $^{17}$O-NMR INVESTIGATION OF INTRACHELATE TAUTOMERISM OF ACYLMETHYLPYRIDINES

V. V. Lapachev, S. A. Stekhova,
I. Ya. Mainagashev, M. A. Fedotov,
V. E. Khall, and V. P. Mamaev

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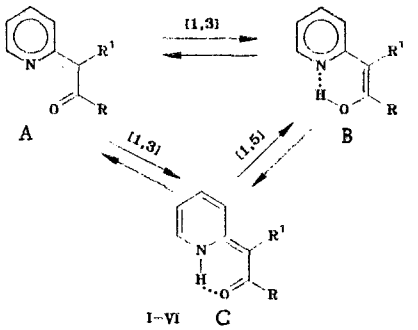
Intrachelate [1, 5]-sigmatropic tautomerism in a series of acylmethylpyridines has been studied by $^{14}$N- and $^{17}$O-NMR spectroscopy. Principles of tautomer modelling or simulation have been proposed and examined, nitrogen and oxygen chemical shift spectra have been determined, and the accuracy of this method for the determination of tautomer composition has been evaluated. The presence of acceptor (electron withdrawing) substituents in the acylmethyl side-chain fragment has been found to stabilize the NH-tautomer.

We have previously studied [2, 3] tautomerism in pyrimidylmalonic and cyanoacetic esters. Due to the low enolizability of the carboxyl groups in these classes of compounds, the enol tautomer B is energetically inaccessible, and solutions of these compounds in $CHCl_3$ and $CCl_4$ are characterized by equilibria of the type A⇄C.




I, VI R=$CH_3$, II R=$C_6H_5$, III R=$CF_3$, IV R=$CH_2Cl$, V R=$CCl_3$; I—V $R^1$=H, VI $R^1$=CN

This type of tautomerism ([1, 3]-sigmatropic tautomerism [4]) is characterized by relatively low rates of interconversion, since symmetry requirements render the intramolecular mechanism of[1, 3]-sigmatropic proton transfer improbable [5]. In the case of easily enolizable ketone groups (R = $CH_3$, $C_6H_5$),[1, 5]-sigmatropic tautomerism of the type B⇄C becomes very rapid; in contrast to [1, 3]-sigmatropic tautomerism, an intramolecular proton transfer mechanism has been advanced for this process [intrachelate tautomerism).

This type of tautomeric equilibrium is of widespread importance in organic chemistry (among enols of β-dicarbonyl compounds, Schiff bases, azo dyes containing ortho-hydroxyphenyl substituents, and enaminocarbonyl compounds, and others).

Interest in studies of intrachelate tautomerism has been stimulated not only by its theoretical importance [6], but also by the feasibility of practical applications of tautomeric chelated systems as light-stabilizers, complex-forming compounds, and photochromic systems.

*For communication 10, see [1].

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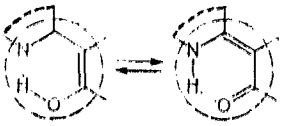


a b

Fig. 1. Structures of chelate fragments: a) iminoenol, and b) enaminocarbonyl.

In addition, this type of tautomerism has not been studied much in heterocyclic systems. This is due mainly to the faster rate of intrachelate proton transfer in these derivatives, which leads to signal coalescence of the exchanging nuclei and thus hinders the use of $^{1}H$- and $^{13}C$-NMR spectroscopy for the determination of tautomer composition. As a result, the generally accepted method of analyzing tautomeric equilibria by NMR studies of model compounds is of little utility for these systems, since their chemical shifts do not differ greatly. Not surprisingly, therefore, the data available concerning the type B⇄C equilibria are inconsistent, even in the case of a very simple model compound, such as acetonylpyridine I [7].

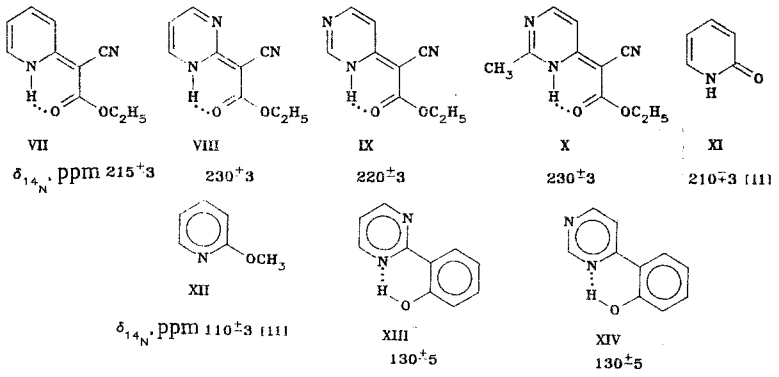
We have hypothesized that consideration of the NMR properties of the nitrogen and oxygen atoms involved in proton migration might yield more useful information concerning the type B⇄C equilibria. The hybridization of these atoms changes during the course of tautomer interconversions, and as a result, the differences in the chemical shift values of the observed nuclei can reach 100 ppm and higher [8, 9]. This, in turn, permits semiquantitative and even in some cases quantitative measurements of tautomer composition.

In the present paper we have used high field $^{14}N$- and $^{17}O$-NMR spectroscopy to study intrachelate (B⇄C) tautomerism in acylmethylpyridines I-VI, and have analyzed the effectiveness of these methods for the study of rapid [1, 5]-sigmatropic tautomerism. Since the rates of A⇄B and A⇄C tautomeric interconversions are slow on the NMR time scale, the concentration of A forms as well as the total amount of B and C forms could be determined by PMR spectroscopy. The ratios of B and C tautomers were evaluated based on the positions of the nitrogen or oxygen atom signals relative to those in model compounds.

Modelling Studies of the Spectral Characteristics of B and C Tautomers. In studies of rapid tautomeric equilibria, the accuracy of equilibrium calculations depends to a large extent on the selection of model compounds. Analysis of literature data has established that the magnitudes of the chemical shifts of nitrogen and oxygen atoms are very sensitive, as might be expected, to conjugative effects as well as to hydrogen bonding [8-10]. For this reason, we rejected the classical approach to selecting tautomer form models (N- and O-methyl derivatives) [11]. Instead, we focused on an approach to selecting model compounds which preserved the structural features of the chelate fragment, namely, the enaminocarbonyl group for type C tautomers and the iminoenol group for type B tautomers (Fig. 1). The peripheral features surrounding the chelate groups have been varied in such a way that one of the forms becomes energetically unfavorable and thus shifts the equilibrium for the model compound almost entirely in favor of one tautomeric form. This approach to model selection is made possible by the fact that nitrogen and oxygen chemical shift values do not depend to a large extent on the nature of their outer surroundings [8-10].

Cyanoacetic esters VII-X were selected as model compounds for $^{14}N$-NMR studies of the NH-tautomers. $^{14}N$- chemical shift comparisons of compounds VII-XI revealed that the position of the NH signal depended only weakly on structural changes in the molecular ($\Delta\delta = \pm 7$ ppm). The similarities in the nitrogen shift values for azinylcyanoacetic esters and 2-pyridone (XI) called our attention; we do not believe that these similarities are coincidental, but rather, that they reflect the amide character of the NH groups in compounds VII-X and XI.

As a result, the two most important factors influencing chemical shifts, namely, conjugation of the carbonyl and amino groups, and hybrization state of the nucleus, are preserved in both cases (the enaminocarbonyl fragment in VII is a vinylog of the amide fragment in XI).

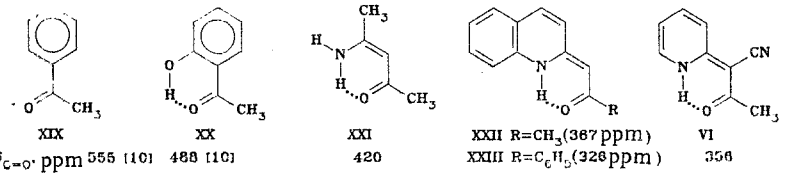



In selecting a model compound for the B tautomer, we considered that this form may be regarded as a vinylog of 2-hydroxypyridine, and thus that, to a first approximation, the $^{14}$N-NMR signals of the enol forms B of acylmethylpyridines can be modelled after the nitrogen atom signal of 2-methoxypyridine XII.* The effect of intramolecular hydrogen bonding shifts the nitrogen atom signal strongly upfield, by almost 20 ppm [9]. The nitrogen atom signals of the enol forms of acylmethylpyridines would thus be expected to occur at approximately −130 ppm. This hypothesis is in excellent agreement with the spectral data for hydroxyphenylpyrimidines XIII and XIV, which, in analogy with form B, possess iminoenol fragments.

In selecting model compounds for the $^{17}$O-NMR spectra of the B forms, we considered compounds XV-XVIII


According to our previous work [12], the position of the signal due to the enol oxygen atom in six-membered ring chelates depends only weakly on the basic portion of the molecule which is involved in intramolecular hydrogen bond formation ($\Delta\delta$ = ±5 ppm), but is more noticeably affected by the presence of substituents attached to the enolizing carbonyl group. For this reason, the enol tautomers can also be modelled using the enol forms of corresponding β-ketoesters; thus, acetonylpyridine is modelled by acetoacetate ester XV, phenacylpyridine by benzoylacetate ester XVI, etc. In this regard, we have found satisfactory agreement of our spectral results with those of the model compound XVIII (compare with XVI), in which the B⇄C equilibrium is shifted almost entirely in favor of the enol form B [13].

The characteristics and extent of conjugative and intramolecular hydrogen bonding effects on the chemical shift values of the carbonyl oxygen atoms can be evaluated in the series of compounds XIX-XXI.




Comparison of the spectral values in compounds XIX-XXI reveals that electron-donating substituents and hydrogen bonding shift the signals upfield. Apparently, the signal of the ylide tautomers of acylmethylpyridines is shifted toward higher field, as shown by the $^{17}$O-NMR chemical shift data for 2-cyanoacetonylpyridine VI and the acetonyl- and phenacylquinolines XXII and XXIII. According to their $^{14}$N-NMR spectra, these compounds exist almost entirely in the form of their ylide tautomers ($-\delta_{NH}$ 199, 223, and 229 ppm, respectively). The

*The $^{14}$N-NMR chemical shifts of azines containing hydroxy groups are hard to measure, since the equilibria involving these compounds are shifted primarily in favor of the oxo forms. The use of methoxy derivatives is justified by comparison with the very small effect of methylation on the $^{14}$N-NMR chemical shift values of hydroxyazines ($\Delta\delta \approx 1$ ppm) [11].

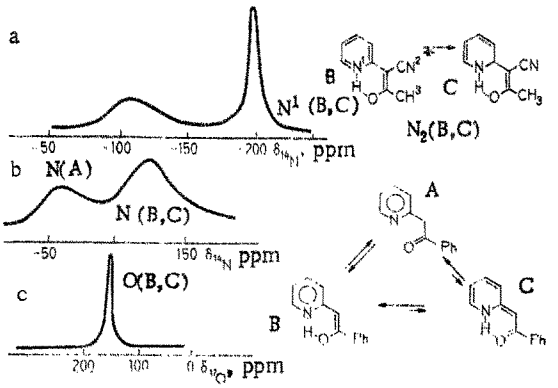



Fig. 2. NMR spectra: a) cyanoacetonylpyridine VI; b and c) phenacylpyridine II.

ylide structure of the quinoline derivatives XXII and XXIII has been confirmed earlier based on their UV and PMR spectroscopic data [14].

Based on the discussion above, we assumed a value of 352 ± 21 ppm for the $^{17}$O-NMR chemical shift of the NH-tautomer.

Accuracy of the $^{14}$N-NMR and $^{17}$O-NMR Methods for the Determination of the NH- and OH-Tautomer Ratio. The use of $^{14}$N- and $^{17}$O-NMR methods in tandem has allowed us to overcome the limitations inherent in each method. The $^{14}$N-NMR method proved to be the more informative means of analyzing mixtures containing a preponderance of the ylide tautomers, since the signal due to the NH group is relatively narrow in these cases and also characteristic in comparison with the nitrogen atom signal in pyridine type compounds (Fig. 2). The signal due to the nitrogen nucleus broadens considerably as the B⇄C tautomer equilibrium is shifted in favor of the enol form. For instance, the width of this signal in the spectrum of 2-cyanoacetonylpyridine (VI), which exists almost entirely in the ylide form, is 320 Hz, whereas the half-width of the 2-phenacylpyridine signal, in which the B⇄C equilibrium is strongly displaced in favor of the enol form, is much greater, $\nu_{1/2}$ = 1300 Hz. In the case of compounds containing significant contributions of the A and B tautomers in solution, the corresponding broad signals sometimes overlap, which complicates determination of the chemical shift values. For example, in the case of 2-phenacylpyridine, in which concentrations of the B and C forms are comparable, the distance between the $^{14}$N-NMR signals of the two forms is on the same order as their line widths (Fig. 2). The determination of the tautomer composition is even more complicated in the case of diazine derivatives, in which the spectra feature an additional signal due to the second nitrogen atom in the ring. In order to overcome the difficulties discussed above, we considered it more expedient to utilize the $^{17}$O-NMR method, in spite of its greater experimental complexity. The use of $^{14}$N- and $^{17}$O-NMR spectroscopy in tandem increases the reliability of the results and decreases the probability of errors due to inadequate model compounds in calculating the tautomer composition or in determining chemical shift values of broad signals, etc. Error values in the tautomer composition results arising from inadequate modelling of the compounds can be evaluated [15, 16] by differentiation of Eq. (1) with respect to two variables, $\Delta\delta_B$ and $\Delta\delta_C$

$$P=\frac{\delta_{obs}-\delta_C}{\delta_B-\delta_C}, \tag{1}$$

where $\delta_{obs}$ is the experimentally determined chemical shift value and $\delta_B$ and $\delta_C$ are the chemical shift values of the model compounds.

$$\Delta P=\frac{\partial P}{\partial \delta_B}\Delta\delta_B+\frac{\partial P}{\partial \delta_C}\Delta\delta_C \quad \text{or}$$
$$\Delta P=\frac{\delta_B-\delta_{obs}}{(\delta_C-\delta_B)^2}\Delta\delta_C+\frac{\delta_{obs}-\delta_C}{(\delta_B-\delta_C)^2}\Delta\delta_B, \tag{2}$$

where $\Delta\delta_{B,C}$ are the errors in modelling tautomers B and C, respectively.

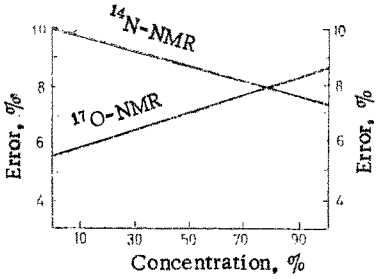



Fig. 3. Dependence of the absolute error in the tautomer composition measurements of acylmethylpyridines (by $^{14}$N- and $^{17}$O-NMR) on the concentration of the C tautomer in the mixture.

TABLE 1. $^{14}$N- and $^{17}$O-NMR Spectral Characteristics and Tautomer Composition for the Acylmethylpyridines I-VI

| Compound | $^{14}$N-NMR spectrum | | $^{17}$O-NMR spectrum | | A/B/C* |
|---|---|---|---|---|---|
| | chemical shift† | B/C‡ | chemical shift† | B/C‡ | |
| I | 130±5 | 100/0 (±10) | 143±3 | 92/8 (±5) | 86:13:1 |
| II | 131±5 | 100/0 (±10) | 125±3 | 90/10 (±5) | 53:45:2 |
| III | 177±3 | 45/55 (±8) | | | 0:45:55 |
| IV | 130±5 | 100/0 (±10) | 160±3 | 82/18 (±5) | 28:59:13 |
| V | 194±3 | 25/75 (±8) | | | 0:25:75 |
| VI | 199±1 | 19/81 (±8) | 356±2 | 0/100 (±7) | 0:19:81 |

*The concentrations of tautomers were calculated from their $^{14}$N-, $^{17}$O-, and $^{1}$H-NMR data; the latter data were also used to determine the A/(B + C) ratio (accuracy ±1%).
†Chemical shift data are reported only for those nitrogen and oxygen atoms involved in proton migration.
‡Absolute errors are given in parentheses.

Analysis of Eq. (2) reveals that in the case of a predominance of the enol tautomer in a mixture ( $\delta_B - \delta_{obs} \approx 0$ ), the error in the tautomer concentration measurement will depend very little on the accuracy of the model for the NH-tautomer. In the case of an equilibrium shifted in the reverse direction ( $\delta_{obs} - \delta_C \approx 0$ ), the error will depend only weakly on the correctness of the OH-tautomer model compound. By inserting values of $\delta_B$ and $\delta_C$ in Eq. (2), we were able to calculate the errors inherent in the measurements of the tautomeric composition of acylmethylazines, as determined by $^{14}$N- and $^{17}$O-NMR spectroscopy (see Table 1). We calculated $\Delta\delta$ values from the chemical shifts of model compounds by taking into account their magnitude and corresponding Student coefficients for a 90% confidence limit [16]: for nitrogen atom signals, $\Delta\delta_B^N = \pm 9$, $\Delta\delta_C^N = \pm 7$ ppm, and for the oxygen atom signals, $\Delta\delta_B^O = \pm 12$, $\Delta\delta_C^O = \pm 22$ ppm. A graph showing the dependence of the error values on the tautomer composition is given in Fig. 3, and indicates that the $^{14}$N-NMR method is more satisfactory in cases where the ylide tautomer predominates (80% and higher), whereas in cases with an NH-tautomer concentration from 0 to 80%, the $^{17}$O-NMR method provides more accurate results.

We should point out that the accuracy of the $^{14}$N- and $^{17}$O-NMR based determination of the enol and ylide tautomer ratio was evaluated based on a wide range of compound types, and was still relatively high. For a narrower class of compounds, such as for instance phenacylpyridines, the accuracy of the intrachelate equilibrium constant measurement approaches the accuracy of PMR measurements made in a stationary (non-exchanging) system (5%), and can be increased even further by more accurate modelling programs.

B⇄C Tautomeric Equilibrium of Acylmethylpyridines. Table 1 summarizes the $^{14}$N- and $^{17}$O-NMR spectral data for the acylmethylpyridines I-VI, and also gives the B/C tautomer ratios which were calculated according to Eq. (1). As can be seen from the Table, there is generally quite good agreement between the $^{14}$N- and $^{17}$O-NMR results, which makes it possible to assign the structures of acylmethylpyridines with a high degree of certainty and also to resolve some of the contradictory literature data [7, 17-23].

Comparison of the $^{14}$N-NMR chemical shift data for acetonylpyridine (I) with that of model compounds reveals that the B⇄C tautomer equilibrium is shifted almost entirely in favor of the enol tautomer. The $^{17}$O-NMR data (see also Table 1), which is more accurate than the $^{14}$N-NMR

method in cases involving a predominance of the enol tautomer, indicates that, in addition to the A and B forms, the ylide tautomer C is also present, although in very small amounts (B/C = 92/8, see [17]). This result is also confirmed by UV spectroscopic analysis; the UV spectrum of acetonylpyridine exhibits a weak long-wavelength absorbance band, $\lambda_{max}$ 380 nm, corresponding to the ylide tautomer (cf. [24]).

In the case of 2-phenacylpyridine (II), the $^{17}$O-NMR data also indicates that the B⇄C equilibrium is shifted almost completely in favor of the OH-tautomer (Table 1). The $^{14}$N-NMR signal due to the enol tautomer is located at −131 ppm, i.e., 20 ppm upfield relative to methoxypyridine. This is consistent with the assumptions which were discussed above concerning modelling of the enol form B.

It was anticipated that introduction of a CN group in the α-position of the side chain to acetonyl- and phenacylpyridine would lead to an increase in the relative stability of the C tautomer [2, 3]. Indeed, the strong downfield shift of the $^{17}$O-NMR signal for compound VI ($\delta_0$ 356 ppm), relative to acetonylpyridine ($\delta_0$ 142 ppm), is consistent with a preponderance of the ylide tautomer C at equilibrium. The $^{14}$N-NMR data are also consistent with this conclusion. Comparison of the $^{14}$N-NMR chemical shift value of cyanoacetonylpyridine ($\delta_N$−199 ppm) with the chemical shift values of model compounds indicates quite clearly that the equilibrium has been shifted strongly in the direction of the NH-tautomer. In summary, therefore, both the $^{14}$N and $^{17}$O-NMR results point to a predominance of the C tautomer in the B⇄C equilibrium of 2-cyanoacetonylpyridine (VI); as a consequence, some of the literature data [21, 23] concerning tautomerism in cyanoacetonylpyridines requires some discussion and refinement.

Based on a study of a series of acylmethylpyridines, Klose and Uhlemann [22] concluded that trifluoroacetonylpyridine III exists entirely in the form of its enol tautomer B. Our $^{14}$N- and $^{17}$O-NMR results, on the other hand, indicate quite clearly that the introduction of acceptor (electron withdrawing) substituents in the β-position of the side chain (as for instance, in the transition from acetonylpyridine to monochloro- trichloro-, and trifluoro-acetonylpyridine) leads to significant destabilization of the keto form A (see Table), and thus increases the concentration of the ylide tautomer; in the case of the trihalo derivatives III and V, the ylide tautomers are the major constituents (present at equilibrium). On the basis of the results obtained for compounds I-VI, it is evident that the position of the B⇄C intrachelate equilibrium is very sensitive to the nature of substituents located in the side chain, and that an increase in the acceptor properties of the substituents favors the NH form C.

We have demonstrated that the application of $^{14}$N- and $^{17}$O-NMR methods in tandem can yield a great deal of information in studies of [1, 5]-sigmatropic tautomerism, and were able to resolve in this manner contradictory literature data concerning the structure of acylmethylpyridines. Further applications of this procedure should be beneficial in establishing the structures of a wider and more important class of heterocyclic derivatives. Analysis of the accuracy of this approach revealed that $^{14}$N- and $^{17}$O-NMR studies of [1, 5]-tautomeric systems which involve changes in the hybridization of the nitrogen and oxygen atoms during the course of tautomer interconversions can generate quantitative measures of the tautomer composition ratios.

## EXPERIMENTAL

Natural isotopic abundance $^{14}$N- and $^{17}$O-NMR spectra were recorded on Bruker CXP-300 (Mechanisms of Catalytic Reactions Research Laboratory, Academy of Sciences of the USSR) and Bruker WH-400 (Bruker Laboratory, Rheinstätten, FRG) spectrometers at operating frequencies of 40.67 and 54.23 (for oxygen) and 21.67 and 28.89 MHz (for nitrogen), respectively. The concentrations of chloroform solutions were 10-20%; the temperature 300°K. The rate of spectral acquisition was 20-50 Hz, the number of spectral acquisitions $10^4$-$10^5$ (for $^{14}$N) and $10^5$-$10^6$ (for $^{17}$O). Chemical shifts are reported relative to external standards, nitromethane ($^{14}$N), and $H_2O$ ($^{17}$O); negative signs correspond to downfield shifts (deshielding).

Compounds I, II [17], VI [23], VII [25], VIII [2], IX [26], X [27], XVII [28], XVIII [13], XXII, and XXIII [29] were all prepared according to literature methods. The synthesis of hydroxyphenylazines XIII and XVI will be described separately.

Acylmethylpyridines III and IV. These were obtained via reaction of picolyllithium with the ethyl esters of trifluoroacetic and chloroacetic acids [30], respectively, and were purified by preparative TLC on silica gel using chloroform–ethyl acetate (2:1). The yellow zones were collected; these gave strong blue color reactions with aqueous ethanolic $FeCl_3$. The

yield of pure trifluoroacetonylpyridine III was 30%, mp 110-113°C (after evaporation and drying in vacuo) [30]. The yield of purified chloroacetonylpyridine IV was 35%. The substance was characterized immediately after purification by TLC (Silufol UV-254, ethyl ether, $R_f$ 0.7) and PMR spectroscopy, although because of its instability during storage (it decomposes within 2-3 days), detailed characterization was not possible. $^{14}$N-NMR spectra of IV were recorded immediately after its purification by TLC. PMR spectrum ($CDCl_3$): 13.31 [0.69 H, br s, OH, NH (B, C)], 8.47-6.80 [4H, m, pyridine ring protons (A, B, C)], 5.52 [0.72 H, s, —CH= (B, C)], 4.19 [0.56 H, s, $CH_2Cl$ (A)], 4.00 [1.44 H, s, $CH_2Cl$ (B, C)], 3.96 [0.56 H, $CH_2$, (A)].

2-Trichloroacetonylpyridine (V). This was prepared analogously to [31]. A solution containing 10 g (0.1 mole) triethylamine and 2.8 g (0.03 mole) 2-methylpyridine in 40 ml benzene was treated stepwise under an argon stream at 0°C with a solution of 18.2 g (0.1 mole) of trichloroacetic anhydride in 10 ml of benzene. The reaction mixture was stirred at room temperature for 3 h, and, after removal of the triethylamine hydrochloride salt precipitate, the benzene solution was evaporated. The residue was extracted with (3 × 20 ml) of boiling petroleum ether. After cooling, the trichloroacetonyl derivative V fell out of solution as yellow crystals. Yield 2.1 g (30%), mp 160-163°C (from petroleum ether). Found, %: C 40.2; H 2.3; N 5.7. $C_8H_6Cl_3NO$. Calculated, %: C 40.3; H 2.5; N 5.9.

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