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The Synthetic Utility of Heteroaromatic Azido Compounds. III. Preparation of Some Furo-, Thieno- and Selenolo[3,2-*b*]pyrroles

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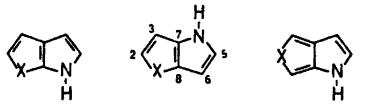
Some 3-azido-2-vinyl derivatives of furan, thiophene, and selenophene have been used for preparation of [3,2-*b*]-fused pyrrole systems by thermal decomposition. One of the resulting derivatives, namely 5-nitroacetylthieno-[3,2-*b*]pyrrole could be transformed to the corresponding unsubstituted thieno[3,2-*b*]pyrrole by alkaline treatment at high temperature. Attempts to obtain the unsubstituted furo- and selenolo-fused systems by this method failed.

The ^1H and ^{13}C NMR parameters for the thieno[3,2-*b*]pyrrole are presented.

Systems consisting of a pyrrole nucleus fused to a furan, thiophene, or selenophene ring are of interest since they are isosteric with indoles, which gives them a potential pharmacological importance. Research in this field has mainly been centered on preparation of analogues of naturally occurring indole derivatives. This is especially the case for the thieno-pyrrole systems; Snyder and his group have prepared a large variety of compounds, perhaps culminating in the synthesis of the thiophene analogues of tryptophan and tryptamine.[1]



Scheme 1.

There are three different *b*-fused isomers (A—C) for each unsubstituted heterocyclic analogue of indole (see Scheme 1).

In the furan series none of the parent compounds is known, and only a few simple derivatives have been described.[2,3] In the thiophene series two of the parent compounds, A and B, are known. Both have been prepared by decarboxylation of the corresponding 5-carboxy derivatives.[4,5] Thieno[3,2-*b*]pyrrole (B) has also been prepared by sodium borohydride reduction of 2*H*-thieno[3,2-*b*]pyrrol-3-one.[6] However, since Hemetsberger *et al.*[3] recently have described a new, easy way to generate 5-carboxy derivatives in these series, the former method seems to be the one of choice. A great number of derivatives of thiophene systems has been reported in the literature. In the selenophene series none of the parent compounds is known and only a few derivatives have been described.[7]

SYNTHESIS

This paper describes a general route to 5-acyl derivatives of furo-, thieno-, and selenolo[3,2-*b*]-pyrroles by thermal cyclization of suitably substituted 3-azidofurans, -thiophenes, and -selenophenes. This type of reaction has been used earlier in the benzene series for preparation of substituted indoles [8] and can mechanistically be regarded as an insertion of the initially generated nitrene into a C—H bond. The azido compounds used as starting materials in this study were 3-azido-2-formylfuran, -thiophene, and -selenophene.[9] The issue at hand was then to convert the formyl function into the necessary vinylic moiety. In principle, this could be done either by Wittig olefin synthesis or by condensation with compounds containing an active methyl or methylene group. The former

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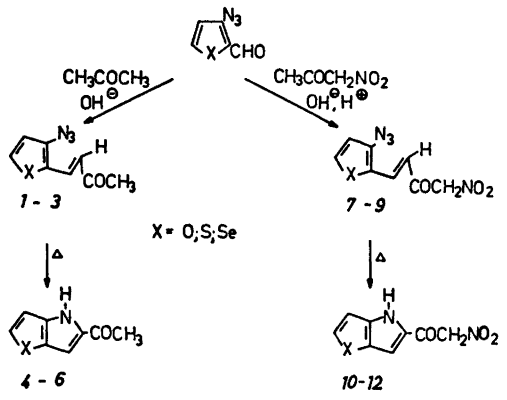


Scheme 2.

method has been shown in this laboratory [10] to be inapplicable in these azido systems, and thus the second method was adopted.

When the azido aldehydes were treated with excess acetone in 2 % sodium hydroxide solution (see Scheme 2), the expected vinylic compounds *1 – 3* were formed in good yields (77 – 92 %). If stronger alkaline solutions were used (> 5 %), the reaction mixtures grew dark and a slow evolution of gas, indicating destruction of the azido function, took place.

These vinylic compounds were then heated in xylene at temperatures of 120 – 130 °C (see Scheme 2) until the evolution of nitrogen gas had ceased. Thus *4 – 6* were obtained in good to excellent yields (69 – 90 %).

Dornow *et al.*[11] have shown that nitroacetone in alkaline medium reacts with aromatic formyl groups to give α,β-unsaturated carbonyl compounds, and that it is the methyl group which participates in the condensation. In order to obtain any significant yields from the reaction of nitroacetone with the azido aldehydes used in this study we found it necessary to modify Dornow's procedure. Thus a much larger amount of alkaline water solution had to be used, probably due to the low solubility of the azido aldehydes in water. We also found it more advantageous to isolate the sodium salt of the product prior to the acidification. Under these conditions (see Scheme 2) the vinylic compounds *7 – 9* were obtained in good yields (65 – 72 %). These vinylic compounds were then heated in an inert solvent under the same conditions as described above for compounds *1 – 3* (see Scheme 2). The heating was continued until no asymmetric N_3-stretching absorption was evident from the IR spectra of the reaction mixture. This gave *10 – 12* in moderate to good yields (54 – 78 %). In the cyclization of the furan compound *7* the reaction was accompanied by extensive tar formation. This could perhaps be due to a sensitivity of the furan ring to the acidic methylene group in the side-chain, at these temperatures.

Russian workers [12] have shown that 2-acetylindole can easily be isomerized to the 3-acetyl compound by the action of various acids (trifluoroacetic acid, polyphosphonic acid). When *5* was subjected to treatment by these acids, either the starting material was recovered unchanged or only resinous material could be isolated, depending on the reaction conditions. No sign of isomerization was evident in this case.

In a futile effort to reduce the carbonyl function of *11* by the Wolff-Kishner method, it was found by VPC that one of the products was unsubstituted thieno[3,2-*b*]pyrrole (*13*). The procedure was then modified and when *11* was treated with potassium hydroxide in diethylene glycol at 190 – 195 °C, under nitrogen, for one hour, this gave *13* as the major product in a yield of 51 %. This reaction sequence then offers an alternative to Snyder's two previously reported methods for preparing this compound.[4,6] Deswarte [13] and Pearson *et al.*[14] have shown that ω-nitroacetophenone under neutral and alkaline conditions is cleaved to benzoic acid and nitromethane or their anions. In order to demonstrate if this cleavage also occurred under our conditions, ω-nitroacetophenone was treated in the same way as *11*. After acidification, an almost quantitative yield of benzoic acid was obtained and no benzene could be detected by VPC. Since it is known from the literature [15] that at least 2-carboxyindoles can decarboxylate under the influence of alkali, it seems plausible that the reaction of *11* with potassium hydroxide at high temperatures could take place *via* the carboxylate anion. However, it should be pointed out that 5-carboxythieno-[3,2-*b*]pyrrole could not be isolated from these reactions. When *10* and *12* were subjected to the same conditions as described above, tars were formed. Neither the unsubstituted systems nor the 5-carboxy derivatives could be isolated from or detected in these tars.

The results presented above and the availability of a number of different carbonyl compounds capable of reacting in a similar manner shows this to be a useful method for obtaining 5-acyl derivatives in these series. This route could prove to be of synthetic value for the preparation of furan, thiophene, and selenophene analogues of naturally occurring indole derivatives.[16]

SPECTRAL DATA

The IR spectra of the azido compounds prepared in this work showed N_3-asymmetric stretching absorptions in the region of *ca.* 2110 – 2140 cm^{-1}. The fused pyrroles showed characteristic absorptions in the region of *ca.* 3250 – 3400 cm^{-1} due to NH-stretching vibrations.

The ^1H NMR data for most of the compounds are given in the experimental part. The assignments of different bands to the various protons have been based on knowledge of shifts and coupling constants in furans, thiophenes, selenophenes, and indoles, and on comparison with literature data for previously prepared compounds in these series.[17,18] The ^1H NMR spectra for the vinylic compounds *1 – 3* and *7 – 9* showed vicinal coupling constants of the magnitude 15.5 – 16.6 Hz indicating an exclusive *trans* configuration for these compounds.

As far as we know, no ^1H NMR spectral data for the unsubstituted thieno[3,2-*b*]pyrrole (*13*) have been hitherto reported. Therefore the spectrum of this compound, in carbon tetrachloride, was analyzed as a 5-spin system in an iterative mode utilizing an extended version of the QCPE program UEAITR (No. 188).[19] The results of this treatment are as follows: δ 6.84 (H-2), 6.48 (H-3), 7.32 (H-4), 6.46 (H-5), 6.22 (H-6). $J_{23} = 5.35$ Hz; $J_{25} = 1.40$ Hz; $J_{36} = 0.70$ Hz; $J_{45} = 2.55$ Hz; $J_{46} = 1.80$ Hz; $J_{56} = 3.00$ Hz.

We have also determined the ^{13}C NMR parameters for thieno[3,2-*b*]pyrrole (*13*). This was done with deuteriochloroform as solvent and deuterium as internal lock signal. The shifts were obtained from the proton decoupled spectre using TMS as internal standard. The assignments of shifts and coupling constants were made as described below.

The proton decoupled spectra showed six distinct signals. Two of these, at 121.9 and 138.6 ppm, were of low intensity indicating that they arise from the quaternary, bridging carbon atoms (C-7 and C-8, see Scheme 1). However, it is not evident which one is which since it is difficult to estimate the size of the mesomeric and inductive effects of the heteroatoms at these positions. Since the undecoupled spectrum showed signs of long-range couplings between carbon atoms and the nitrogen proton, and since we felt it safe to assume that such couplings could only occur to a significant extent with the carbon atoms in the pyrrole part of the molecule, we tried to eliminate these couplings in order to facilitate the assignments of the remaining four peaks. Addition of piperidine to a dioxan solution of pyrroles gives a rapid hydrogen exchange which effectively eliminates the couplings between the α- and β-protons and the nitrogen proton.[20] In order to ascertain if this was also the case for thieno-[3,2-*b*]pyrrole (*13*) we added a few drops of piperidine to a solution in deuteriochloroform. The ^1H NMR spectra showed a complete decoupling of the nitrogen proton couplings as did also the ^{13}C NMR spectra.

This result clearly indicated that the signals at δ 101.3 and 123.0 correspond to the peripheral carbon atoms in the pyrrole ring while those at δ 111.2 and 123.7 correspond to those in the thiophene ring. Comparison with literature data for the direct carbon-hydrogen couplings in pyrrole ($J_{C\alpha H\alpha}$ 184 Hz, $J_{C\beta H\beta}$ 170 Hz)[21] gives the assignments of carbons 5 and 6 (see Scheme 1). Further proof for this can be found from the fact that a small downfield shift (~0.2 ppm) was observed for the peak assigned to carbon 5 when piperidine was added to the sample. A similar but larger effect was also observed in the ^1H NMR spectra for the 5-proton when piperidine was added. It seems that the closeness to the centre where exchange is taking place gives rise to a downfield shift. The assignment of carbons 2 and 3 (see Scheme 1) was made by comparison with literature data for direct couplings and long-range couplings for thiophene compounds.[22] The ^{13}C parameters found were thus: δ 123.7 (C-2), 111.2 (C-3), 123.0 (C-5), 101.3 (C-6), 121.9 [C-7 (or C-8)], 138.6 [C-8 (or C-7)]. $J_{C_2H_2}$ 185 Hz, $J_{C_2H_3}$ 6.8 Hz, $J_{C_3H_3}$ 170 Hz, $J_{C_3H_2}$ 4.6 Hz, $J_{C_3H_5 \text{ or } H_6}$

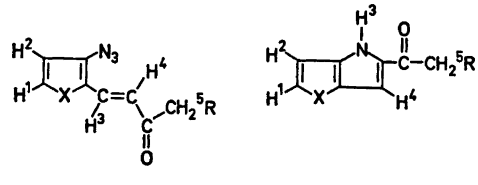
0.7 Hz, $J_{C_5H_5}$ 185 Hz, $J_{C_5H_4}$ 4.1 Hz, $J_{C_5H_5}$ 8.4 Hz, $J_{C_6H_6}$ 176 Hz, $J_{C_6H_4}$ 5.9 Hz, $J_{C_6H_5}$ 8.2 Hz, $J_{C_6H_2 \text{ or } H_3}$ 1.4 Hz.

It is interesting to note that the α-carbon in the thiophene part of the molecule resonates at lower field than the β-carbon. This is the opposite of what has been found for thiophene itself.[22] A similar but smaller reversing effect has also been demonstrated in the ^{13}C NMR spectra of benzo[*b*]thiophene.[23]

Another point of interest is that there are long-range couplings between the two rings. Thus carbon 3 couples with one of the protons in the pyrrole moiety and carbon 6 couples with one of the thiophene protons. Some pertinent information about which protons these carbons are coupled to could probably be obtained from deuteration experiments. However, due to the lability of the thieno[3,2-*b*]-pyrrole system, no efforts in this direction have been made. Similar long-range couplings have been observed in other systems.[24]

EXPERIMENTAL

The ^1H NMR spectra were obtained with a Varian A-60 high resolution spectrometer and a Jeol MH-100 spectrometer. The ^1H NMR data given below refers to the following protons:



X = O, S, Se
R = H, NO_2

The ^{13}C NMR spectra were recorded on a Jeol FX-60 spectrometer. The IR spectra were recorded on a Perkin-Elmer spectrometer model 257. The gas chromatograph used was a Perkin-Elmer 900 analytical instrument (OV-25, 3 %, Chrom Q, 3 m; BDS, 10 %, Chrom W., 2 m). Mass spectra were obtained with an LKB 9000 mass spectrometer. Elementary analyses were carried out at the Analytical Department of the Chemical Institute and by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr.

trans-*4-(3-Azido-2-furyl)-3-buten-2-one* (*1*). To a solution of 1.5 g of sodium hydroxide in 75 ml of water, 6.7 g (0.049 mol) of 3-azido-2-formylfuran [9] in 30 ml of acetone was added. The resulting heterogeneous mixture was stirred at room temperature for one hour and then cooled in ice. The resulting precipitate was filtered off and recrystallized from methanol, giving 7.5 g (85 %) of the product with m.p. ~105 °C (decomp.). IR spectrum (KBr): N_3= 2120 cm^{-1}. NMR spectrum ($CDCl_3$): δ 7.46 (H-1), 6.49 (H-2), 7.22 (H-3), 6.52 (H-4), 2.30 (H-5); $J_{1,2}$ 2.2 Hz, $J_{3,4}$ 15.9 Hz. [Found: C 54.2; H 4.03; N 24.3; m.wt. 177. Calc. for $C_8H_7N_3O_2$: C 54.2; H 3.99; N 23.7; m.wt. 177.18].

trans-*4-(3-Azido-2-thienyl)-3-buten-2-one* (*2*) was prepared as described above for *1* from 2.0 g of sodium hydroxide, 100 ml of water, 10.0 g (0.0654 mol) of 3-azido-2-formylthiophene [9] and 35 ml of acetone. This gave after recrystallization from methanol 11.0 g (92 %) of the product, m.p. ~105 °C (decomp.). IR spectrum (KBr): N_3= 2120 cm^{-1}. NMR spectrum ($CDCl_3$): δ 7.42 (H-1), 6.95 (H-2), 7.58 (H-3), 6.42 (H-4), 2.30 (H-5); $J_{1,2}$ 5.6 Hz, $J_{2,3}$ 0.8 Hz, $J_{3,4}$ 16.6 Hz. [Found: C 49.5; H 3.65; S 16.5; m.wt. 193. Calc. for $C_8H_7N_3OS$: C 49.7; H 3.66; S 16.6; m.wt. 193.24].

trans-*4-(3-Azido-2-selenyl)-3-buten-2-one* (*3*) was prepared as described above for *1* from 1.0 g of sodium hydroxide, 50 ml of water, 6.0 g (0.030 mol) of 3-azido-2-formylselenophene [9] and 25 ml of acetone. This gave after recrystallization from methanol 5.5 g (77 %) of the product, m.p. 87.0 – 90.0 °C (decomp.). IR spectrum (KBr): N_3= 2110 cm^{-1}. NMR spectrum ($CDCl_3$): δ 8.04 (H-1), 7.23 (H-2), 7.64 (H-3), 6.25 (H-4), 2.87 (H-5); $J_{1,2}$ 5.9 Hz, $J_{3,4}$ 16.0 Hz. [Found: C 40.1; H 2.94; Se 32.9; m.wt. 241. Calc. for $C_8H_7N_3OSe$: C 40.0; H 2.94; Se 32.9; m.wt. 240.14].

5-Acetylfuro[3,2-b]pyrrole (*4*). 5.2 g (0.029 mol) of 4-(3-azido-2-furyl)-3-buten-2-one (*1*) was dissolved in 175 ml of xylene. The mixture was heated at 120 – 130 °C with stirring and kept at this temperature until the evolution of nitrogen gas had ceased (30 – 45 min). The solution was then allowed to attain room temperature, whereupon the solvent was removed by evaporation. The dark residue was filtered off and repeatedly washed with low-boiling petroleum ether. Charcoal treatment and recrystallization from toluene gave 3.0 g (69 %) of the product, m.p. 184.5 – 187.0 °C. IR spectrum (KBr): NH = 3280 cm^{-1}, CO = 1630 cm^{-1}. NMR spectrum (DMSO-d_6): δ 7.82 (H-1), 6.62 (H-2), 11.7 (H-3), 6.98 (H-4), 2.45 (H-5); $J_{1,2}$ 2.2 Hz, $J_{2,4}$ 0.8 Hz, $J_{3,4}$ 1.7 Hz. [Found: C 64.8; H 4.78; N 9.27; m.wt. 149. Calc. for $C_8H_7NO_2$: C 64.4; H 4.74; N 9.39; m.wt. 149.16].

5-Acetylthieno[3,2-b]pyrrole (*5*) was prepared as described above for *4* from 7.5 g (0.039 mol) of 4-(3-azido-2-thienyl)-3-buten-2-one (*2*) in 200 ml of xylene. Recrystallization from toluene gave 5.8 g (90 %) of the product, m.p. 160.5 – 163.0 °C. IR spectrum (KBr): NH = 3295 cm^{-1}, CO = 1630 cm^{-1}. NMR spectrum (DMSO-d_6): δ 7.59 (H-1), 7.02 (H-2), 11.9 (H-3), 7.30 (H-4), 2.45 (H-5); $J_{1,2}$ 5.4 Hz, $J_{2,4}$ 0.8 Hz, $J_{3,4}$ 2.2

Hz. [Found: C 58.2; H 4.24; S 19.2; m.wt. 165. Calc. for C_8H_7NOS: C 58.2; H 4.28; S 19.4; m.wt. 165.22].

5-Acetylselenolo[3,2-b]pyrrole (6) was prepared as described above for *4* from 4.2 g (0.017 mol) of 4-(3-azido-2-selenyl)-3-buten-2-one (*3*) in 125 ml of xylene. Charcoal treatment and recrystallization from toluene gave 3.0 g (82 %) of the product, m.p. 167.0 – 168.0 °C. IR spectrum (KBr): NH = 3250 cm^{-1}, CO = 1625 cm^{-1}. NMR spectrum (DMSO-d_6): δ 8.04 (H-1), 7.27 (H-2), 11.9 (H-3), 7.29 (H-4), 2.30 (H-5); $J_{1,2}$ 6.0 Hz, $J_{3,4}$ 0.7 Hz. [Found: C 45.4; H 3.36; Se 37.2; m.wt. 213. Calc. for C_8H_7NOSe: C 45.3; H 3.33; Se 37.2; m.wt. 212.12].

trans-*4-(3-Azido-2-furyl)-1-nitro-3-buten-2-one (7)*. 10.0 g (0.0730 mol) of 3-azido-2-formylfuran [9] and 10.0 g (0.0971 mol) of nitroacetone [19] were dispersed in 400 ml of 5 % sodium hydroxide solution. The heterogeneous mixture was stirred at room temperature for 24 h and during this time a voluminous, yellow precipitate, consisting of the sodium salt of the product, was formed. This precipitate was filtered off and as fast as possible added with stirring to 300 ml of ice water containing 14 ml of conc. hydrochloric acid. The stirring was then continued for 30 min, whereupon the now distinctly orange precipitate was filtered off and allowed to dry. This orange substance was treated with 25 ml of methanol at a temperature of 35 – 40 °C for 5 min, with stirring. The colour of the solid material changed during this operation from orange to yellow. The mixture was cooled in ice and the solid material filtered off. This gave 11.2 g (70 %) of the product. An analytical sample which was obtained by recrystallization from ethanol showed an IR spectrum identical to that of the crude product; m.p. 81.5 – 83.0 °C. IR spectrum (KBr): N_3 = 2120 cm^{-1}, CO = 1665 cm^{-1}. NMR spectrum (DMSO-d_6): δ 7.97 (H-1), 6.70 (H-2), 7.35 (H-3), 6.51 (H-4), 6.05 (H-5); $J_{1,2}$ 2.0 Hz, $J_{3,4}$ 15.5 Hz. [Found: C 43.4; H 2.75; N 25.2; m.wt. 222. Calc. for $C_8H_6N_4O_4$: C 43.2; H 2.73; N 25.2; m.wt. 222.18].

trans-*4-(3-Azido-2-thienyl)-1-nitro-3-propen-2-one (8)* was prepared as described above for *7* from 13.0 g (0.0850 mol) of 3-azido-2-formylthiophene,[9] 9.7 g (0.094 mol) of nitroacetone [19] and 800 ml of 5 % sodium hydroxide solution. This gave after treatment with warm methanol 14.6 g (72 %) of the product. An analytical sample which was obtained by recrystallization from ethanol showed an IR spectrum identical to that of the crude product; m.p. ~105 °C (decomp.). IR spectrum (KBr): N_3 = 2140 cm^{-1}, CO = 1675 cm^{-1}. NMR spectrum (DMSO-d_6): δ 7.89 (H-1), 7.26 (H-2), 7.65 (H-3), 6.57 (H-4), 6.02 (H-5); $J_{1,2}$ 5.3 Hz, $J_{3,4}$ 15.7 Hz. [Found: C 40.1; H 2.66; S 13.5; m.wt. 238. Calc. for $C_8H_6N_4O_3S$: C 40.3; H 2.54; S 13.5; m.wt. 238.24].

trans-*4-(3-Azido-2-selenyl)-1-nitro-3-propen-2-one (9)* was prepared as described above for *7* from 2.5 g (0.013 mol) of 3-azido-2-formylselenophene,[9] 1.5 g (0.015 mol) of nitroacetone [19] and 160 ml of 5 % sodium hydroxide solution. However, the reaction time in this case was 48 h. After treatment with warm methanol, 2,7 g of the crude product was obtained. Recrystallization from ethanol gave 2.4 g (65 %) of the product; m.p. ~105 °C (decomp.). IR spectrum (KBr): N_3 = 2105 cm^{-1}, CO = 1685 cm^{-1}. NMR spectrum (DMSO-d_6): δ 8.48 (H-1), 7.51 (H-2), 7.71 (H-3), 6.52 (H-4), 5.96 (H-5); $J_{1,2}$ 6.0 Hz, $J_{3,4}$ 15.6 Hz. [Found: C 33.7; H 2.29; Se 27.8; m.wt. 286. Calc. for $C_8H_6N_4OSe$: C 33.7; H 2.13; Se 27.7; m.wt. 285.14].

5-Nitroacetylfuro[3,2-b]pyrrole (10). 11.2 g (0.0505 mol) of *trans*-4-(3-azido-2-furyl)-1-nitro-3-buten-2-one (*7*) was dissolved in 350 ml of xylene. The mixture was heated at 120 – 125 °C with stirring until its IR spectrum (film) showed no more asymmetric N_3-stretching absorption. The solution was then allowed to attain room temperature, whereupon the solvent was removed by evaporation. The dark residue was filtered off and repeatedly washed with low-boiling petroleum ether. The solid was then transferred to a Soxhlet apparatus and continuously extracted with 350 ml of methanol for 5 days. Evaporation of the solvent gave 5.3 g (54 %) of the product. An analytical sample, obtained by recrystallization from methanol, showed an IR spectrum identical with that of the crude product, m.p. 202.5 – 205.0 °C (decomp.). IR spectrum (KBr): NH = 3290 cm^{-1}, CO = 1640 cm^{-1}. NMR spectrum (DMSO-d_6): δ 7.94 (H-1), 6.68 (H-2), 12.0 (H-3), 7.15 (H-4), 6.12 (H-5); $J_{1,2}$ 2.2 Hz, $J_{2,4}$ 0.9 Hz, $J_{3,4}$ 1.5 Hz. [Found: C 49.1; H 3.14; O 33.1; m.wt. 194. Calc. for $C_8H_6N_2O_4$: C 49.5; H 3.12; O 33.0; m.wt. 194.16].

5-Nitroacetylthieno[3,2-b]pyrrole (11) was prepared as described above for *10* from 10.2 g (0.0429 mol) of *trans*-4-(3-azido-2-thienyl)-1-nitro-3-propen-2-one (*8*) in 500 ml of xylene. In this case, however, the crude product, obtained after evaporation of xylene and thorough washing with petroleum ether, was treated with 600 ml of boiling methanol and filtered while hot. The filtrate was evaporated to dryness to give 7.0 g (78 %) of the product. An analytical sample, obtained by recrystallization from methanol, showed an IR spectrum identical with that of the crude product, m.p. 171.5 – 174.5 °C (decomp.). IR spectrum (KBr): NH = 3320 cm^{-1}, CO = 1645 cm^{-1}. NMR spectrum (DMSO-d_6): δ 7.70 (H-1), 7.06 (H-2), 12.4 (H-3), 7.47 (H-4), 6.20 (H-5); $J_{1,2}$ 5.3 Hz, $J_{2,4}$ 0.6 Hz, $J_{3,4}$ 1.5 Hz. [Found: C 45.5; H 2.91; S 15.1; m.wt. 210. Calc. for $C_8H_6N_2O_3S$: C 45.7; H 2.88; S 15.3; m.wt. 210.22].

5-Nitroacetylselenolo[3,2-b]pyrrole (12) was prepared as described above for *10* from 3.5 g (0.012 mol) of *trans*-4-(3-azido-2-selenyl)-1-nitro-3-propen-2-one (*9*) in 150 ml of xylene. In this case, however, the crude product, obtained after evaporation of xylene and thorough

washing with petroleum ether, was treated with 500 ml of boiling methanol and charcoal and filtered while hot. The filtrate was evaporated to dryness, yielding 2.3 g (74 %) of the product. An analytical sample, obtained by recrystallization from methanol, showed an IR spectrum identical with that of the crude product, m.p. 177.0 – 181.0 °C (decomp.). IR spectrum (KBr): NH = 3320 cm^{-1}, CO = 1640 cm^{-1}. NMR spectrum (DMSO-d_6): δ 8.15 (H-1), 7.25 (H-2), 12.4 (H-3), 7.40 (H-4), 6.15 (H-5); $J_{1,2}$ 5.7 Hz. [Found: C 37.4; H 2.40; Se 30.7; m.wt. 258. Calc. for $C_6H_5N_2O_2Se$: C 37.4; H 2.36; Se 30.7; m.wt. 257.12].

*Thieno[3,2-*b*]pyrrole (13).* 2.5 g (0.012 mol) of 5-nitroacetylthieno[3,2-*b*]pyrrole (*11*) and 2.8 g of potassium hydroxide were dispersed in 50 ml of diethylene glycol. The mixture was heated to 190 – 195 °C with stirring and nitrogen inlet, and kept at this temperature for one hour. After attaining room temperature, the black solution was poured into 200 ml of water and the resulting mixture extracted four times with 75 ml of ether. The combined ether phases were washed once with 40 ml of water and dried over magnesium sulfate. Evaporation of the solvent gave 1.1 g of an oil which was immediately transferred to a sublimation apparatus. At 60 – 80 °C/1.2 mmHg, 0.75 g (51 %) of product condensed on the water-cooled sublimation finger; m.p. 24 – 26 °C (lit. value:[6] 25 – 28 °C). IR spectrum (film): NH = 3400 cm^{-1}. NMR spectrum (CCl_4): see text.

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