INDOLE DERIVATIVES.

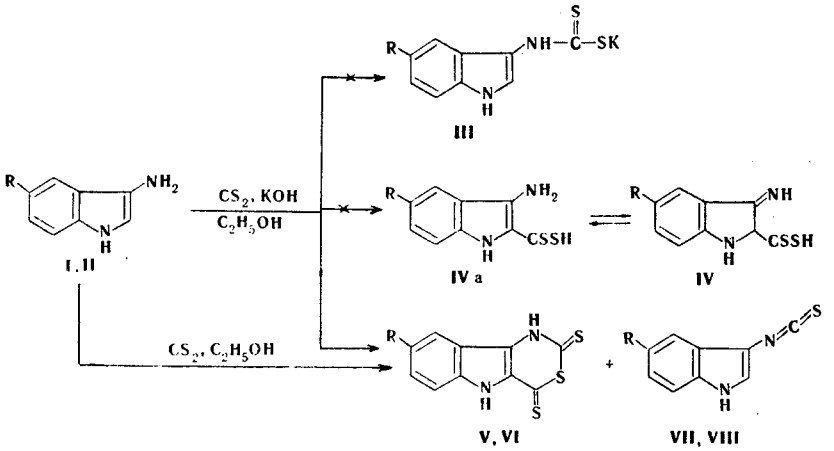
CXVII.* REACTION OF 3-AMINOINDOLES WITH CARBON DISULFIDE. CONVENIENT ONE-STEP SYNTHESIS OF 3-INDOLYL ISOTHIOCYANATES AND INDOLO[2,3-d]-1,3-THIAZINES

V. S. Velezheva, A. V. Yarosh, T. A. Kozik, and N. N. Suvorov

UDC 547.754'869.1.07

A new one-step method was developed for the preparation of 3-indolyl isothiocyanates by reaction of 3-aminoindoles with carbon disulfide in the presence of sodium ethoxide. It is shown that indolo[2,3-d]-1,3-thiazines are obtained from 3-aminoindoles and carbon disulfide when extraneous bases are absent. The structures of the compounds are confirmed by data from their IR, UV, PMR, and mass spectra.

The reactions of 3-aminoindole (I), to the properties of which little study has yet been devoted, with carbon disulfide were investigated. One might have expected that 3-aminoindole (I) would form, under conditions typical for the preparation of dithiocarbamic acid salts (from the amine, carbon disulfide, KOH, and alcohol) [2], either salt III or, like enamines [3] and 1-acetylindoxyl [4, 5], 3-imino-2-dithiocarboxylic acid IV and 3-amino-2-dithiocarboxylic acid IVa, respectively, as well as products of subsequent transformations. The analogy with 1-acetylindoxyl follows from the fact, which we observed in [1], that 3-aminoindole in a number of cases behaves like indoxyl derivatives.



I, V, VII R = H; II, VI, VIII R = Br

In fact, indolothiazine V (32%) and isothiocyanate VII (3%) were obtained instead of III, IV, and IVa under the indicated conditions.

Thiazine V was also obtained from amine I and carbon disulfide (a no less than twofold excess as compared with the amine) in alcohol in the absence of extraneous bases. In this case thiazine V is obtained in highest yield (62%) and is the most pure product.

It seemed of interest to ascertain the pathways of formation of thiazine V and isothiocyanate VII.

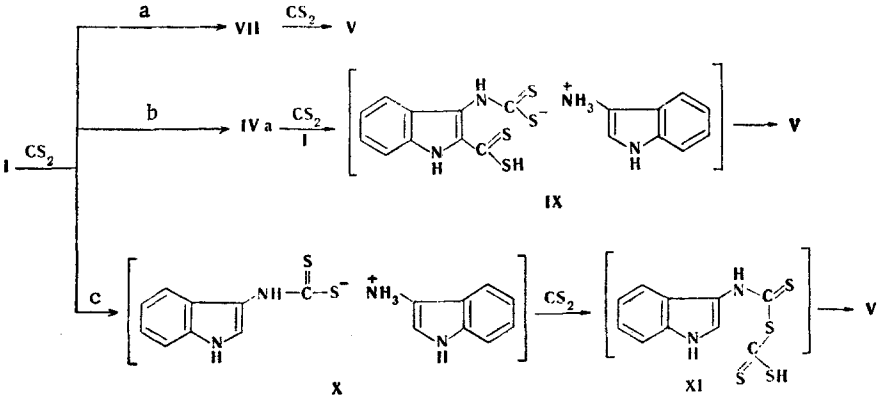
*See [1] for communication CXVI.

D. I. Mendeleev Moscow Institute of Chemical Technology, Moscow 125047. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1497-1503, November, 1978. Original article submitted December 21, 1977.

0009-3122/78/1411-1217$07.50

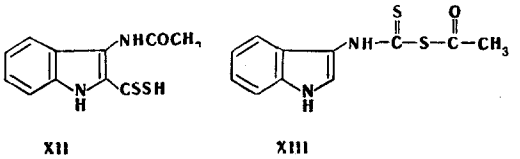
With allowance for the information available in the literature [2-5], one could conceive of three schemes for the formation of triazine V (in the absence of extraneous bases):

a) Amine I is converted to isothiocyanate VII and then to thiazine V under the influence of 1 mole of carbon disulfide; b) amine I is converted to 2-dithiocarboxylic acid IVa and then to salt IX and thiazine V under the influence of another mole of carbon disulfide and 3-aminoindole; c) amine I is converted to dithiocarbamate X, which reacts with another mole of carbon disulfide to give thioanhydride XI and then thiazine V.



Scheme a was excluded from consideration after we established that isothiocyanate VII does not react with carbon disulfide.

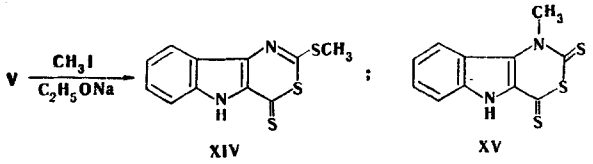
To choose between schemes b and c we decided to isolate the precursor of thiazine V in the form of the relatively stable acetyl derivative at a point at which the reaction of 3-aminoindole with carbon disulfide was not yet complete. To accomplish this we added acetic anhydride to the reaction mixture after 5 min; in the case where scheme b is valid one might have expected the formation of acetyl derivatives XII, whereas in the case of scheme c one might have expected the formation of anhydride XIII.



Instead of XII and XIII we isolated only isothiocyanate VII (6%) in addition to 3-acetamidoindole (61%). However, its production constituted evidence in favor of the formation of thioanhydride XIII as an intermediate and, in turn, in favor of the formation of thiazine V via scheme c. This explanation is confirmed by the literature data on the conversion of difficult-to-obtain acyldithiocarbamates, obtained by the action of acyl halides on dithiocarbamic acid salts by heating to 100°C, to amides and to isothiocyanates under the influence of KOH [6, 7]. In the present case the latter process is evidently a spontaneous one.

The formation of the 3-aminoindole salt (X) of 3-dithiocarbamic acid from amine I and carbon disulfide (in the absence of extraneous bases, in which case aromatic amines do not react at all with carbon disulfide) can be explained by the higher basicity of 3-aminoindole as compared with aromatic amines [8-10].

The reaction for the preparation of indolothiazines is evidently typical for 3-aminoindoles. Thus, 8-bromothiazine (VI) was obtained in 63% yield from 5-bromo-3-aminoindole (II).



Like tetrahydrobenzothiazines [11], indolothiazine V reacts with sodium ethoxide to give stable sodium salt Va, which reacts with methyl iodide to give S-methylation product XIV.

The isomeric (with respect to thio ether XIV) N-methylthiazine structure XV is excluded on the basis of the fact that the mass spectrum of XIV contains the peak of an [M — SCH_3] fragment ion.

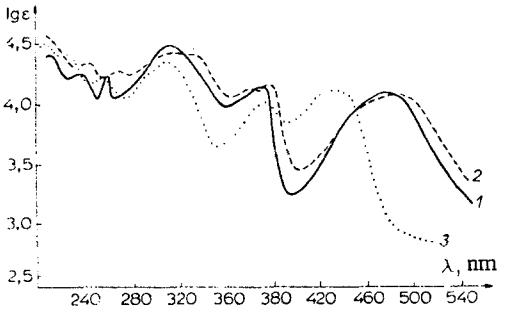


Fig. 1. UV spectra in alcohol: 1) 5H-2-mercapto-4-thioxoindolo[2,3-d]-1,3-thiazine (V); 2) 5H-2-mercapto-8-bromo-4-thioxoindolo[2,3-d]-1,3-thiazine (VI); 3) 5H-2-methylthio-4-thioxoindolo[2,3-d]-1,3-thiazine (XIV).

The same hypsochromic shift of the absorption bands that was previously observed in the UV spectra of tetrahydro- and dihydro-2-thiothazines, which exist in the thione form, as compared with their 2-thiol derivatives [12] is characteristic for the UV spectra of thiazine V and its S-methyl derivative (XIV). These data constitute evidence in favor of the thione structure of thiazine V (Fig. 1).

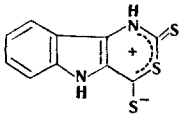
The UV spectrum of 8-bromothiazine VI has the form characteristic for the spectrum of thiazine V (Fig. 1).

2-Mercaptothiazine and its thio ether have high and almost identical stabilities with respect to electron impact (W_M = 20.2 and 19.5, respectively) and also have fragmentation pathways of similar character. The formation of [M − CSH] and [M − CS_2] fragment ions in the fragmentation of the molecular ion of thiazine V is probably due to prior opening of the thiazine ring at the $C_{(2)}$—$S_{(3)}$ bond. The presence in the mass spectrum of the thiazine of a weak-intensity [M − CS] peak at 206 can be explained by the existence of the thione form of the thiazine and opening of the ring at the $S_{(3)}$—$C_{(4)}$ bond.

The PMR spectra of solutions of thiazines V and VI in d_6-DMSO contain signals of four and three, respectively, aromatic protons and NH protons.

The IR spectra of thiazines V and VI contain absorption bands of NH and C=S groups but, unlike the spectra of tetrahydrobenzothiazines, which have a mesoionic structure [11], do not contain the absorption at 2550-2600 cm^{-1} that is characteristic for the stretching vibrations of the SH group.

To solve the problem of the possibility of the existence of thiazine V in mesoionic form XVI we made an attempt to use data from the x-ray electron spectra.



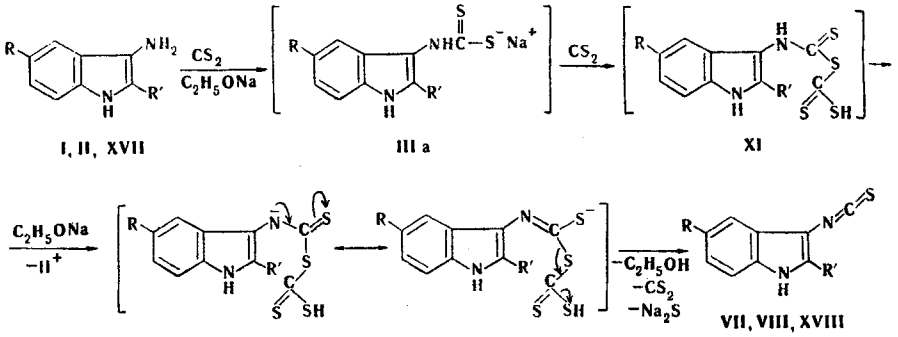
XVI

However, we found that we could not arrive at a choice between structures V and XVI by this method, since the investigated compound decomposes under the influence of x-ray beams.

In our explanation of the pathway of formation of isothiocyanate VII from amine I and carbon disulfide in alcohol in the presence of KOH we proceeded from the following data. In view of the fact that isothiocyanate VII is obtained along with thiazine V under these conditions, it may be assumed that their common precursor in this case is thioanhydride XI. To this one must add that N-substituted carbethoxydithiocarbamates (which are converted via the Kaluza reaction [13] to isothiocyanates by heating to 100°C or by the action of bases) can also be regarded as the corresponding thioanhydrides.

If the proposed scheme for the formation of isothiocyanate VII is valid, the use of strong bases in amounts that are twice the amount of the amine should increase its yield.

The role of the base reduces 1) to the formation of 3-indolyldithiocarbamate salt III; and 2) to detachment of a proton from intermediate thioanhydride XI.

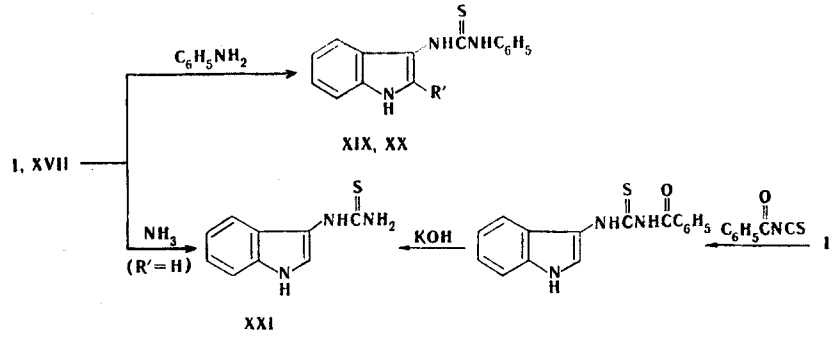


I, VII R=R'=H; II, VIII R=Br, R'=H; XVII, XVIII R=H, R'=CH_3

After we established that isothiocyanate VII remains unchanged in an alcohol solution of sodium ethoxide at room temperature for a long time without appreciable signs of decomposition, we used sodium ethoxide (two equivalents) in alcohol as the base for the conversion of amine I to isothiocyanate VII. The yield of isothiocyanate VII increased to 60% in this case.

Two equivalents of ethylmagnesium bromide [1] or diethylamine and hydrogen peroxide [15] have been previously used in one-step methods for the conversion of amines to isothiocyanates under the influence of carbon disulfide.

Our one-step method for the preparation of isothiocyanate VII was also found to be suitable for the preparation of isothiocyanates containing substituents in the benzene and pyrrole rings. Isothiocyanates VIII and XVIII were obtained in 64 and 40% yields under the same conditions from 5-bromo- and 2-methyl-3-aminoindoles II and XVII.



I, XIX, XXI R=H; XVII, XX R=CH_3

Thus we have developed a new one-step method for the preparation of 3-indolyl isothiocyanates from 3-aminoindoles and carbon disulfide.

The structure of isothiocyanate VII was confirmed by the results of elementary analysis and data from its IR, PMR, and mass spectra, as well as by conversion to thioureas XIX and XXI. Thiourea XXI was also obtained by alternative synthesis from 3-aminoindole (I) and benzoyl isothiocyanate.

The structures of isothiocyanates II and XVII are confirmed by data from the IR and mass spectra and by conversion to thiourea XX.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in d_6-DMSO were obtained with a JNM-4H-100 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 50 eV and a cathode emission current of 1.25 mA. The identities of the compounds obtained in the various experiments were proved by thin-layer chroma-

tography (TLC) on Silufol UV-254, the IR spectra, and the absence of melting-point depressions for mixtures with authentic samples.

Reaction of 3-Aminoindole with Carbon Disulfide in the Presence of Potassium Hydroxide. A solution of 0.68 g (10 mmole) of KOH in 1 ml of water and 0.64 ml (11 mmole) of carbon disulfide were added successively to a solution of 0.66 g (5 mmole) of 3-aminoindole I in 15 ml of alcohol, and the mixture was stirred for 2 h. The alcohol was then removed by evaporation, and the residue was dissolved in 30 ml of 5% aqueous KOH solution. The alkaline solution was extracted with chloroform, and the aqueous layer was neutralized with acetic acid. The resulting precipitate was removed by filtration, washed with water, and dried in vacuo to give 0.4 g (32%) of thiazine V. The chloroform solution was dried with $MgSO_4$ and applied to a column filled with neutral aluminum oxide (elution with chloroform). The solvent was removed from the eluate by evaporation to give 0.03 g (3%) of isothiocyanate VII.

5H-2-Mercapto-4-thioxoindolo[2,3-d]-1,3-thiazine (V). A 1.2-ml (20 mmole) sample of carbon disulfide was added to a solution of 1.32 g (10 mmole) of amine I in 10 ml of absolute alcohol, and the mixture was stirred at room temperature for 2 h. The resulting precipitate was removed by filtration and washed with alcohol to give 1.54 g (62%) of a product with mp 295-296°C (dec., by reprecipitation from acetone solution by pouring into heptane). Mass spectrum, m/e: 250 (100), 249 (2), 217 (74), 206 (2), 205 (36), 173 (14), 173 (14), 130 (3), 129 (19), 102 (15). IR spectrum (cm^{-1}): 3330 s, 3270 shoulder (NH), and 1010 s (C=S). PMR spectrum: 12.14 (1H, s, NH) and 7.08-8.40 ppm (4H, m, indole ring CH). Found: C 48.4; H 2.5; N 11.2; S 37.9%. $C_{10}H_6N_2S_3$. Calculated: C 48.4; H 2.4; N 11.2; S 38.4%.

5H-2-Mercapto-4-thioxo-8-bromoindolo[2,3-d]-1,3-thiazine (VI). Thiazine VI [2.07 g (64%)], with mp 315-316°C (dec., from alcohol), was similarly obtained from 2.11 g (10 mmole) of 5-bromo-3-aminoindole and 1.2 ml (20 mmole) of carbon disulfide. IR spectrum (cm^{-1}): 3330 s, 3310 s (NH) and 1010 s (C=S). PMR spectrum: 12.16 (1H, s, NH) and 7.34-8.52 ppm (3H, m, indole ring CH). Found: Br 23.8; N 8.1%. $C_{10}H_5BrN_2S_3$. Calculated: Br 24.3; N 8.5%.

Reaction of 3-Aminoindole with Carbon Disulfide in the Presence of Acetic Anhydride. A 0.64-ml (11 mmole) sample of carbon disulfide was added to a solution of 0.66 g (5 mmole) of 3-aminoindole (I) in 20 ml of absolute alcohol, 5 min after which 0.5 ml (5 mmole) of acetic anhydride was added, and the mixture was stirred for 1 h. The solvent was then removed by evaporation, and the residue was dissolved in 40 ml of chloroform. The chloroform solution was washed with water, dried with $MgSO_4$, and evaporated to a volume of 5 ml. The precipitate that formed on standing was removed by filtration and washed with 5 ml of chloroform to give 0.53 g (61%) of 3-acetamidoindole with mp 160-162°C (from water). The mother liquor was applied to a column (2 by 50) filled with neutral aluminum oxide and eluted with chloroform. The solvent was evaporated from the eluate to give 0.05 g (6%) of isothiocyanate VII.

5H-2-Mercapto-4-thioxoindolo[2,3-d]-1,3-thiazine Sodium Salt (Va). A 2.5-g (10 mmole) sample of thiazine V was added to a solution of sodium ethoxide, prepared from 0.28 g (10 mmole) of sodium in 50 ml of absolute alcohol, and the mixture was stirred for 10 min. The alcohol was removed by evaporation to a volume of 5 ml, the concentrate was filtered, and the filtrate was poured with stirring into 100 ml of absolute ether. The resulting precipitate was removed by filtration to give 2.5 g (92%) of a product with mp 348-349°C (dec.). PMR spectrum: 11.20 (1H, s, NH) and 7.00-7.98 ppm (4H, m, indole ring CH).

5H-2-Methylthio-4-thioxoindolo[2,3-d]thiazine (XIV). A 1.0-ml (16 mmole) sample of methyl iodide was added to a solution of salt Va, prepared from 0.23 g (10 mmole) of sodium and 2.5 g (10 mmole) of thiazine V in 30 ml of alcohol, and the mixture was heated for 30 min. The alcohol was removed by evaporation, and the residue was dissolved in 5 ml of acetone and applied to a column (2 by 50) filled with neutral aluminum oxide and eluted with chloroform. The solvent was removed from the eluate by evaporation to give 1.53 g (58%) of a product with mp 219-220°C (from alcohol). Mass spectrum, m/e: 264 (100), 263 (3), 249 (5), 220 (16), 218 (26), 217 (95), 205 (12), 173 (16), 141 (3), 129 (14), 102 (11). IR spectrum (cm^{-1}): 3345 m, 3290 s (NH), and 1010 s (C=S). PMR spectrum: 12.26 (1H, s, NH), 7.20-8.08 (4H, m, indole ring CH), and 2.84 ppm (3H, s, CH_3). Found: C 50.2; H 3.1; N 10.6; S 35.6%. $C_{11}H_8N_2S_3$. Calculated: C 50.0; H 3.6; N 10.6; S 36.4%.

3-Indolyl Isothiocyanate (VII). A) A 1.28-ml (22 mmole) sample of carbon disulfide and a solution of 1.32 g (10 mmole) of 3-aminoindole (I) in 30 ml of absolute alcohol were added to a solution of sodium ethoxide, prepared from 0.46 g (20 mmole) of sodium in 15 ml of absolute alcohol, and the mixture was stirred at room temperature for 1 h. The solvent was

removed by evaporation in vacuo at no higher than 40°C, and the residue was dissolved in chloroform. The chloroform solution was washed with water, dried with $MgSO_4$, and applied to a column (2 by 50) filled with neutral aluminum oxide (elution with chloroform). The solvent was removed from the eluate by evaporation to give 1.04 g (60%) of a product with mp 80-81°C (from petroleum ether). IR spectrum (cm^{-1}): 3400 s (indole NH) and 2160 s (N=C=S). Found: C 62.1; H 3.6; N 16.5; S 18.2%; M 174 (by mass spectrometry). $C_9H_6N_2S$. Calculated: C 62.0; H 3.5; N 16.1; S 18.4%; M 174.

B) The reaction was carried out as in method A, after which the alcohol was removed by evaporation to dryness, and the residue was extracted with boiling petroleum ether (15 3-ml portions). The hot solution was filtered through activated charcoal, and the filtrate was evaporated to a volume of 10 ml and cooled. The resulting precipitate was removed by filtration to give 0.43 (25%) of product.

5-Bromo-3-indolyl Isothiocyanate (VIII). This compound was obtained in analogy with the synthesis of isothiocyanate VII (by method A) from 1.05 g (5 mmole) of 5-bromo-3-aminoindole, 1.28 ml (11 mmole) of carbon disulfide, and 0.23 g (10 mmole) of sodium. The yield was 0.81 g (64%). Found: Br 31.6; N 10.7%; M^+ 253 (by mass spectrometry). $C_9H_5BrN_2S$. Calculated: Br 31.6; N 11.1%; M 253.

2-Methyl-3-indolyl Isothiocyanate (XVIII) and N-Phenyl-N'-(2-methyl-3-indolyl)thiourea (XX). A 0.64-ml (11 mmole) sample of carbon disulfide and a solution of 0.72 g (5 mmole) of 2-methyl-3-aminoindole in 10 ml of absolute alcohol were added to a solution of sodium ethoxide, prepared from 0.23 g (10 mmole) of sodium in 15 ml of absolute alcohol, and the mixture was stirred for 2 h. The alcohol solution was filtered through activated charcoal, and the solvent was removed from the filtrate by evaporation. The residue was extracted with boiling petroleum ether (10 3-ml portions), and the hot solution was filtered and evaporated to give 0.38 g (40%) of isothiocyanate XVIII in the form of an oil. IR spectrum in chloroform (cm^{-1}): 3500 s (indole NH) and 2160 s (N=C=S).

Isothiocyanate XVIII was dissolved in 2 ml of benzene, 0.23 ml (2.5 mmole) of aniline was added, and the mixture was heated for 30 min. The solvent was removed by evaporation, and the residue was crystallized by the addition of ether. Workup gave 0.46 g (79%) of thiourea XX with mp 246-247°C (from alcohol). IR spectrum (cm^{-1}): 3410 s (indole NH), 3350 m and 3160 s (NH and NH_2), and 1270 s (C=S). Found: N 14.5; S 10.7%. $C_{16}H_{15}N_3S$. Calculated: N 14.9; S 11.4%.

N-Phenyl-N'-(3-indolyl)thiourea (XIX). A 0.1-ml (1 mmole) sample of aniline was added to a solution of 0.19 g (1 mmole) of isothiocyanate VII in 2 ml of benzene, and the mixture was heated for 30 min. The benzene was then removed by evaporation, and the residue was crystallized by the addition of ether. The precipitate was removed by filtration and washed with ether to give 0.2 g (75%) of a product with mp 198-199°C (from alcohol). IR spectrum (cm^{-1}): 3410 s (indole NH), 3330 and 3190 s (NH and NH_2), and 1270 s (C=S). Found: N 15.5; S 11.3%. $C_{15}H_{13}H_3S$. Calculated: N 15.7; S 12.0%.

3-Indolylthiourea (XXI). A) Ammonia was passed into a heated solution of 0.17 g (1 mmole) of isothiocyanate VII in 5 ml of benzene in the course of 30 min, after which the mixture was cooled, and the precipitate was removed by filtration and washed with benzene to give 0.17 g (91%) of a product with mp 209-210°C (from alcohol). IR spectrum (cm^{-1}): 3360 (indole NH), 3280 s and 3180 s (NH and NH_2), and 1240 s (C=S). Found: N 22.3; S 16.6%. $C_9H_9N_3S$. Calculated: N 22.0; S 16.8%.

B) A 1.17-g (10 mmole) sample of benzoyl chloride was added to a solution of 0.34 g (11 mmole) of ammonium thiocyanate in 5 ml of dry acetone, and the mixture was heated with stirring for 5 min. A solution of 1.32 g (10 mmole) of 3-aminoindole in 10 ml of absolute tetrahydrofuran was added to the resulting benzoyl isothiocyanate in such a way that the mixture boiled gently. It was then poured with stirring into water, and the precipitated N-(3-indolyl)-N-benzoylthiourea was separated. The crystals were heated with 30 ml of 20% NaOH solution for 5 min, and the resulting solution was filtered through activated charcoal. The filtrate was acidified to pH 4-5 with concentrated hydrochloric acid, and the precipitate was removed by filtration and washed with water to give 1.24 g (65%).

LITERATURE CITED

1. V. S. Velezheva, V. N. Gunar, M. V. Balyakina, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 7, 939 (1978).

2. T. Takeshima, N. Fukada, M. Muraoka, and T. Miyauchi, J. Synth. Org. Chem., Jpn., 31, 811 (1973).
3. T. Takeshima, T. Miyauchi, N. Fukada, and S. Koshisava, J. Chem. Soc., Perkin I, No. 10, 1009 (1973).
4. J. Taminaga, C. Tamora, S. Sato, T. Hata, R. Natsuki, J. Matsuda, and J. Kobayashi, Chem. Pharm. Bull, 21, 1651 (1973).
5. J. Taminaga, J. Matsuda, and J. Kobayashi, J. Pharm. Soc. Jpn., 95, 980 (1975).
6. W. Braun, Ber., 36, 3520 (1903).
7. E. Hodkins and W. P. Reeves, J. Org. Chem., 29, 3098 (1964).
8. A. V. Yarosh, V. S. Velezheva, T. A. Kozik, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 4, 481 (1977).
9. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Methuen (1962).
10. R. Reynaud, Bull. Soc. Chim. France, No. 12, 4957 (1967).
11. T. Takeshima, T. Hayauchi, M. Muraoka, and T. Matsuoka, J. Org. Chem., 32, 980 (1967).
12. G. L. Garraway, J. Chem. Soc., B, No. 1, 92 (1966).
13. L. Kaluza, Monatsh., 33, 964 (1912).
14. S. Sakai, F. Fryinami, and F. Aisawa, Bull. Chem. Soc. Jpn., 48, 2981 (1975).
15. J. S. Johovi, U. Agarawala, and P. B. Rao, Indian J. Chem., 8, 759 (1970).

RESEARCH ON LACTAMS.

XXXII.* ANOMALOUS FISCHER REACTION OF α-OXOCAPROLACTAM O-PHENYLOXIME

R. G. Glushkov, I. M. Zasosova, I. M. Ovcharova, N. P. Solov'eva, O. S. Anisimova, and Yu. N. Sheinker

UDC 547.891'728'814

The reaction of O-phenylhydroxylamine hydrochloride with α-oxocaprolactam gave α-oxocaprolactam O-phenyloxime, which gave two substances — 1,2,3,4-tetrahydropyrido[2,3-c]coumarin as the principal product and 1-oxo-10a-hydroxy-1H-2,3,4,5,5a,10a-hexahydrobenzofuro[2,3-c]azepine as the minor product — under the conditions of the Fischer reaction. The minor product was converted to 1-oxo-1H-2,3,4,5-tetrahydrobenzofuro[2,3-c]azepine in quantitative yield by dehydration in trifluoroacetic acid.

Like the corresponding arylhydrazones, the O-phenyloximes of carbonyl compounds undergo the Fischer reaction to give benzofuran derivatives [2]. In particular, 1-oxo-1H-2,3,4,5-tetrahydrobenzofuro[3,2-c]azepine derivatives were obtained by this method from substituted 2,4-dioxohexahydroazepines and O-phenylhydroxylamine [3].

In the present research we attempted to synthesize 1-oxo-1H-2,3,4,5-tetrahydrobenzofuro[2,3-c]azepine (I) with α-oxocaprolactam (II) as the starting compound [4]. α-Oxocaprolactam O-phenyloxime (IV) was obtained by reaction of II with O-phenylhydroxylamine hydrochloride (III). It follows from the PMR spectrum that phenyloxime IV is a mixture of two geometrical isomers, since doubling of the signals of the protons of the CH_2 group in the 4 position of the azepine ring (multiplets at 2.41 and 2.66 ppm) and of the NH group (triplets at 8.17 and 8.33 ppm) is observed in its spectrum, along with multiplets at 1.65 [5,6-$(CH_2)_2$], 3.11 (7-CH_2), and 6.85-7.35 ppm (aromatic protons).

In an attempt to convert phenyloxime IV to I under the conditions of the preparation of substituted benzofurans from O-phenyloximes [2] we isolated two substances: a major product (V) with empirical formula $C_{12}H_{11}NO_2$ and mp 141-143°C, and a minor product with empirical formula $C_{12}H_{13}NO_3$ and mp 188-190°C. On the basis of the spectral data it was established

*See [1] for communication XXXI.

S. Ordzhonikidze All-Union Scientific-Research Pharmaceutical-Chemistry Institute, Moscow 119021. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1504-1507, November, 1978. Original article submitted January 21, 1978.

0009-3122/78/1411-1223$07.50