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REACTIONS OF AZIDOAZOLOPYRIDAZINES WITH 1,3-DICARBONYL COMPOUNDS

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Abstract—Azidoazoloazines react with 1,3-dicarbonyl compounds to give cycloaddition products, 1,2,3-triazole derivatives, whose structures have been established by chemical transformations and spectroscopic data.

As a part of our studies of azolo- and azidopyridazines, in particular those having an attached azido group,[1-4] and the possibility of azidotetrazolo isomerization of these compounds,[5] we report their reactions with 1,3-dicarbonyl compounds. It is well known that alkyl or aryl azides react with active methylene compounds, in particular with 1,3-diketones or keto esters[6] to form 1,2,3-triazoles. So far, the corresponding heterocyclic azides have not been investigated in this respect and, in addition, the possibility of nitrene formation[7,8] makes these azides worthy of investigation.

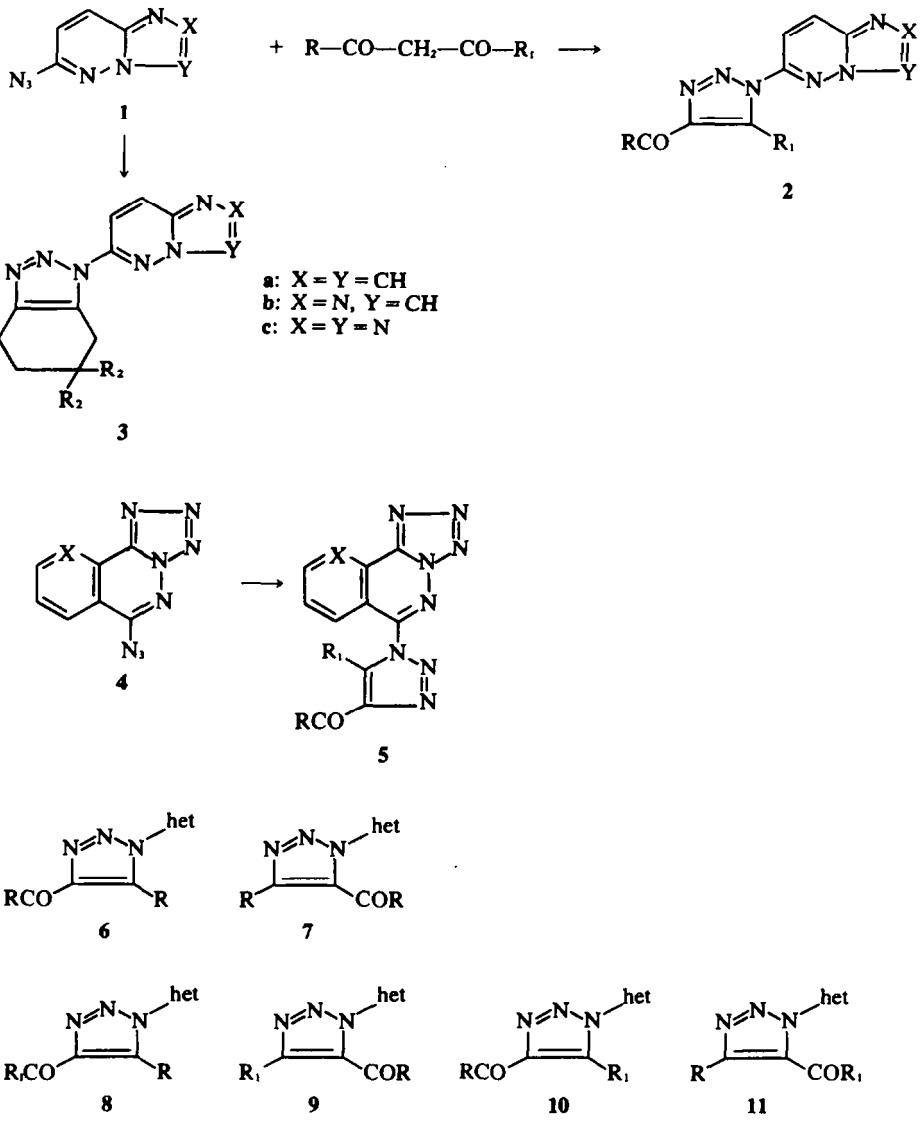
We have reacted 6 - azidoimidazo (1,2 - b)-, 6-azido - s - triazolo - (4,3 - b)-, 6 - azidotetrazolo (1,5 - b)-, 6 - azidopyrido (2,3 - d) - tetrazolo (1,5 - b) pyridazine or 6 - azidotetrazolo (1,5 - b) phthalazine with different 1,3 - dicarbonyl compounds such as acetylacetone, benzoylacetone, ethyl acetoacetate or benzoylacetate, diethyl acetonedicarboxylate, 1,3 - cyclohexanedione and its 5,5 - dimethyl analogue. Treatment of the corresponding heterocyclic azide with equimolar amount of the 1,3-dicarbonyl compound afforded products of the type **2**, **3** or **5** as concluded on the basis of analytical and spectroscopic data. In principle, there are two possible 1,2,3 - triazole ring formulations, **6** or **7**, whereas with unsymmetrical 1,3 - dicarbonyl compounds four possible structures, **8–11**, are conceivable. In order to clarify the structures of the cycloaddition products, several observations have to be taken into account.

In all cases, as concluded from NMR evidence, only one cycloadduct was formed and isolated. This parallels, for example, the specificity of cycloaddition of phenyl azide to enamines[9] where only one kind of cycloaddition product, resulting from electronic control, was formed. The reaction between **1c** and 1,3 - indanedione in the presence of triethylamine afforded besides 6 - aminotetrazolo (1,5 - b) pyridazine also 2 - diazo - 1,3 - indanedione[10] in high yield. This indicates that the reaction took place via the intermediates **12**, **13** and **14** to give **15**. If the reaction would follow in the opposite sense and involve as intermediate **16**, 1 - diazo - 2,3 - indanedione **17** or its decomposition products would be expected along with 6 - aminoazolopyridazine. The same observations, regarding the formation of 2 - diazo - 1,3 - indanedione could be made in the case of **1a**, **1b** or **4** (X = CH) as starting material.

The analogous reactions of the corresponding azidoazolopyridazines with acetylacetone could be followed in a NMR probe. Here, 3 - diazo - 2,4 - pentanedione[11] was detected among the decomposition products. A singlet at $\tau = 7{\cdot}63$ for both methyl groups is compatible only with a symmetrical structure, i.e. 3 - diazo - 2,4 - pentanedione. The same pattern could be observed when decomposing compound **2c** ($R = R_1 = Me$) in a separate experiment. At room temperature and in the presence of triethylamine, $t_{1/2}$ was about 45 min and 6 - aminotetrazolo (1,5 - b) pyridazine and 3 - diazo - 2,4 - pentanedione were formed. The same diazo compound was formed upon decomposition of compound **5** (X = CH, $R = R_1 = Me$) in the presence of triethylamine. On hand of all these results, structures **7**, **9** or **11** for cycloaddition products can be excluded.

By analogy with the above observations, it is possible to formulate the cycloaddition products with 1,3 - cyclohexanedione or its 5,5 - dimethyl analogue as **3**, with ethyl acetoacetate or benzoylacetate as **2** or **5** and with diethyl acetonedicarboxylate as **2** ($R_1 = CH_2COOEt$, R = OEt). The cycloaddition product formed with benzoylacetone, however, can be formulated to have either structure **8** or **10** (R = Me, R_1 = Ph). From the NMR spectrum of the product it became evident that the signal for the phenyl group is typical for a benzoyl group and this would correspond to a 4 - benzoyl derivative of 1,2,3 - triazole (**2**, R = Ph, R_1 = Me). This holds for all cycloaddition products with benzoylacetone.

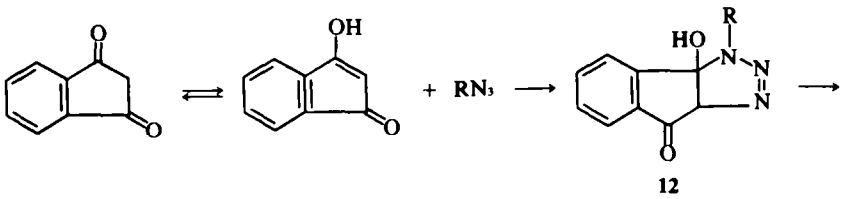
6 - Azidopyrido (2,3 - d) tetrazolo (1,5 - b) pyridazine (**4**, X = N) formed a cycloaddition product only with acetylacetone, whereas in all other



cases the corresponding 6-amino heterocycle was isolated. If the above mentioned azide was heated in an ethanolic solution of ethyl acetoacetate for 12 h it was transformed into a mixture of the isomeric 6 - aminopyrido (2,3 - d)- and 6 - aminopyrido (3,2 - d) tetrazolo (1,5 - b) pyridazine. The same mixture resulted when the compound reacted in a solution of diethyl acetonedicarboxylate in n-butanol. This indicates that prior to the reaction with the reactive methylene compound azido-tetrazolo isomerization, as already observed earlier,[12] took place. The preference for the formation of aminoheterocycles could be observed also in several other experiments, in particular when these reactions were conducted in the presence of a base.

4-Acetyltriazole derivatives of **2a** and **2b** reacted with hydrazine in two ways. Depending upon the reaction conditions, either the triazoline part is split off during the hydrazinolysis to give the corresponding 6 - hydrazinoazolopyridazine, or the corresponding hydrazone or phenylhydrazone (**18**) was formed. If a suspension of the hydrazone in toluene was heated under reflux for several hours the hydrazino function added to the triazole ring to give a pyrazolotriazole derivative (**19**). In all other cases hydrazinolysis afforded 6-hydrazinoazolopyridazines.

No cycloaddition products could be obtained from diethyl malonate and the azido heterocycles were transformed quantitatively into the corresponding 6 - aminoazolopyridazines. This is most probably due to a triazolo - diazo ring - chain tautomerism and subsequent decomposition into



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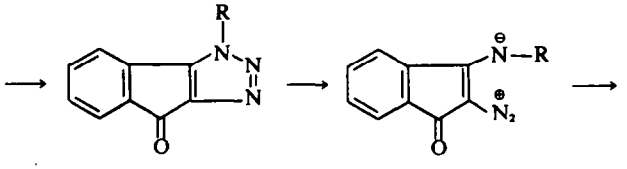

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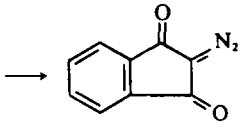

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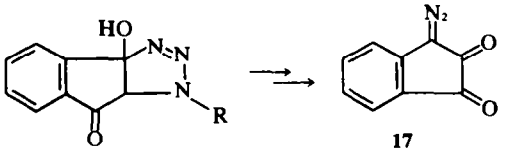

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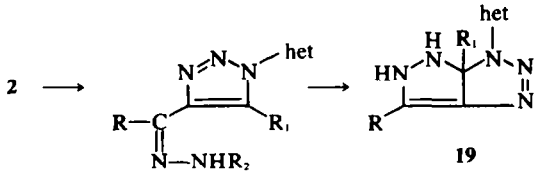

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het: a-imidazo(1,2-b)pyridazinyl-6'b-s-triazolo(4,3-b)pyridazinyl-6'-

the amino derivative. This type of tautomerism has been reported previously.[13]

EXPERIMENTAL

M.ps were determined on a Kofler apparatus. Spectral data were obtained from a JEOL-C-60HL NMR spectrometer and Hitachi-Perkin-Elmer RMU-6L mass spectrometer.

4 - *Benzoyl* - 5 - *methyl* - 1 - (*tetrazolo* (1,5*b*) *pyridazinyl* - 6') - 1*H*, 1,2,3 - *triazole* (**2c**, R = Ph, R_1 = Me). A mixture of compound **1c** (1·62 g; 0·01 mole), benzoylacetone (1·62 g; 0·01 mole) and ethanol (10 ml) was heated under reflux for 3 h. The separated product was filtered off and crystallized from ethanol and N,N - dimethylformamide. Yield 0·45 g (15%), m.p. 235–236°. The same product was obtained when the reaction was conducted in the presence of triethylamine (2 ml). NMR: (DMSO-d_6): τ = 1·50 (d, H_7), 0·85 (d, H_8), 6·98 (s, Me), 2·40 and 1·80 (m, Ph), J_{H_7,H_8} = 9·5 Hz. (Found: C, 54·98; H, 3·43; N, 36·70. Calc. for $C_{14}H_{10}N_8O$: C, 54·89; H, 3·29; N, 36·60%).

In the same manner the following compounds were prepared:

Compound **3c** (R_2 = H) in 63% yield, m.p. 244–245°. NMR (DMSO-d_6): τ = 1·48 (d, H_7), 0·95 (d, H_8), 7·5 (m, 5-CH_2), 6·60 (t, 7-CH_2), 7·5 (m, 6-CH_2), J_{H_7,H_8} = 9·5 Hz. (Found: C, 47·06; H, 3·43; N, 43·70. Calc. for $C_{10}H_8N_8O$: C, 46·89; H, 3·15; N, 43·76%.)

Compound **3c** (R_2 = Me) was obtained after 5 days of reflux in 28% yield, m.p. 213–214°. NMR (DMSO-d_6): τ = 1·55 (d, H_7), 1·00 (d, H_8), 7·42 (s, 5-CH_2), 6·65 (s, 7-CH_2), 8·85 (s, 6-Me), J_{H_7,H_8} = 9·5 Hz. (Found: C, 50·92; H, 4·29; N, 39·41. Calc. for $C_{12}H_{12}N_8O$: C, 50·70; H, 4·25; N, 39·44%).

Compound **2b** (R = Ph, R_1 = Me), m.p. 262–265° (18% yield). (Found: C, 58·95; H, 3·93; N, 32·14. Calc. for $C_{15}H_{11}N_7O$: C, 59·01; H, 3·63; N, 32·12%).

Compound **3b** (R_2 = H), m.p. 252–253° (20% yield). NMR (DMSO-d_6): τ = 2·03 (d, H_7), 1·37 (d, H_8), 0·30 (s, H_3), 7·50 (m, 6- and 5-CH_2), 6·60 (t, 7-CH_2), $J_{7,8}$ = 9·5 Hz. (Found: C, 51·53; H, 3·78; N, 38·25. Calc. for $C_{11}H_9N_7O$: C, 51·77; H, 3·55; N, 38·43%).

Compound **5** (X = CH, R = OEt, R_1 = Me), m.p. 270–273° (46% yield). (Found: C, 51·98; H, 3·90; N, 34·70. Calc. for $C_{14}H_{12}N_8O_2$: C, 51·84; H, 3·74; N, 34·56%). NMR (DMSO-d_6): τ = 7·67 (s, 5-Me), 5·95 (q, CH_2CH_3), 8·78 (t, CH_2CH_3), J_{Et} = 7·2 Hz, τ = 1·2 and 1·9 (m, $H_{7,8,9,10}$).

Compound **5** (X = CH, R = OEt, R_1 = Ph) was obtained in 38% yield, m.p. 244–249°. NMR (DMSO-d_6) τ = 2·60 (broad s, 5-Ph), 5·84 (q, CH_2CH_3), 8·80 (t, CH_2CH_3), 1·75 and 1·25 (m, $H_{7,8,9,10}$), J_{Et} = 7·2 Hz. (Found: C, 59·20; H, 3·92; N, 29·00. Calc. for $C_{19}H_{14}N_8O_2$: C, 59·05; H, 3·66; N, 29·01%).

4 - *Benzoyl* - 5 - *methyl* - 1 - (*imidazo* [1,2 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2a**, R = Ph, R_1 = Me). Compound **1a** (1·6 g), benzoylacetone (1·62 g) and few drops of ethanol were heated under reflux for 6 h on water bath. The separated product was collected, washed with ethanol and crystallized from ethanol and N,N - dimethylformamide (3:1). Yield 1·9 g (62%), m.p. 165°. Mass spectrum: M^+ = 304; NMR (DMSO-d_6): τ = 1·82 (d, H_2), 1·63 (d, H_3), 1·90 (d, H_7), 1·62 (d, H_8), 7·18 (s, 5-Me), 2·40 and 1·90 (m, 4-Ph), $J_{2,3}$ = 1·0, $J_{7,8}$ = 9·5 Hz. (Found: C, 62·95; H, 3·99; N, 27·46. Calc. for $C_{16}H_{12}N_6O$: C, 63·15; H, 3·98; N, 27·62%).

4 - *Carbethoxy* - 5 - *methyl* - 1 - (s - *triazolo* [4,3 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2b**, R = OEt, R_1 = Me). Compound **1b** (0·8 g) and ethyl acetoacetate (5 ml) were heated at 130° for 5 h. The separated product was filtered off and crystallized from ethanol (0·78 g, 57%), m.p. 175°. NMR (DMSO-d_6, 118°): τ = 0·28 (d, H_3), 2·02 (d, H_7), 1·28 (dd, H_8), 7·10 (s, 5-Me), 5·55 (q, $COOCH_2CH_3$), 8·60 (t, $COOCH_2CH_3$), J_{Et} = 7·5, $J_{3,8}$ = 0·8, $J_{7,8}$ = 10·5 Hz. (Found: C, 48·19; H, 4·00; N, 35·76. Calc. for $C_{11}H_{11}N_7O_2$: C, 48·35; H, 4·06; N, 35·88%).

In the same manner were prepared:

4 - *Carbethoxy* - 5 - *carbethoxymethyl* - 1 - (s - *triazolo* [4,3 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2b**, R = OEt, R_1 = CH_2COOEt), in 41% yield, m.p. 142–143°. NMR (DMSO-d_6): τ = 0·0 (d, H_3), 2·3 (d, H_7), 1·30 (dd, H_8), 5·40 (s, CH_2COOEt), 5·80 (q, 5-$CH_2CO_2CH_2CH_3$), 8·85 (t, 5-$CH_2CO_2CH_2CH_3$), 5·60 (q, 4-$CO_2CH_2CH_3$), 8·70 (t, 4-$CO_2CH_2CH_3$), J_{Et} = 7·2 Hz. (Found: C, 48·39; H, 4·41; N, 28·78. Calc. for $C_{14}H_{13}N_7O_4$: C, 48·70; H, 4·38; N, 28·39%).

4-*Acetyl*-5-*methyl*-1-(*tetrazolo* [1,5-b] *pyridazinyl*-6') - 1H - 1,2,3 - *triazole* (**2c**, R = R_1 = Me) was obtained in 87% yield, m.p. 214°. NMR (DMSO-d_6): τ = 1·62 (d, H_7), 1·0 (d, H_8), 7·08 (s, 5-Me), 7·32 (s, 4-MeCO), $J_{7,8}$ = 9·4 Hz. (Found: C, 44·08; H, 3·40; N, 45·74. Calc. for $C_9H_8N_8O$: C, 44·26; H, 3·30; N, 45·89%).

4 - *Carbethoxy* - 5 - *methyl* - 1 - (*tetrazolo* [1,5 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2c**, R = OEt, R_1 = Me), m.p. 175° (yield 61%). NMR (DMSO-d_6): τ = 1·62 (d, H_7), 0·98 (d, H_8), 7·13 (s, 5-Me), 5·65 (q, 4-$CO_2CH_2CH_3$), 8·68 (t, 4-$CO_2CH_2CH_3$), $J_{7,8}$ = 9·5, J_{Et} = 7·2 Hz. (Found: N, 40·63. Calc. for $C_{10}H_{10}N_8O_2$: N, 40·86%).

4 - *Acetyl* - 5 - *methyl* - 1 - (s - *triazolo* [4,3 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2b**, R = R_1 = Me), m.p. 204–205° (from ethanol, 68% yield). NMR (DMSO-d_6): τ = 0·05 (d, H_3), 1·95 (d, H_7), 1·15 (d, H_8), 7·10 (s, 5-Me), 7·30 (s, 4-MeCO), $J_{3,8}$ = 0·8, $J_{7,8}$ = 9·5 Hz. (Found: C, 49·45; H, 4·06; N, 40·61. Calc. for $C_{10}H_9N_7O$: C, 49·38; H, 3·73; N, 40·31%).

The product, when heated with hydrazine hydrate for 1 h, was transformed in 80% yield into 6 - hydrazino - s - triazolo (4,3 - b) - pyridazine, identical with an authentic specimen. If the same reaction was performed in ethanol (4 h, reflux) the corresponding hydrazone (**18b**, R = R_1 = Me, R_2 = H) was formed. M.p. 195°, from the melt new crystals separated and they melted at 250–260° (yield 67%, crystallized from ethanol). (Found: C, 47·15; H, 4·54; N, 48·91. Calc. for $C_{10}H_{11}N_9$: C, 46·68; H, 4·31; N, 49·01%).

4 - *Carbethoxy* - 5 - *phenyl* - 1 - (*tetrazolo* [1,5 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2c**, R = OEt, R_1 = Ph). A suspension of **1c** (0·81 g) in methanol (10 ml) was treated with ethyl benzoyl-acetate (0·96 g) and triethylamine (0·5 ml). The mixture was heated under reflux for 15 min, the separated product was collected and crystallized from ethanol and N,N - dimethylformamide (2:1), m.p. 210–211° (1·48 g, 88%). NMR (DMSO-d_6): τ = 2·00 (d, H_7), 1·10 (d, H_8), 5·72 (q, 4-$CO_2CH_2CH_3$), 8·85 (t, 4-$CO_2CH_2CH_3$), 2·65 (s, 5-Ph), $J_{7,8}$ = 9·6 Hz. (Found: C, 53·70; H, 3·73; N, 33·72. Calc. for $C_{15}H_{12}N_8O_2$: C, 53·57; H, 3·60; N, 33·32%).

In the same manner were prepared:

4 - *Carbethoxy* - 5 - *carbethoxymethyl* - 1 - (*tetrazolo* [1,5 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2c**, R = OEt, R_1 = CH_2COOEt), m.p. 147° (from ethanol, 82% yield), after 1 h of heating under reflux. NMR (DMSO-d_6, 50°): τ = 1·36 (d, H_7), 0·74 (d, H_8), 5·65 (q, 4-$CO_2CH_2CH_3$), 8·62 (t, 4-$CO_2CH_2CH_3$), 5·38 (s, 5-CH_2COOEt), 5·77 (q, 5-$CH_2CO_2CH_2CH_3$), 8·75 (t, 5-$CH_2CO_2CH_2CH_3$) J_{Et} = 6·7 Hz. (Found: C, 45·10; H, 4·28; N, 32·65. Calc. for $C_{13}H_{14}N_8O_4$: C, 45·09; H, 4·08; N, 32·36%).

4 - *Carbethoxy* - 5 - *phenyl* - 1 - (s - *triazolo* [4,3 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2b**, R = OEt, R_1 = Ph), m.p. 157° (from ethanol, 75% yield). NMR: (DMSO-d_6, 71°): τ = 0·50 (d, H_3), 2·38 (d, H_7), 1·40 (dd, H_8), 5·70 (q, 4-$CO_2CH_2CH_3$), 8·80 (t, 4-$CO_2CH_2CH_3$), 2·50 (s, 5-Ph), $J_{3,8}$ = 0·8, $J_{7,8}$ = 9·5, J_{Et} = 7·5 Hz. (Found: C, 56·76; H, 4·11; N, 30·01. Calc. for $C_{16}H_{13}N_7O_2$: C, 57·31; H, 3·91; N, 29·24%).

Reaction between 6-azidopyrido (2,3-d) *tetrazolo* (1,5-b) *pyridazine and acetylacetone.* Compound **4** (X = N) (0·53 g) and acetylacetone (0·25 g) were heated at 130° for 30 min. Upon cooling the product was collected and it was a mixture of 6 - aminopyrido (2,3 - d) tetrazolo (1,5 - b) pyridazine and of compound **5** (X = N, R = R_1 = Me) in a ratio of about 3:1, from the NMR spectrum.

If the above reaction was performed in the presence of sodium methylate (1 h) only the 6-amino compound was obtained in 80% yield, m.p. 297° (from ethanol and N,N - dimethylformamide) (lit.[1] gives m.p. > 285°. Also if the reaction was performed in the presence of other bases (diethylamine, aniline or N - methylaniline) only the 6-amino compound was formed.

4 - *Carbethoxy* - 5 - *phenyl* - 1 - (*imidazo* [1,2 - b] *pyridazinyl* - 6') - 1H - 1,2,3 - *triazole* (**2a**, R = OEt, R_1 = Me). (a) A mixture of **1a** (0·8 g), ethanol (15 ml), ethyl benzoylacetate (0·96 g) and triethylamine (0·5 ml) was heated under reflux for 2 h. Upon standing on ice overnight, the separated product was filtered off and crystallized from ethanol and N,N - dimethylformamide, 3:1 (yield 1·2 g, 72%), m.p. 116°.

(b) A mixture of **1a** (0·8 g) and ethyl benzoylacetate (4 ml) was heated at 130° for 5 h. Upon cooling, n-hexane (20 ml) was added and the mixture was left on ice overnight. The product was filtered off, washed with n-hexane

and crystallized from chloroform and n-hexane (1:5) (0·9 g, 54% yield), m.p. 116°. (Found: C, 61·18; H, 4·30; N, 24·84. Calc. for $C_{17}H_{14}N_6O_2$: C, 61·07; H, 4·22; N, 25·14%).

1 - (*Imidazo* [1,2 - b] *pyridazinyl* - 6') - 1*H* - 4,5,6,7 - *tetrahydrobenzotriazol* - 4 - *one* (**3a**, R_2 = H). A mixture of **1a** (0·8 g), cyclohexane - 1,3 - dione (0·56 g) and few drops of triethylamine was gently heated until the product separated. It was crystallized from ethanol and N,N - dimethylformamide (4:1) (yield 1·0 g, 78%), m.p. 265–267° (d). NMR (DMSO-d_6): τ = 2·25 (d, H_7), 1·70 (d, H_8), 2·19 (d, H_2), 1·80 (d, H_3), 6·65 (t, 7-CH_2), 7·50 (m, 5- and 6-CH_2), $J_{2,3}$ = 1·0, $J_{7,8}$ = 9·5 Hz. (Found: C, 56·46; H, 3·99; N, 33·02. Calc. for $C_{12}H_{10}N_6O$: C, 56·68; H, 3·96; N, 33·06%).

The 6,6 - dimethyl analog (**3a**, R_2 = Me) was prepared similarly (8 h reflux) in 85% yield, m.p. 235° (from ethanol and N,N - dimethylformamide, 2:1). (Found: C, 59·67; H, 5·10; N, 30·06. Calc. for $C_{14}H_{14}N_6O$: C, 59·56; H, 5·00; N, 29·77%).

4 - *Carbethoxy* - 5 - *methyl* - 1 - (*imidazo* [1,2 - b] *pyridazinyl* - 6') - 1*H* - 1,2,3 - *triazole* (**2a**, R = OEt, R_1 = Me). Compound **1a** (1·6 g) was suspended in ethyl acetoacetate (5 ml) and the mixture was heated at 140° for 7 h. The separated product was dissolved in hot ethanol, filtered from the insoluble residue, the filtrate treated with charcoal and upon cooling the separated product was collected (yield 59%), m.p. 168°. NMR ($CDCl_3$): τ = 2·15 (d, H_2), 2·00 (dd, H_3), 2·25 (d, H_7), 1·85 (dd, H_8), 7·05 (s, 5-Me), 5·55 (q, 4-$CO_2CH_2CH_3$), 8·55 (t, 4-$CO_2CH_2CH_3$), J_{Et} = 7·2, $J_{2,3}$ = 1·2, $J_{3,8}$ = 0·3, $J_{7,8}$ = 9·5 Hz. (Found: C, 53·08; H, 4·58; N, 31·04: Calc. for $C_{12}H_{12}N_6O$: C, 52·93; H, 4·44; N, 30·87%).

In a likewise manner were prepared: 4 - *Carbethoxy*-5-*carbethoxymethyl*-1-(*imidazo* [1,2-b] *pyridazinyl*-6')-1*H*-1,2,3-*triazole* (**2a**, R = OEt, R_1 = CH_2COOEt). Excess of diethyl acetonedicarboxylate was distilled off in vacuo at the end of the reaction. The residue was crystallized from ethanol (a small quantity of N,N - dimethylformamide was added) (yield 45%), m.p. 104–106°. NMR (DMSO-d_6): τ = 2·15 (d, H_2), 1·82 (dd, H_3), 2·28 (d, H_7), 2·62 (dd, H_8), 5·52 (s, 5-CH_2COOEt), 5·95 (q, 5-$CH_2CO_2CH_2CH_3$), 8·88 (t, 5-$CH_2CO_2CH_2CH_3$), J_{Et} = 7·5 Hz; τ = 5·65 (q, 4-$COOCH_2CH_3$), 8·65 (t, 4-$CO_2CH_2CH_3$), J_{Et} = 7·2 Hz. (Found: C, 52·16; H, 4·69; N, 24·24. Calc. for $C_{15}H_{16}N_6O_4$: C, 52·32; H, 4·68; N, 24·41%).

4 - *Acetyl* - 5 - *methyl* - 1 - (*imidazo* [1,2 - b] *pyridazinyl* - 6') - 1*H* - 1,2,3 - *triazole* (**2a**, R = R_1 = Me) was obtained in 91% yield, m.p. 190° (from ethanol). NMR (DMSO-d_6): τ = 2·00 (d, H_2), 1·50 (dd, H_3), 2·20 (d, H_7), 1·50 (dd, H_8), 7·20 (s, 5-Me), 7·32 (s, 4-MeCO), $J_{2,3}$ = 1·2, $J_{3,8}$ = 0·6, $J_{7,8}$ = 9·5 Hz. (Found: C, 54·34; H, 4·33; N, 34·88. Calc. for $C_{11}H_{10}N_6O$: C, 54·54; H, 4·16; N, 34·70%).

The compound, when heated with hydrazine for 1 h, was transformed in 71% yield into 6 - hydrazinoimidazo (1,2 - b) pyridazine, identical with an authentic specimen, m.p. 225°. If the same reaction was conducted in an ethanolic solution (3 h) the corresponding hydrazone (**18a**, R = R_1 = Me, R_2 = H) was obtained, m.p. 190–191° (from ethanol). NMR (DMSO-d_6): τ = 2·12 (d, H_2), 1·62 (dd, H_3), 2·32 (d, H_7), 1·62 (dd, H_8), 7·78 (s, 4MeC=), 7·30 (s, 5-Me), 3·6 (broad, NH), $J_{2,3}$ = 1·2; $J_{3,8}$ = 0·6, $J_{7,8}$ = 9·5 Hz. (Found: C, 51·51; H, 4·82; N, 43·96. Calc. for $C_{11}H_{12}N_8$: C, 51·55; H, 4·72; N, 43·73%).

Similarly, the phenylhydrazone (**18a**, R = R_1 = Me, R_2 = Ph) was prepared, m.p. 203° (from ethanol and N,N - dimethylformamide, 1:2). (Found: N, 33·82. Calc. for $C_{17}H_{16}N_8$: N, 33·72%).

1 - (*s* - *Triazolo* [4,3 - b] *pyridazinyl* - 6') - 4,6a - *dimethyl* - 5,6 - *dihydro* - 6a*H* - *pyrazolo* (3,4 - d) - 1,2,3 - *triazole* (**19b**, R = R_1 = Me). A suspension of the hydrazone (**18b**, R = R_1 = Me, R_2 = H) (0·257 g) in toluene (5 ml) was heated under reflux for 3 h. The product was crystallized from ethanol and N,N - dimethylformamide (3:1), m.p. 256° (yield almost quantitative). NMR (DMSO-d_6, 40°): τ = 0·43 (d, H_3), 2·83 (d, H_7), 1·54 (dd, H_8), 7·42 (s, 4-Me), 7·51 (s, 6a-Me), 3·02 (broad, NH), $J_{3,8}$ = 0·8, $J_{7,8}$ = 9·7 Hz. (Found: C, 46·81; H, 4·68; N, 48·79. Calc. for $C_{10}H_{11}N_9$: C, 46·68; H, 4·31; N, 49·01%).

1 - (*Imidazo* [1,2 - b] *pyridazinyl* - 6') - 4,6a - *dimethyl* - 5,6 - *dihydro* - 6a*H* - *pyrazolo* (3,4 - d) - 1,2,3 - *triazole* **19a**, R = R_1 = Me) was prepared in an analogous way, m.p. 203° (from ethanol and N,N - dimethylformamide, 4:1). NMR (DMSO-d_6, 83°): τ = 2·40 (d, H_2), 2·00 (dd, H_3), 3·19 (d, H_7), 2·05 (dd, H_8), 7·46 (s, 4-Me), 7·58 (s, 6a-Me), 3·25 (broad, NH), $J_{2,3}$ = 1·2, $J_{3,8}$ = 0·6, $J_{7,8}$ = 9·6 Hz. (Found: C, 51·42; H, 4·68; N, 43·93. Calc. for $C_{11}H_{12}N_8$: C, 51·55; H, 4·72; N, 43·73%).

6 - *Methoxytetrazolo* (1,5 - b) *pyridazine*. Compound **2c** (R = R_1 = Me) (0·6 g) was heated under reflux with a methanolic solution of sodium methylate (prepared from 0·1 g sodium and 10 ml of methanol) for 10 min. From the chilled solution the product separated (0·29 g, 79%) and had m.p. 154° (lit.[14] m.p. 154·5°). The same product was obtained if the azido compound was heated in the presence of acetylacetone and triethylamine for 5 min.

Reaction between 6 - *azidotetrazolo* (1,5 - b) *pyridazine and indane* - 1,3 - *dione*. A suspension of indane - 1,3 - dione (0·73 g) in ethanol (15 ml) was treated with triethylamine (2 ml) and cooled to 0°. Under stirring, **1c** (0·81 g) was added portion-wise and the mixture was held at 0° for 3 h. After standing at room temperature for 30 min, the product was filtered off, suspended in ethanol (15 ml), heated to 50°, filtered and the filtrate evaporated to dryness in vacuo at room temperature. The insoluble part was 6 - aminotetrazolo (1,5 - b) pyridazine (0·69 g, 88%). The product which was obtained from the filtrate was crystallized from ethanol to give pure 2 - diazo - 1,3 - indanedione (0·85 g), m.p. 150° (lit[10] m.p. 149°) and mixed m.p. with an authentic specimen undepressed.

In an analogous way indane - 1,3 - dione reacted with compounds **4** (X = CH), **1a** and **1b** to give the corresponding amino derivatives and **15**.

Reaction between 6 - *azidotetrazolo* (1,5 - b) *pyridazine and acetylacetone*. A mixture of **1c** (32 mg), acetylacetone (20 mg), DMSO-d_6 (0·5 ml) and triethylamine (30 mg) was placed in a NMR probe at room temperature. After 40 min the reaction mixture contained about 1/3 of the starting azide, 1/3 of compound **2c** (R = R_1 = Me) and 1/3 of 6 - aminotetrazolo (1,5 - b) pyridazine. A complete conversion could be observed after 20 h.

The same conversion could be observed when compound **2c** (R = R_1 = Me) (49 mg) was mixed with DMSO-d_6 (0·5 ml) and triethylamine (30 mg) and the reaction followed in a NMR probe at room temperature. After 45 min about 50% of the starting compound was transformed into 6 - aminotetrazolo (1,5 - b) pyridazine.

The same conversion was observed either with **4** (X = CH) in the presence of acetylacetone and triethylamine in DMSO-d_6 or if compound **5** (X = CH, R = R_1 = Me) was decomposed in the presence of triethylamine. Both reactions were followed in a NMR probe at 100° and in the first case the formation of the corresponding amino compound was complete in 10 min, whereas in the second case 5 min were necessary for completion.

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