for 2 h. The mixture was poured into water and extracted by ether; the extract was washed with water and dried over $MgSO_4$; the solvent was distilled off; and the residue was distilled in vacuo. Alcohols (IIIa-f) were obtained (see Table 1).

Pyrethroids (IVa-d), (Va-e) (VIa-d). A solution of 6 mmoles of the chlorides of the corresponding acids in 10 ml of absolute benzene was added gradually at 18-20°C to a solution of 5 mmoles of alcohols (IIIa-e) and 5 mmoles of dry Py in 20 ml of absolute benzene, and the mixture was left to stand for 12 h at 20°C. The mixture was poured into water and extracted by ether. The extract was washed with 3% HCl, water, a saturated $NaHCO_3$ solution, and water again and dried over $MgSO_4$, and the ether was distilled in vacuo. The oil obtained was chromatographed on 200 g of silica gel, eluting the pyrethroids (IVa-e), (Va-e), and (VIa-e) with a heptane–ether mixture (99:1 → 9:1) (see Table 2).

## CONCLUSIONS

1. A general method was developed for synthesizing substituted α-trichloromethylbenzyl alcohols from acylals of aromatic aldehydes.

2. A series of pyrethroids of a new type with an α-trichloromethyl group in the alcoholic fragment of the molecule was synthesized.

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# INTERACTION OF 2,6- AND 2,5-DISUBSTITUTED AROMATIC AMINES WITH SECONDARY α-CHLOROALKENES


I. B. Abdrakhmanov, G. B. Shabaeva, N. G. Nigmatullin, and G. A. Tolstikov



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New aromatic amines with allyl-type substituents in the para position of the benzene ring have been obtained by the reaction of some secondary α-chloroalkenes with 2-methyl-6-ethylaniline and 2,5-xylidine.

Cyclic α-chloroalkenes only give products of ortho substitution with 2,5-xylidine; this is as a result of the Claisen rearrangement of the corresponding N-alkenylamines which are formed at the first stage. The formation of the p isomer of 2,5-xylidine proceeds as a result of the ortho–para migration of the allyl fragments.

The Claisen rearrangement of aromatic N-allylamines is a convenient method for the synthesis of the corresponding o isomers; this also applies in the series of phenylallyl ethers. However, this method is not strictly selective since significant amounts of the p products are also formed together with the o isomers in the majority of the known cases. In connection with this, it was of interest to develop preparative methods for the synthesis of the individual isomers, particularly the C-alkenylamines substituted in position 4 of the benzene ring, by varying the substitution of the aromatic nucleus of the initial amine. Moreover, the identification of the route of the rearrangement, as dependent on the structure of the allyl fragment and the position of the substituents in the benzene nucleus of the amino substrate, will permit the confirmation of the mechanism of the investigated process.

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0568-5230/86/3506-1245 $12.50

TABLE 1. Characteristics of the Compounds Obtained

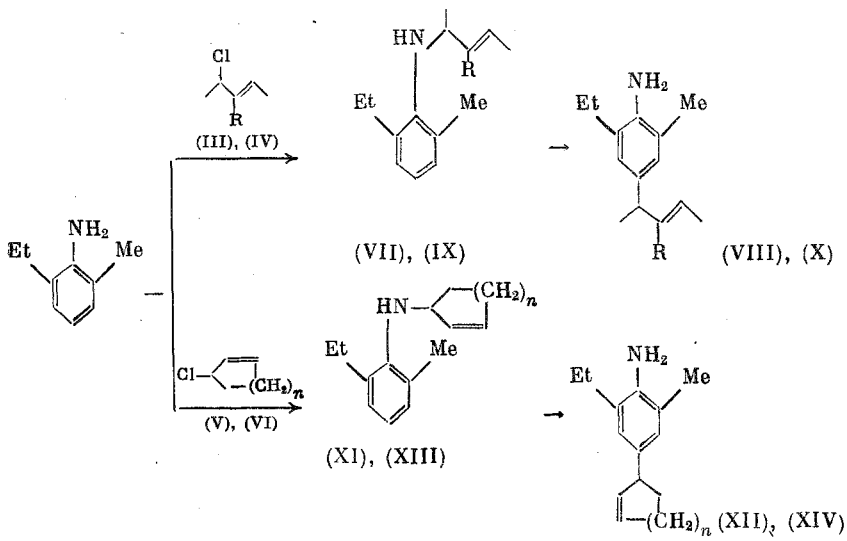
| Compound | bp, °C (p, mm of Hg stem) | Yield,% | $n_D^{20}$ | Found, % | | | Empirical formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | | C | H | N |
| N-(1-Methyl-2-butenyl)-2,6-methylethylaniline (VII) | 118–120(2) | 95 | 1,5238 | 81,97 | 10,01 | 6,52 | $C_{14}H_{21}N$ | 82,07 | 10,30 | 6,89 |
| 4-(1-Methyl-2-butenyl)-2,6-methylethylaniline (VIII) | 140–142(3) | 92 | 1,5425 | 81,93 | 10,30 | 6,68 | | | | |
| N-(2-Chloro-1-methyl-2-butenyl)-2,6-methylethylaniline (IX) | 138–140(2) | 78 | 1,5361 | 71,45 | 8,43 | 5,74 | $C_{14}H_{20}NCl$ | 70,73 | 8,42 | 5,89 |
| 4-(2-Chloro-1-methyl-2-butenyl)-2,6-methylethylaniline (X) | 147–149(2) | 89 | 1,5550 | 70,86 | 8,56 | 5,48 | | | | |
| N-(2-Cyclopentenyl)-2,6-methylethylaniline (XI) | 136–138(5) | 84 | 1,5491 | 83,44 | 9,43 | 6,90 | $C_{14}H_{19}N$ | 83,58 | 9,45 | 6,96 |
| 4-(2-Cyclopentenyl)-2,6-methylethylaniline (XII) | 144–146(2) | 76 | 1,5637 | 83,36 | 9,87 | 6,42 | | | | |
| N-(2-Cyclohexenyl)-2,6-methylethylaniline (XIII) | 132–134(3) | 86 | 1,5820 | 83,60 | 10,05 | 6,15 | $C_{15}H_{22}N$ | 83,33 | 10,18 | 6,48 |
| 4-(2-Cyclohexenyl)-2,6-methylethylaniline (XIV) | 150–152(2) | 80 | 1,5531 | 83,00 | 9,99 | 6,75 | | | | |

Note. For (IX): found Cl 14.38%; calculated 14.94%. For (X): found Cl 14.70%.

TABLE 2. IR and PMR Spectra of the Compounds Obtained

| Compound | IR Spectrum ($\nu$, $cm^{-1}$) | PMR Spectrum ($\delta$, ppm) |
|---|---|---|
| (VII) | 3353, 1510, 978 | 1,01 t (3H, $CH_3$), 1,2 t (3H, $CH_3$), 1,56 d (3H, $CH_3$), 2,1 s (3H, $CH_3$), 2,55 q (2H, $CH_2$), 2,6 s (1H, NH), 3,58 m (1H, CH), 5,41m (2H, CH=CH), 6,8 m (3H, ArH) |
| (VIII) | 3380, 3462, 1510, 980 | 1,13 d (3H, $CH_3$), 1,25 t (3H, $CH_3$), 1,65 d (3H, $CH_3$), 2,03 s (3H, $CH_3$), 2,38 q (2H, $CH_2$), 3,05 q (1H, CH), 3,6 s (2H, $NH_2$), 5,46 m (2H, CH=CH), 6,61 s (2H, ArH) |
| (IX) | 3390, 1620, 920, 745 | 1,01 t (3H, $CH_3$), 1,36 d (3H, $CH_3$), 1,6 d (3H, $CH_3$), 2,08 s (3H, $CH_3$), 2,55 q (2H, $CH_2$), 3,3 s (1H, NH), 3,78 q (1H, CH), 5,36 q (1H, CH=CCl), 6,76 m (3H, ArH) |
| (X) | 3370, 3390, 1625, 910, 880 | 1,3 t (3H, $CH_3$), 1,38 d (3H, $CH_3$), 1,66 d (3H, $CH_3$), 2,05 s (3H, $CH_3$), 2,4 q (2H, $CH_2$), 3,16 s (2H, $NH_2$), 3,53 m (1H, CH), 5,46 q (1H, CH=CCl), 6,6 s (2H, ArH) |
| (XI) | 3380, 1605, 759 | 1,08 t (3H, $CH_3$), 1,75 m (4H, $CH_2$), 2,6 s (3H, $CH_3$), 3,00 s (1H, NH), 3,06 q (2H, $CH_2$), 3,58 m (1H, CH), 5,5m (2H, CH=CH), 6,79 m (3H, ArH) |
| (XII) | 3430, 3380, 1610, 1560, 870, 710 | 1,08 t (3H, $CH_3$), 1,6 m (4H, $CH_2$), 1,81 s (3H, $CH_3$), 2,2 q (2H, $CH_2$), 3,08 s (2H, $NH_2$), 3,5 m (1H, CH), 5,6 m (2H, CH=CH), 6,5 s (2H, ArH) |
| (XIII) | 3350, 1590, 1420, 750 | 1,016 t (3H, $CH_3$), 1,5–2,2 m (6H, $3CH_2$), 2,58 q (2H, $CH_2$), 2,68 s (3H, $CH_3$), 2,85s (1H, NH), 3,9 m (1H, CH), 5,68s (2H, CH=CH), 6,81 m (3H, ArH) |
| (XIV) | 3380, 3470, 1590 | 1,15 t (3H, $CH_3$), 1,41–2,00 m (6H, $3CH_2$), 2,18 s (3H, $CH_3$), 2,53 q (2H, $CH_2$), 2,9 s (2H, $NH_2$), 3,51 m (1H, CH), 5,63 m (2H, CH=CH), 6,8 s (2H, ArH) |

With this object, we studied the rearrangement in the interaction of 2-methyl-6-ethylaniline (I) and 2,5-xylidine (II) with some readily available α-chloroalkenes. Thus, good yields of the 4-alkenyl derivatives of amine (I) were obtained on heating amine (I) with 4-chloro-2-pentene (III), 3,4-dichloro-2-pentene (IV), 3-chlorocyclopentene (V), and 3-chlorocyclohexene (VI) (1:5 molar ratio of the chloroalkene to the amine; 1-4 h; 170°C) (Table 1).




R = H(III), (VII), (VIII); Cl(IV), (IX), (X); $n$ = 1 (V), (XI), (XII); 2(VI), (XIII), (XIV).

The structure of the products was confirmed by spectral methods. Characteristic bands of the primary $NH_2$ group (3380-3470 $cm^{-1}$) as well as the trans [980 $cm^{-1}$ for amines (VIII) and (X)] and cis [720 $cm^{-1}$ for amines (XII) and (XIV)] double bonds are present in the IR spectra of amines (VIII), (X), (XII), and (XIV).

The PMR spectra of these amines are characterized by a two-proton singlet of the aromatic protons at 6.5 ppm, which clearly indicates the substitution at position 4 of the

TABLE 3. Characteristics of the Compounds Obtained

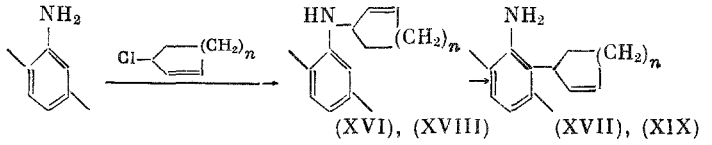
| Compound | bp, °C (p, mm of Hg stem) | Yield,% | $n_D^{20}$ | Found, % | | | Empirical formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | | C | H | N |
| N-(2-Chloro-1-methyl-2-butenyl)-2,5-dimethylaniline (XX) | 144–145 (10) | 69 | 1,5465 | 70,33 | 8,01 | 6,24 | $C_{13}H_{18}NCl$ | 69,80 | 8,05 | 6,27 |
| 4-(2-Chloro-1-methyl-2-butenyl)-2,5-dimethylaniline (XXII) | 155–157 (4) | 65 | 1,5730 | 70,54 | 8,00 | 6,24 | | | | |
| N-(2-Cyclopentenyl)-2,5-dimethylaniline (XVI) | 122–124 (2) | 77 | 1,5621 | 82,90 | 9,08 | 7,16 | $C_{13}H_{17}N$ | 83,42 | 9,09 | 7,48 |
| 6-(2-Cyclohexenyl)-2,5-dimethylaniline (XVII) | 142–145 (3) | 79 | 1,5740 | 83,74 | 9,57 | 6,32 | | | | |
| N-(2-Cyclohexenyl)-2,5-dimethylaniline (XVIII) | 138–140 (2) | 76 | 1,5600 | 83,32 | 9,66 | 6,74 | $C_{14}H_{19}N$ | 83,58 | 9,45 | 6,98 |
| 6-(2-Cyclohexenyl)-2,5-dimethylaniline (XIX) | 160–162 (3) | 81 | 1,5731 | 83,12 | 9,44 | 6,88 | | | | |

TABLE 4. IR and PMR Spectra of the Compounds Obtained

| Compound | IR Spectrum ($\nu$, $cm^{-1}$) | PMR Spectum ($\delta$, ppm) |
|---|---|---|
| (XX) | 3390, 1600, 1515, 998, 928, 750 | 1,138 d (3H, $CH_3$), 1,66 d (3H, $CH_3$), 2,03 s (3H, $CH_3$), 2,6 s (3H, $CH_3$), 3,63 s (1H, NH), 4,01 q (1H, CH), 5,65 q (1H, CH), 6,01 s (1H, ArH), 6,3 d (1H, ArH), 6,75 d (1H, ArH) |
| (XXI) | 3470, 3390, 1625, 920, 800 | 1,45 d (3H, $CH_3$), 1,78 d (1H, $CH_3$), 2,03 s (3H, $CH_3$), 2,25 s (3H, $CH_3$), 3,50 s (2H, $NH_2$), 4,00 q (1H, CH), 5,73 q (1H, CH=CCl), 6,35 d (1H, ArH), 6,71 d (1H, ArH) |
| (XXII) | 3460, 3380, 1630, 1510, 1300, 990, 920 | 1,25 d (3H, $CH_3$), 1,58 d (3H, $CH_3$), 1,58 d (3H, $CH_3$), 1,96 s (3H, $CH_3$), 2,0 s (3H, $CH_3$), 3,58 q (1H, CH), 5,28 q (1H, CH=CCl), 6,25 s (1H, ArH), 6,75 s (1H, ArH) |
| (XVI) | 3425, 1610, 1520, 1300, 800, 740 | 1,94 s (3H, $CH_3$), 2,22 s (3H, $CH_3$), 2,32 m (4H, $CH_2$), 2,32 m (4H, $CH_2$), 3,18 s (1H, NH), 5,80 m (4H, CH=CH), 6,30 d (2H, ArH), 6,74 d (1H, ArH) |
| (XVII) | 3480, 3390, 1620, 800, 735 | 1,98 s (3H, $CH_3$), 2,23 s (3H, $CH_3$), 2,6 m (4H, $CH_2$), 3,66 s (2H, $NH_2$), 4,2 m (1H, CH), 5,86 m (2H, CH=CH), 6,3 d (1H, ArH), 6,65 d (1H, ArH) |
| (XVIII) | 3350, 1610, 1580, 1520, 800, 720 | 1,62 m (6H, $CH_2$), 1,98 s (3H, $CH_3$), 2,22 s (3H, $CH_3$), 3,23 s (1H, NH), 3,32 m (1H, CH), 5,20 s (2H, CH=CH), 6,26 d (2H, ArH), 6,28 d (1H, ArH) |
| (XIX) | 3470, 3380, 1620, 1470, 900, 735 | 1,73 m (6H, $CH_2$), 1,98 s (3H, $CH_3$), 2,16 s (3H, $CH_3$), 3,58 s (2H, $NH_2$), 3,92 m (1H, CH), 5,20 s (2H, CH=CH), 6,26 d (1H, ArH), 6,28 d (1H, ArH) |

benzene ring. The olefinic protons give multiplets in the region of 5.41-5.63 ppm (Table 2).

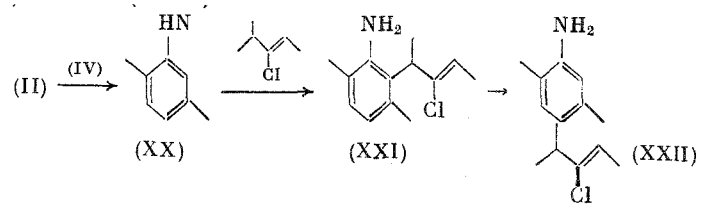
Amine (II) reacts with these α-chloroalkenes with the selective formation of o and p isomers depending on the structure of the allyl fragment. Thus, good yields of the products of the ortho migration of the allyl fragments were obtained by the reaction of (II) with α-chloroalkenes (V) and (VI) according to [1] (Table 3).




(XVI), (XVIII) (XVII), (XIX)

$n = 1$ (XVI), (XVII); 2 (XVIII), (XIX).

α-Chloroalkene (IV) forms the product of the para rearrangement – 2,5-dimethyl-4-(2-chloro-1-methyl-2-butenyl)aniline (XXII) – with a good yield under these conditions with amine (II).




The structure of (XVII), (XIX), and (XXII) was confirmed by spectral methods. The bands of the primary $NH_2$ group and the double bonds of the alkenyl substituents are also present in the IR spectra (cf. Table 3).

The position of the alkenyl substituent in the aromatic nucleus was confirmed from the PMR spectra of (XVII), (XIX), and (XXII). The aromatic protons of the benzene ring of 2,5-xylidine appear in the form of two groups of signals – a one-proton singlet at 6.01 ppm and two doublets in the region of 6.3-6.75 ppm. The absence of the one-proton singlet at 6.01 ppm and the presence of the indicated doublets serve as a reliable confirmation of the ortho position of the alkenyl substituent in (XVII) and (XIX). Two one-proton singlets indicate the para position of the alkenyl substituent in (XXII) (Table 4).

We have proposed [2] that the formation of the aromatic o- and p-C-alkenylamines by the scheme worked out is the result of the Claisen rearrangement of the aromatic N-alkenylamines

which are formed in the first stage. For the confirmation of this, we synthesized the corresponding N-alkenyl precursors from amines (I) and (II) and α-chloroalkenes (III)-(VI) according to [3]. The IR spectra of these compounds contain bands of the secondary NH group (3400 $cm^{-1}$); in other respects they are similar to the IR spectra of the rearrangement products. The ratio of the intensities of the signals of the protons of the benzene ring and the $NH_2$ group changes in the PMR spectra of these amines.

There are three aromatic protons in the N-alkenyl derivatives of (I). They appear in the form of multiplets at 6.8 ppm in (VII), (IX), (XI), and (XIII) as was anticipated; whereas the corresponding derivatives of (II) – (XVI), (XVIII), and (XX) – give the same splitting for the cleavage of the aromatic protons as the unsubstituted (II).

On comparison of the properties of the N-alkenyl derivatives obtained with the products initially formed by the reaction of (I) and (II) with α-chloroalkenes, their complete identity was established.

Moreover, the isolated N-substituted amines (VII), (IX), (XI), (XIII), (XVI), (XVIII), and (XX) were readily converted to the rearrangement products. It was established that the product of the para rearrangement (XXII) is formed as a result of the subsequent ortho–para migration of the alkenyl substituent. As a confirmation of this, the intermediate o isomer, identified as 6-(2-chloro-1-methyl-2-butenyl)-2,5-xylidine (XXI), was isolated by chromatography on a column with $Al_2O_3$ from the reaction mixture resulting from the brief heating of (II) with α-chloroalkene (IV). The same groups of nonequivalent protons are preserved in the PMR spectrum of the given isomer, but the character of the splitting of the aromatic protons changes. The one-proton singlet at 6.01 ppm disappears, and the two adjoining aromatic protons give the expected doublets at 6.35 and 6.71 ppm. The principal possibility for the conversion of the o isomer (XXI) to the product of the para rearrangement (XXII) was previously shown by us. Therefore, the simple and practicable synthesis of the alkenylated derivatives of amines (I) and (II), which are promising in a practical connection, was developed. This consisted of the Claisen rearrangement of the corresponding N-alkenylamines which are obtained by the direct interaction of the utilized amines with some secondary α-chloroalkenes. The formation of these derivatives shows the coincidence of the course of the Claisen rearrangement, observed in these systems, with the classical variant which was studied in a series of allylphenyl ethers. However, the absence of the products of the para-Claisen rearrangement in the reaction of amine (II) with the cyclic α-chloroalkenes (V) and (VI) indicates the necessity for a more detailed study of the mechanism of the given process.

## EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer. The PMR spectra were obtained on a Tesla BS-487B instrument. The GLC analysis was performed on a Khrom-5 chromatograph, utilizing a column 3.7 by 3 mm of SE-30 on Chromaton DMCS in a current of helium. The compounds 3-chlorocyclopentene and 3-chlorocyclohexene were obtained by known methods directly before use.

General Method for the Isolation of Compounds (VIII), (X), (XII), (XIV), (XVII), (XIX), and (XXII). To 0.5 mole of 2-methyl-6-ethylamine (I) were added 0.1 mole of the α-chloroalkene (III)-(VI), and the mixture was held for 1-3 h at 170°C [for 5 h at 200°C in the case of (XXII)]. The mixture was cooled, and the solidified mass was treated with a 20% solution of alkali. The organic layer was separated and dried over KOH. The products (VIII), (X), (XII), (XIV), (XVII), (XIX), and (XXII) were isolated by vacuum distillation.

The compound 6-(2-chloro-1-methyl-2-butenyl)-2,5-dimethylaniline (XXI) was isolated by column chromatography on $Al_2O_3$ (act. II). The eluent was a 3:4 mixture of chloroform and petroleum ether. The yield was 56%. It had $R_f$ 0.57 and $n_D^{20}$ 1.5500. Found: C 70.21; H 8.04; N 5.98%. $C_{13}H_{18}NCl$. Calculated: C 69.80; H 8.05; N 6.27%.

## CONCLUSIONS

1. New aromatic amines with allyl-type substituents in the para position of the benzene ring were obtained as a result of the Claisen rearrangement in the reaction of secondary α-chloroalkenes with 2-methyl-6-ethylaniline and 2,5-xylidine.

2. It was established that only the products of the ortho substitution are given from the cyclic α-chloroalkenes and 2,5-xylidine, whereby their formation was caused by the rearrangement of the corresponding N-alkenylamines which were obtained in the first stage.

3. The para isomer of the 2,5-xylidine – 2,5-dimethyl-4-(2-chloro-1-methyl-2-butenyl)aniline – is formed in sequence as a result of the ortho–para migration of the allyl substituent.

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# SYNTHESIS AND CRYSTAL STRUCTURE OF 3-(1,5-DIMETHYL-4-(1H)-PYRIDON-3-YL)-2-CYANOTHIOBUTYRAMIDE


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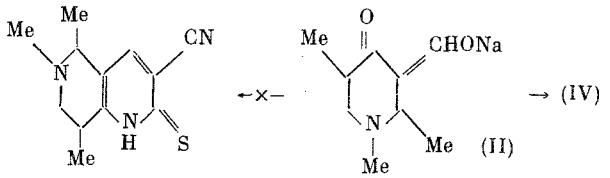
UDC 542.91:548.312.5:547.398.4

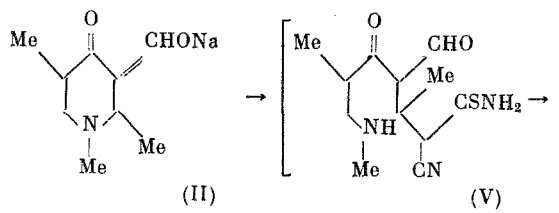

In a search for new biologically active compounds, we have examined methods of preparing condensed pyridinethiones from 1,2,5-trimethyl-4-piperidone (I). One method of synthesis of 3-cyano-2(1H)-pyridinethiones is by reaction of β-dicarbonyl compounds with cyanothioacetamide (CTAA) [1]. However, reaction of the salt (II), obtained by formylating (I), with CTAA in the presence of acetic acid gave, instead of the expected naphthyridone (III), a compound (IV) whose structure was difficult to establish reliably from its UV, IR, and PMR spectra.




In order to establish the structure of (IV), it was submitted to x-ray structural examination.

## DISCUSSION OF RESULTS

As will be seen from Fig. 1, which shows the geometry of the molecule of (IV), and from the bond lengths and valence angles given in Tables 1 and 2, compound (IV) is 3-(1,5-dimethyl-4(1H)-pyridon-3-yl)-2-cyanothiobutyramide. The formation of (IV) may be described as follows. It appears that in the first stage of the reaction the CTAA anion attacks the 2 position of the heterocycle in salt (II), resulting in cleavage of the $N^1-C^2$ bond and the formation of the intermediate (V). Subsequent inversion (V) → (VI), intramolecular condensation, and dehydrogenation gives the 4(1H)-pyridone (IV)





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