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# SYNTHESIS OF PYRIDAZINE DERIVATIVES—XXVIII

## TETRAZOLO-AZIDO ISOMERIZATIONS IN SOME FUSED TETRAZOLOPYRIDAZINES[1]

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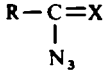
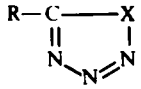
**Abstract**—It has been found that in certain cases azidotetrazolopyridazines can isomerize. 6-Azido-7-methyltetrazolo[1·5-*b*]pyridazine isomerizes into 6-azido-8-methyltetrazolo[1·5-*b*]pyridazine by simultaneous ring opening of the tetrazolo ring and cyclization of the azido group. Similarly, 6-azidopyrido-[3·2-*d*]tetrazolo[5·1-*b*]pyridazine isomerizes to the thermodynamically more stable 6-azidopyrido[2·3-*d*]-tetrazolo[5·1-b]pyridazine.

IN ADDITION to our publications on tetrazolopyridazines, including reports on tetrazolo-azido transformations in some fused azolopyridazines,[2] isomeric tetrazolo-pyridopyridazines[3,4] and other polyazaheterocycles,[5,6] the present communication presents evidence for tetrazolo-azido isomerizations in some fused tetrazolopyridazines.



I



II

Several heterocyclic systems where the azide group is adjacent to an annular nitrogen have been investigated in order to establish their structures and the possibility of cyclization to a fused tetrazolo ring. From the chemistry of the related open chain analogues, represented with the structure I it is well known that the heteroatom or group X (X = O, S, $NR_1$, $CR_2R_3$) is mainly responsible for the conversion of I into the cyclic form II. The electronegative character of X which may be influenced by the electron donating power of eventually attached functions ($NR_1$, $CR_2R_3$) determines thus the stability of the azide or tetrazole form, respectively. In this manner, if groups $R_1$, $R_2$, $R_3$ are electron withdrawing they undoubtedly exert a stabilizing influence on the azido form. There are several examples of open chain azides which agree with this observation.[7–15]

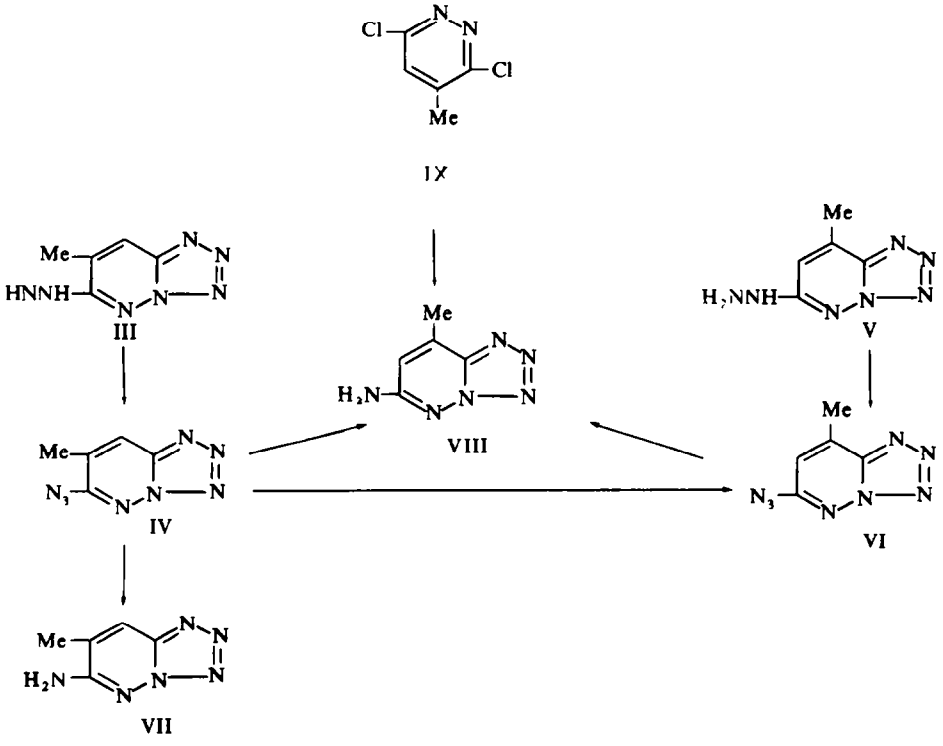
The above generalization can be equally well applied to heterocyclic systems containing the prerequisite arrangement of azide and azomethine group(s).[16–19] Temperature and solvent effects are sometimes also important. In the pyridazine series the generation of an azide group adjacent to a ring nitrogen involves immediate cyclization to stable tetrazolo[1.5-*b*]pyridazines.[2,20–27] An exception is 3-azido-pyridazine-1-oxide which exists exclusively in the azide form and the destabilization

of the tetrazolo ring in this case is in agreement with the above discussion. Deoxygenation spontaneously generates the fused tetrazolo ring.[26]

Similarly, a fused azolo ring stabilizes another azido group as is the case with 6-azidotetrazolo[1.5-*b*]pyridazine.[2,26,27] Further investigations in related systems has shown that two isomeric methyl 6-azidotetrazolo[1.5-*b*]pyridazines can be prepared.

Treatment of the isomeric 7-methyl- and 8-methyl-6-hydrazinotetrazolo[1.5-*b*]-pyridazines with nitrous acid afforded each of the isomeric azides IV and VI. Both compounds are stable and on the basis of IR (strong asymmetric stretching absorption at 2132 and 2169 $cm^{-1}$, respectively, characteristic for azide[28,29]) and NMR spectra the proposed structures are fully justified. Examination of their solutions in different solvents at low and room temperature gave no indication of an equilibrium either between the isomers or between different tautomeric forms.

The isomer IV has a higher m.p. and we could observe that from the melt a new compound separated upon cooling and this was identified as the lower melting isomer VI. With the intention to prepare one of both azide isomers, we treated 3,6-dichloro-4-methylpyridazine (IX) with sodium azide in ethylene glycol. Instead of the expected product we isolated 6-amino-8-methyltetrazolo[1.5-*b*]pyridazine (VIII). Apparently reduction of the azido group took place and this could be verified in a separate experiment with the parent azide X, which under similar conditions was transformed into XI. The solvent was undoubtedly involved as hydrogen source. A similar case of oxidation-reduction of an azidohydroquinone to aminoquinone was reported recently.[30]



The isomeric amines VII and VIII were also obtained by hydrogen sulphide reduction of the corresponding azides. Furthermore, an interesting transformation results when the azide IV is heated in 2-ethoxyethanol. The product VIII is probably produced via isomerization to VI and subsequent reduction of the azido function.

By means of NMR spectra it is possible to follow the conversion of the azide IV into the isomer VI. Samples of a hot solution of IV in dimethyl sulphoxide-$d_6$ were taken at different time intervals since the isomerization is measurably slow. The changes in signals for the Me group, characteristic for each isomer, are shown on Fig. 1.

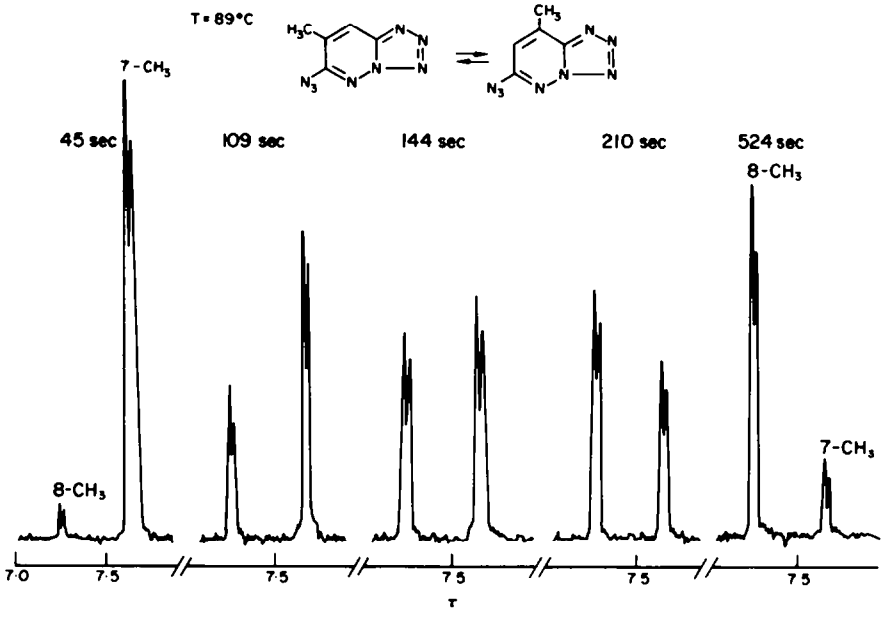
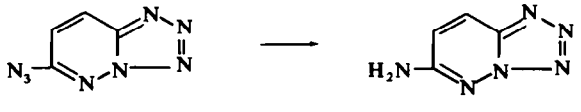



FIG. 1

In order to determine the enthalpy change $\Delta H$ accompanying the above isomerization, the concentration of each isomers in equilibrium (dimethyl sulphoxide-$d_6$ as solvent) was determined by measuring the corresponding signal areas at 89° and 94°. From the temperature dependence of the equilibrium constants the value $\Delta H = -5{\cdot}9$ kcal/mol was calculated. The Arrhenius activation energy, $E_a$, was calculated from the rate constants[31] and found to be 20·5 kcal/mol. This value is comparable with the activation energy for the conversion of some guanylazides into 5-aminotetrazoles.[8]

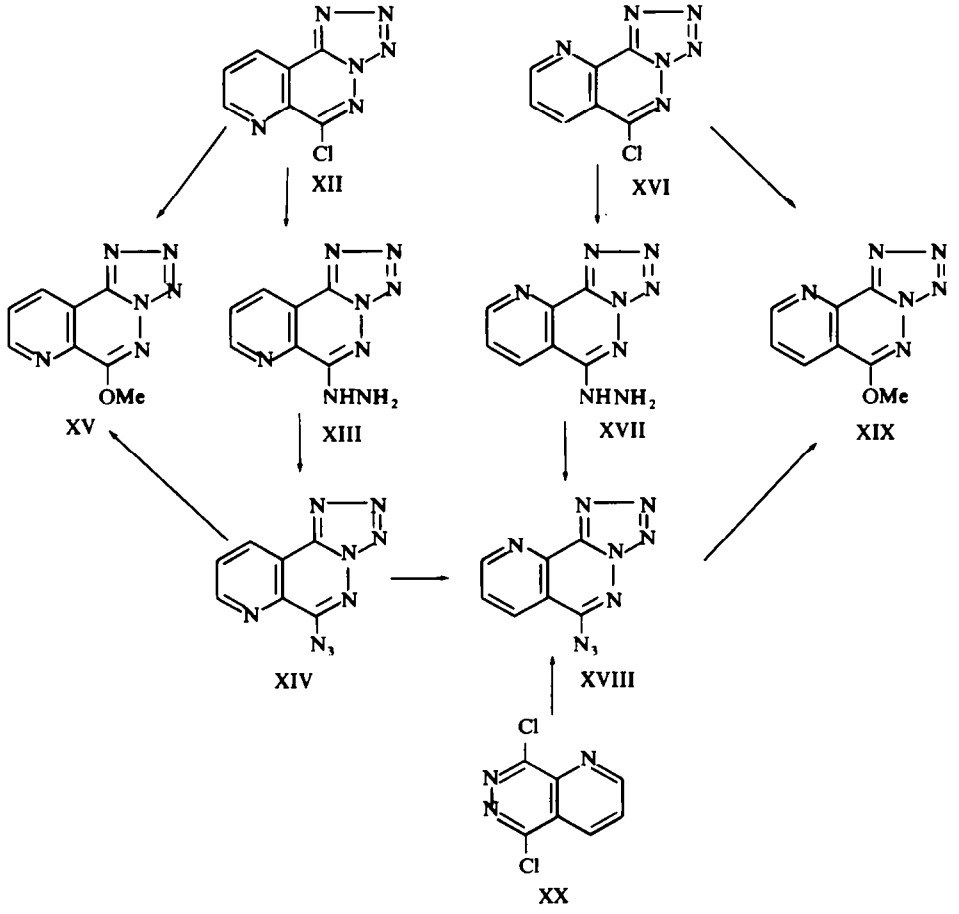


X XI

This type of isomerization is the first to be noted in the heterocyclic series, but another example was found in the related pyridopyridazine series.

From the isomeric 6-chloropyrido[3.2-*d*]tetrazolo[5.1-*b*]pyridazine (XII) and 6-chloropyrido[2.3-*d*]tetrazolo[5.1-*b*]pyridazine (XVI) the corresponding azidotetrazolo compounds XIV and XVIII were prepared via the hydrazines XIII and XVII. The confirmation of their structures followed from their conversion into each of the isomeric methoxy compounds XV and XIX, obtainable also from the isomeric XII and XVI. Treatment of 5,8-dichloropyrido[2.3-*d*]pyridazine (XX) with ethanolic socium azide afforded only the thermodynamically more stable isomer XVIII. Both azido compounds are soluble in conc sulphuric acid upon heating and upon cooling the unchanged compounds separated from the solution.

The conversion of the lower melting isomer XIV (m.p. 180–182°) into the higher melting XVIII (m.p. 197°) takes place during heating. This indicates the same tendency as discussed before with azidotetrazolopyridazines to assume the thermodynamically more stable tetrazole isomer. IR spectra (intense azide bands at 2119 and 2141 $cm^{-1}$, respectively) and NMR spectra are in accord with the proposed structures.



## EXPERIMENTAL

M.ps (Kofler m.p. apparatus) are corrected; IR spectra: Infracord Model 137 as mulls in Nujol; NMR spectra: Varian A-60 spectrometer, TMS as internal standard.

*6-Hydrazino-7-methyltetrazolo*[1,5-b]*pyridazine* (III)

A mixture of 6-chloro-7-methyltetrazolo[1.5-b]pyridazine[20] (0·85 g) and 80% hydrazine hydrate (8 ml) was heated under reflux for 15 min. The mixture was chilled on ice, the separated crystals were filtered off, washed with water and dried. Upon crystallization from a mixture of N,N-dimethylformamide and EtOH (4:1) the pure compound had m.p. 285–287°; yield 0·73 g (88%). (Found: C, 36·36; H, 4·67; N, 59·31; $C_5H_7N_7$ requires: C, 36·36; H, 4·27; N, 59·37%).

*6-Azido-7-methyltetrazolo*[1.5-b]*pyridazine* (IV)

Compound III (330 mg) was dissolved in 5N HCl (6 ml), the soln cooled on ice and to the stirred soln $NaNO_2$ aq (150 mg in 2 ml of water) was added dropwise. After the addition was complete and the mixture was left to stand on ice for 30 min. the crude product was separated, dried and crystallized from 50% EtOH; m.p. 113–114°; yield 290 mg (82%). Upon cooling the melt, a compound with m.p. 87–92° crystallized and proved to be impure isomer VI; IR spectrum (Nujol): 2132 $cm^{-1}$ ($N_3$); NMR spectrum: $CF_3COOH$, room temp: $\tau$ = 1·57 (d, $H_8$), 7·42 (d, 7-$CH_3$); $J$ = 1·2 c/s ($H_8$, 7-Me); $CD_3COCD_3$, −30°: $\tau$ = 1·53 (d, $H_8$), 7·60 (d, 7-Me). (Found: C, 34·32; H, 2·47; N, 63·44; $C_5H_4N_8$ requires: C, 34·09; H, 2·29; N, 63·62%).

*6-Amino-7-methyltetrazolo*[1.5-b]*pyridazine* (VII)

Compound IV (88 mg) was dissolved in hot EtOH (5 ml) and $H_2S$ was introduced during 5 min. The solvent was evaporated *in vacuo* to half of its original volume, iced water (5 ml) was added and the mixture was left to stand on ice for 1 hr. The separated crystals were filtered off (40 mg, 53%) and crystallized from 50% EtOH, m.p. 320–323° (dec, some decomposition was observed at about 310°); IR spectrum (Nujol): 3356 and 3205 $cm^{-1}$ ($NH_2$). (Found: C, 40·08; H, 4·25; N, 56·12; $C_5H_6N_6$ requires: C, 39·99; H, 4·03; N, 55·98%).

*6-Hydrazino-8-methyltetrazolo*[1.5-b]*pyridazine* (V)

This compound was prepared from 6-chloro-8-methyltetrazolo[1.5-b]pyridazine[20] (0·85 g) as described for the isomeric III, yield 0·67 g (81%); m.p. 247–248° (from N,N-dimethylformamide and EtOH, 1:1). (Found: C, 36·52; H, 4·46; N, 59·44; $C_5H_7N_7$ requires: C, 36·36; H, 4·27; N, 59·37%).

*6-Azido-8-methyltetrazolo*[1.5-b]*pyridazine* (VI)

Compound V (495 mg) was treated with $HNO_2$, as described in the synthesis of the isomeric IV. The crude product (380 mg, 72%) was purified by crystallization from 50% EtOH, m.p. 95°; IR spectrum (Nujol): 2169 $cm^{-1}$ ($N_3$); NMR spectrum: $CF_3COOH$, room temp; $\tau$ = 2·81 (d, $H_7$), 7·15 (d, 8-Me); $J$ = 1·2 c/s ($H_7$, 8-Me); $CD_3COCD_3$, −30°: $\tau$ = 2·67 (d, $H_7$), 7·23 (d, 8-Me). (Found: C, 34·26; H, 2·52; N, 63·54; $C_5H_4N_8$ requires: C, 34·09; H, 2·29; N, 63·62%).

*6-Amino-8-methyltetrazolo*[1.5-b]*pyridazine* (VIII)

(i) Compound VI (176 mg) was treated with $H_2S$ as described in the case of the isomeric IV. The crude product (86 mg, 57%) was crystallized from 50% EtOH and had m.p. 302–303°; IR spectrum (Nujol): 3289 and 3145 $cm^{-1}$ ($NH_2$), no azide band. (Found: C, 39·95; H, 4·34; N, 56·17; $C_5H_6N_6$ requires: C, 39·99; H, 4·03; N, 55·98%).

(ii) Compound IX[32–35] (1·63 g), sodium azide (1·30 g) and ethylene glycol (15 ml) were heated under reflux for 20 min. The dark soln was cooled and poured onto about 40 g of crushed ice. The crude product was filtered off (0·8 g, 53%) and a sample crystallized for analysis from 50% EtOH; m.p. 302–303°, mixed m.p. with the compound prepared as described under (i) was undepressed and IR spectra were identical. If instead of ethylene glycol 2-ethoxyethanol was used as solvent the product was obtained in almost the same yield.

(iii) Compound IV (176 mg) was heated in 2-ethoxyethanol (2 ml) under reflux for 20 min. The ice cold soln was diluted with n-hexane (5 ml) and the separated product filtered off. Upon crystallization from 50% EtOH the compound had m.p. 302–303° and was identified as 6-amino-8-methyltetrazolo[1.5-b]-pyridazine (m.m.p. and IR spectra).

*6-Aminotetrazolo[1.5-b]pyridazine* (XI)

A soln of X[2] (1·62 g) in ethylene glycol (10 ml) was treated as described for the synthesis of VIII under (iii). The dark brown crude product (0·45 g, 33%) was crystallized from N,N-dimethylformamide, m.p. 312–315°, mixed m.p. with an authentic specimen[2] was undepressed; IR spectrum (Nujol): 3378, 3300, 3175 $cm^{-1}$ ($NH_2$).

*Isomerization of 6-azido-7-methyltetrazolo[1.5-b]pyridazine into 6-azido-8-methyltetrazolo[1.5-b]pyridazine*

The azide IV (176 mg) was heated with toluene (2·5 ml) under reflux for 15 min. To the cold reaction mixture n-hexane (10 ml) was added and the separated product was obtained in almost quantitative yield. A sample was crystallized from 50% EtOH to give the pure isomeric azide VI, m.p. 95°, mixed m.p., IR and NMR spectra were identical.

For the determination of rate constants and equilibria in dimethylsulphoxide-$d_6$ measurements at 89 and 94° were made. Ten measurements at different time intervals were recorded and the temp was verified by difference in chemical shift of two signals of ethylene glycol. From the temp dependence of the equilibrium constants the value $\Delta H$ was calculated using the equation:

$$\log\frac{K_2}{K_1} = -\frac{\Delta H}{4{\cdot}576}\left[\frac{1}{T_2} - \frac{1}{T_1}\right].$$

It was found that $\Delta H = -5{\cdot}9 \pm 0{\cdot}5$ kcal/mol.

For calculation of Arrhenius activation energy the following equation has been employed:[31]

$$\log\frac{k_2}{k_1} = -\frac{E_a}{4{\cdot}576}\left[\frac{1}{T_2} - \frac{1}{T_1}\right].$$

The determined rate constants, $k$, were: $k_1 = 3{\cdot}33 \times 10^{-3}$ $sec^{-1}$ and $k_2 = 5{\cdot}01 \times 10^{-3}$ $sec^{-1}$ and the calculated $E_a = 20{\cdot}5 \pm 1{\cdot}0$ kcal/mol.

*6-Hydrazinopyrido[3.2-d]tetrazolo[5.1-b]pyridazine* (XIII)

A suspension of XII[3] (618 mg) in 80% hydrazine hydrate (3 ml) was heated under reflux for 5 min, the reaction mixture chilled on ice and the separated product filtered off. Upon crystallization from EtOH and N,N-dimethylformamide, 2:1, the pure compound (350 mg, 58% yield) had m.p. 274°. (Found: C, 41·73; H, 3·10; N, 55·25; $C_7H_6N_8$ requires: C, 41·58; H, 2·99; N, 55·43%).

*6-Azidopyrido[3.2-d]tetrazolo[5.1-b]pyridazine* (XIV)

Compound XIII (291 mg) was dissolved in 50% AcOH (5 ml), the soln cooled on ice and during stirring a soln of $NaNO_2$ in water (110 mg in 15 ml) was added dropwise. Upon standing on ice for 2 hr, the product was separated and crystallized from N,N-dimethylformamide and EtOH (1:1), yield 220 mg (72%); m.p. 180–182°. From the melt a crystalline product separated and this had m.p. 195–197° (compound XVIII); IR spectrum (Nujol): 2119 $cm^{-1}$ ($N_3$); NMR spectrum: $CF_3COOH$: $\tau = 0{\cdot}28$ ($H_8$, q), 1·37 (q, $H_9$), 0·42 (q, $H_{10}$); $CD_3SOCD_3$: 0·55 (q, $H_8$), 1·82 (q, $H_9$), 0·91 (q, $H_{10}$); $J_{8,9} = 5{\cdot}5$; $J_{9,10} = 8{\cdot}0$; $J_{8,10} = 1{\cdot}8$. (Found: C, 39·77; H, 1·55; N, 59·02; $C_7H_3N_9$ requires: C, 39·45; H, 1·42; N, 59·14%).

*6-Methoxypyrido[3.2-d]tetrazolo[5.1-b]pyridazine* (XV)

(i) The azide XIV (213 mg) was heated in a soln of NaOMe in MeOH (prepared from 0·04 g Na and 2 ml MeOH) on a water bath for 1 hr. The reaction mixture was evaporated *in vacuo* to dryness, water (1 ml) was added and the separated product filtered off. Upon crystallization from N,N-dimethylformamide and EtOH (1:1) the pure compound (150 mg, 75%) had m.p. 243–245°. (Found: C, 47·68; H, 3·32; N, 41·54; $C_8H_6N_6O$ requires: C, 47·52; H, 2·99; N, 41·57%).

(ii) A similar procedure was applied to XII (1·03 g) and the product was obtained in 54% yield (0·54 g). Mixed m.p. with the compound prepared as described under (i) was without depression.

*6-Hydrazinopyrido[2.3-d]tetrazolo[5.1-b]pyridazine* (XVII)

Compound XVI (412 mg) was suspended in 80% hydrazine hydrate (2 ml). After an exothermic reaction, the mixture was heated to boiling, the starting compound dissolved completely and the formed product separated. Upon heating the mixture for 5 min and after cooling to room temp, the product was separated,

washed with cold water and crystallized from N,N-dimethylformamide and EtOH (1:1), yield 367 mg (94%); m.p. 282–284°. (Found: C, 41·82; H, 3·25; N, 55·72; $C_7H_6N_8$ requires: C, 41·58; H, 2·99; N, 55·43%).

6-*Azidopyrido*[2.3-d]*tetrazolo*[5.1-b]*pyridazine* (XVIII)

(i) This compound was prepared from XVII (194 mg), AcOH (4 ml of 50%) and $NaNO_2$ aq (75 mg in 1 ml water) as described for the isomeric XIV. The product (140 mg, 68% yield) was crystallized from EtOH and N,N-dimethylformamide (1:1), m.p. 197° (dec); IR spectrum (Nujol): 2141 $cm^{-1}$ ($N_3$); NMR spectrum: $CF_3COOH$: $\tau$ = 0·67 (q, $H_7$), 1·44 (q, $H_8$), 0·25 (q, $H_9$); $CD_3SOCD_3$: $\tau$ = 1·40 (q, $H_7$), 1·92 (q, $H_8$), 0·62 (q, $H_9$). $J_{7,9}$ = 1·8; $J_{7,8}$ = 8·0; $J_{8,9}$ = 5·5. The compound is photochromic. (Found: C, 39·72; H, 1·76, N, 59·02; $C_7H_3N_9$ requires: C, 39·45; H, 1·42; N, 59·14%).

(ii) A suspension of XX (4·0 g) and sodium azide (5·2 g) in EtOH (70 ml) was heated under reflux for 3 hr. The cooled reaction mixture was poured into iced water (100 ml), the inorganic salts dissolved and the residue filtered off and washed with water and dried (3·0 g, 71% yield). Upon crystallization from EtOH and N,N-dimethylformamide (1:1) the compound melted at 197° (dec). Mixed m.p. with the compound prepared as described under (i) was undepressed and IR spectra were identical.

6-*Methoxypyrido*[2.3-d]*tetrazolo*[5.1-b]*pyridazine* (XIX)

(i) Compound XVIII (0·53 g) was converted into XIX by applying the procedure described for the synthesis of XV from XIV. The pure compound (0·3 g, 61% yield) was obtained after crystallization from EtOH and N,N-dimethylformamide (2:1), m.p. 230–231°. (Found: C, 47·80; H, 2·86; N, 41·55; $C_8H_6N_6O$ requires: C, 47·52; H, 2·99; N, 41·57%).

(ii) Using a similar procedure and starting with XVI (1·03 g) the product XIX was obtained in 47% yield, m.p. 230–231°, mixed m.p. with the compound obtained as described under (i) was undepressed and IR spectra were identical.

*Isomerization of* 6-*azidopyrido*[3.2-d]*tetrazolo*[5.1-b]*pyridazine into* 6-*azidopyrido*[2.3-d]*tetrazolo*-[5.1-b]*pyridazine*

Compound XIV (50 mg) in a glass tube (about 5 mm) was placed in a preheated oil bath at 184°. After melting, crystals separated and the tube was left at the same temp for 2 min. The cooled solid was dissolved in N,N-dimethylformamide (0·5 ml), the soln was filtered and EtOH (2 ml) was added. After standing for 1 hr on ice the crystals were collected and a mixed m.p. and IR spectral comparison with an authentic specimen showed the compound was identical with XVIII.

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