3-Diazopyrazolo[3,4-*b*]pyridine, A Versatile Synthon for New Heterocyclic Systems

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3-Diazopyrazolo[3,4-*b*]pyridine was synthesized and its transformations were investigated. With reactive methylene compounds the corresponding hydrazones are formed and they can be cyclized into condensed 1,2,4-triazine derivatives. With amines of thiols the diazo compound forms triazenes or diazosulfides. From hydrazines tetrazenes are formed first and they give upon fragmentation a mixture of N-N or C-N bond fission products. The diazo compound undergoes cycloaddition, reacting as a 1,2-dipole. 3-Azidopyrazolo[3,4-*b*]pyridine was prepared and converted into the tetrazolo isomer, whereas the 3-amino compound was used for the synthesis of some pyridopyrazolopyrimidines.

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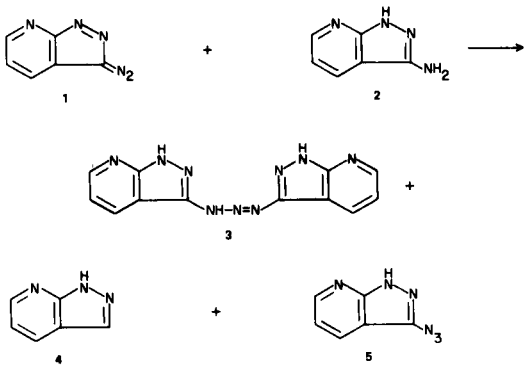
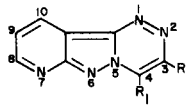
In our previous communications we have shown the utility of heterocyclic diazo compounds in organic synthesis (1-8). In addition, these compounds were also valuable for aza-transfer studies (9-12). Moreover, several heterocyclic diazo compounds possess biological activity. For example, 5-diazouracil inhibits cell division (13), causes an increase in the mean cell volume (14) and has a broad-spectrum *in vitro* activity against pathogenic bacteria (15). On the other hand, pyrazolopyrimidines which are purine analogs, were shown to have useful properties as antimetabolites in purine biochemical synthesis (16-19). All this prompted us to investigate the chemistry of pyrazolopyridines and in particular that of 3-diazopyrazolo[3,4-*b*]pyridine.

The preparation of the starting compound presented at the beginning some difficulties since the normal diazotization procedure of 3-aminopyrazolo[3,4-*b*]-pyridine afforded a mixture of the parent compound (**4**), the azide (**5**) and the triazene (**3**) together with the anticipated diazo compound (**1**). That this mixture originates from the initially formed triazene (**3**) could be established by a separate experiment between the amine and the diazo compound. Here too, a mixture of all above mentioned products was identified in the reaction mixture. The diazo compound (**1**) could be prepared in fair yield by very slow diazotization and from the diazonium

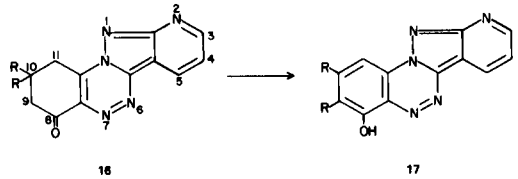




No.	R	R_1
13	COMe	Me
14	COPh	Me
15	COOEt	Me

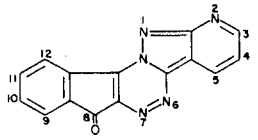
tetrafluoroborate upon neutralizaiton the free diazo compound was obtained.

The diazo compound (**1**) reacted with reactive methylene groups to give the corresponding hydrazones **6-12** (or tautomers). These, when heated alone, in an ethanolic or *N,N*-dimethylformamide solution were cyclized, but in the presence of some mineral acid the cyclization of some hydrazones was accomplished already in 10 minutes. For the tricycle **13** the structure follows straightforward, whereas for **14** also the alternative structure, *i.e.* as 3-acetyl-4-phenyl derivative is theoretically possible. The later structure could be eliminated on account of nmr and mass spectroscopic data, and for **15** an alternative structure of a condensed triazinone is excluded for the same reason.



Similarly for the cyclization product **16** (R = H) several tautomeric structures involving keto-enol forms or different position of the double bond in the carbocyclic part of the molecule are possible. From nmr spectrum only structure **16** (R = H) is compatible with three methylene groups. Similarly, for the dimethyl analog (**16**, R = Me), in the nmr spectrum two singlets for two methylene groups and a singlet for both methyl groups are discernible, and this eliminates other possible tautomeric structures. On heating alone or in the presence of concentrated sulfuric acid both compounds are aromatized

to **17**. However, in the case of the dimethyl analog the nmr spectrum of the aromatized product shows signals for three pyridine protons at τ = 1.1 (m) and 2.52 (dd) with J = 4.6 and 8.0 Hz, an aromatic proton at τ = 2.16 (s) and two methyl singlets at τ = 7.46 and 7.67. Since both methyl groups are magnetically nonequivalent, it follows that during aromatization a methyl group has migrated to the neighbouring position. That migration occurred to position 9 and not to position 11 of this tetracycle follows from correlation of chemical shifts with the unsubstituted analog (**17**, R = H), the signal for H_{11} being more shielded than that for H_9. From indane-1,3-dione, the pentacyclic compound (**18**) was obtained in a similar manner upon



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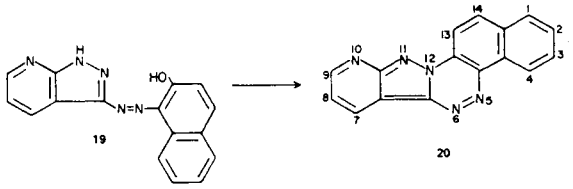
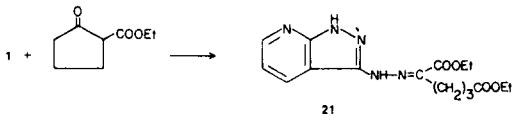
prolonged heating in concentrated sulfuric acid. The diazo compound (**1**) when coupled to 2-naphthol gives the azo compound **19** which could be cyclized subsequently into the pentacyclic compound **20**.



19 **20**

An unusual reaction could be observed when **1** reacted with ethyl cyclopentanone-2-carboxylate. Instead of the anticipated coupling product the hydrazone of diethyl α-ketoadipate (**21**) was isolated, indicating that cleavage



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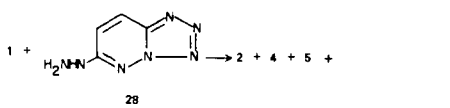
of the cyclopentanone ring occurred during the reaction. This is comparable to the known Japp-Klingemann reaction (20) in which coupling of diazonium salts and cyclic β-keto esters produced ring-opened products (21,22).

3-Diazopyrazolo[3,4-*b*]pyridine reacts with various primary or secondary amines and thiols to give the corresponding triazenes or diazosulfides. With hydrazines tetrazenes are formed first and they decompose subsequently into various products. The isolated or identified



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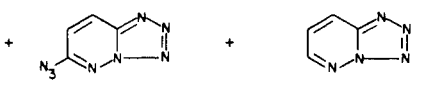
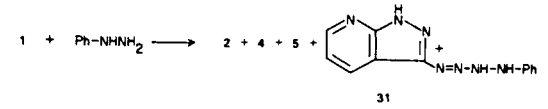


29 **30**

products from the reaction between the diazo compound (**1**) and phenylhydrazine correspond to fission of the



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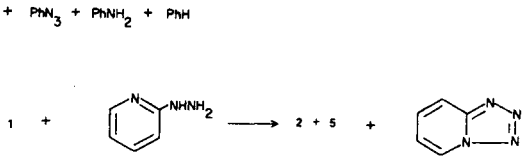

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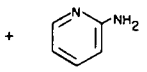

tetrazene (**31**) at all N-N and C-N bonds, giving a mixture of compounds **2**, **4**, **5**, benzene, aniline and phenylazide. The decomposition of the tetrazene (**31**) in dimethyl sulfoxide at moderate temperature, when followed by nmr, is accompanied by CIDNP effect, indicating a homolytic cleavage of the tetrazene into an intermediate radical pair before formation of the observed decompositions products (23). The identification of all above mentioned products supports also the structure of a 1,4-tetrazene as we have already shown in other cases with the aid of labelled tetrazenes (10). In a similar manner, compound **1** reacts also with **28** to give a mixture of **2**, **4**, **5**, **29** and **30**, or with hydrazine to give a mixture of compounds **3**, **4** and **5**, or with 2-hydrazinopyridine to give compounds **2**, **5**, **32** and 2-aminopyridine. Decomposition of the triazene (**24**) in the presence of concentrated hydrobromic acid afforded a mixture 3-bromopyrazolo[3,4-*b*]pyridine and 2-bromopyridine, indicating cleavage at both sides of the triazene group.

Some photochemical experiments were also performed in order to establish the stability and reactivity of **1**. The diazo compound (**1**), when photolized in methanol gives the parent compound (**4**), whereas in benzene, the 3-phenyl analog was obtained in good yield.

In view of the known reactivity of diazo compounds in cycloaddition reactions, heterocyclic diazo compounds with the diazo group at position *ortho* to a ring nitrogen are of particular interest since they can be regarded as 1,2-, 1,3- or 1,4-dipoles. So far, in most cycloadditions they react as 1,3-dipoles (8), although for 3-diazo-4,5-dicyanoimidazole cycloaddition is reported in which it reacts as a 1,2-dipolar species (24). Pyrazolo[3,4-*b*]pyridine-3-diazonium tetrafluoroborate reacted with 2,3-dimethylbutadiene at 0° to give a product to which the structure

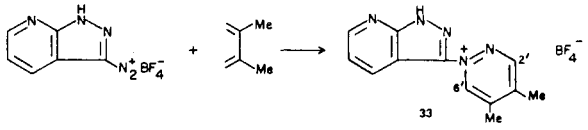

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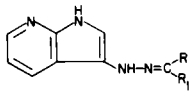
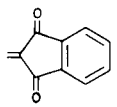
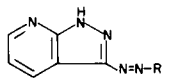
Table I



Compound No.	R	R_1	M.p. °C	Formula	Analytical data Calculated	Analytical data Found	Mass spectrum M^+	Nmr data (τ)
6	COMe	COMe	180-184 (a)	$C_{11}H_{11}N_5O_2$	C 53.87 H 4.52 N 28.56	C 54.04 H 4.71 N 28.39	245 (100%)	
7	COPh	COMe	159-162	$C_{16}H_{13}N_5O_2$	C 62.53 H 4.26 N 22.79	C 62.60 H 4.57 N 22.82	307 (10%)	DMSO-d_6: 1.44 (m, H_4), 3.0 (dd, H_5), 1.44 (m, H_6), 2.0-2.85 (m, Ph), 7.45 (s, Me), $J_{4,5}$ = 8.2, $J_{5,6}$ = 4.2 Hz.
8	COMe	COOEt	174-176	$C_{12}H_{13}N_5O_3$	C 52.36 H 4.76 N 25.43	C 52.47 H 4.75 N 25.30	275 (84%)	
9	COPh	COOEt	163-165	$C_{17}H_{15}N_5O_3$	C 60.53 H 4.48 N 20.76	C 60.60 H 4.59 N 20.91	337 (18%)	DMSO-d_6: 1.45 (m, H_4), 3.15 (dd, H_5), 1.45 (m, H_6), 2.0-2.65 (m, Ph), 5.62 (q, $COOCH_2Me$), 8.70 (t, $COOCH_2CH_3$), $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.5, $J_{5,6}$ = 4.5, J_{Et} = 7.0 Hz.
10	-$CO(CH_2)_3CO$-		252-257	$C_{12}H_{11}N_5O_2$	C 56.02 H 4.31 N 27.33	C 57.32 H 4.74 N 26.94	257 (25%)	DMSO-d_6 (60°): 1.45 (m, H_4), 2.76 (dd, H_5), 1.45 (m, H_6), 7.4 (m, 4′-CH_2, 6′-CH_2), 7.95 (m, 5′-CH_2), $J_{4,5}$ = 8.0, $J_{5,6}$ = 5.0 Hz.
11	-$COCH_2C(Me)_2CH_2CO$-		195-198	$C_{14}H_{15}N_5O$	C 58.93 H 5.30 N 24.55	C 59.15 H 5.28 N 24.85	285 (100%)	DMSO-d_6: 1.32 (m, H_4), 2.64 (m, H_5), 1.32 (m, H_6), 7.35 (s, 4′-CH_2, 6′-CH_2), 8.92 (s, Me).
12			269-272 (a)	$C_{15}H_9N_5O_2$	C 61.85 H 3.11 N 24.05	C 61.56 H 3.21 N 24.21	291 (44%)	DMSO-d_6 (120°): 1.45 (dd, H_4), 2.73 (dd, H_5), 1.38 (dd, H_6), 2.08 (s, H_4, H_5, H_6, H_7), $J_{4,5}$ = 7.2, $J_{4,6}$ = 1.5, $J_{5,6}$ = 5.0 Hz.

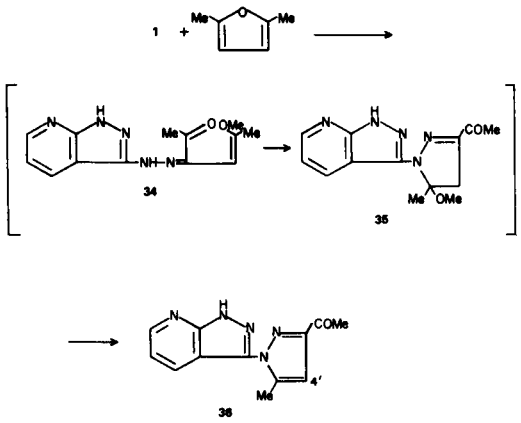
(a) Conversion to a cyclic product.

Table II

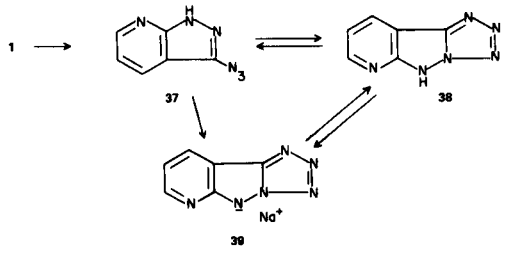


Compound No.	R	M.p. °C	Solvent for crystallization	Formula	Analytical data Calculated	Found	Mass Spectrum M^+	Nmr (τ)
22	$-NEt_2$	196-199	benzene	$C_{10}H_{14}N_6$	C 55.03 H 6.47 N 38.51	C 54.89 H 6.50 N 38.68	218 (100%)	Deuteriochloroform: 1,5 (dd, H_4), 2.88 (dd, H_5), 1.38 (dd, H_6), 6.53 [q, $N(CH_2Me)_2$], 8.65 [t, $N(CH_2CH_3)_2$], $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.8, $J_{5,6}$ = 5.0, J_{Et} = 7.0 Hz.
23	-NHPh	196-198	ethanol and aniline	$C_{12}H_{10}N_6$	C 60.49 H 4.23 N 35.28	C 60.33 H 4.31 N 34.91	238 (9%)	DMSO-d_6: 1,48 (m, H_4), 2.65 (m, H_5), 1.48 (m, H_6), 2.65 (m, Ph).
24		160-170 dec.	ethanol and *N,N*-dimethyl-formamide	$C_{11}H_9N_7$	C 55.22 H 3.79	C 54.67 H 4.28	239 (19%)	DMSO-d_6: 1.40 (m, H_4), 2.6 to 3.05 (m, H_5), 1.40 (m, H_6), 1.6 (m, H_6'), 2.1 (m, H_4'), 2.5 (dd, H_3'), 2.6 to 3.05 (m, H_5'), $J_{3',4'}$ = 7.5, $J_{4',5'}$ = 7.0, $J_{4',6'}$ = 2.0, $J_{5',6'}$ = 4.8 Hz.
25	-S-Ph	>115 dec.	chloroform and petroleum ether	$C_{12}H_9N_5S$	C 56.45 H 3.55 N 27.43	C 56.84 H 3.16 N 27.55	255 (7%)	DMSO-d_6: 1.77 (dd, H_4), 2.4 (m, H_5), 1.37 (dd, H_6), 2.4 (m, Ph), $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.8, $J_{5,6}$ = 4.4 Hz.
26		137-139 dec.	ethanol (washed)	$C_{11}H_8N_6S$	C 51.56 H 3.15 N 32.80	C 51.26 H 3.33 N 32.73	228 (M^+-N_2) (7%)	DMSO-d_6: 1.55 (dd, H_4), 2.4 to 2.7 (m, H_5), 1.28 (m, H_6), 1.28 (m, H_6'), 1.95 (m, H_3',H_4'), 2.4 to 2.7 (m, H_5'), $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.5, $J_{5,6}$ = 4.5 Hz.
27	$-SCH_2COOEt$	121-124 dec.	ethanol	$C_{10}H_{11}N_5O_2S$	C 45.28 H 4.18 N 26.41	C 45.41 H 4.35 N 26.27		DMF-d_7: 1.28 (dd, H_4), 2.44 (dd, H_5), 1.16 (dd, H_6), 5.26 (s, $-CH_2-$), 5.73 (q, $COOCH_2Me$), 8.72 (t, $COOCH_2CH_3$), $J_{4,5}$ = 8.3, $J_{4,6}$ = 1.6, $J_{5,6}$ = 4.8, J_{Et} = 7.2 Hz.

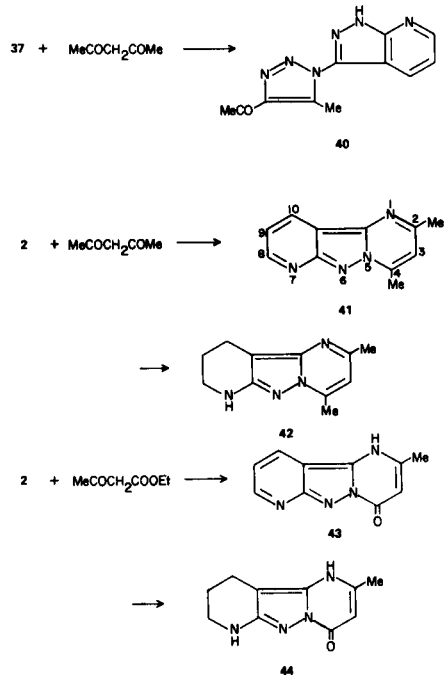
of a 1,2-cycloadduct (**33**) can be assigned on the basis of nmr spectroscipic and analytical data. On the other hand, the reaction between **1** and 2,5-dimethylfuran took a quite different course. The product which was formed after addition of **1** at 0° and then after standing at room temperature had molecular weight 241. This corresponds to an addition product and on the basis of nmr spectroscopic and analytical data, the compound is most adequately represented by the structure **36**. Its formation can be envisaged *via* the intermediates **34** and **35**, which is similar to the reaction with *p*-nitrobenzenediazonium chloride (25).



As a continuation of our interest in azido-tetrazolo isomerizations in the azine series (26), this phenomenon was investigated recently in the thiazolopyridine series (28). Therefore, it seemed worthwhile to examine the hitherto unknown 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine. This could be prepared from **1** and ethanolic hydroxylamine at 0°, whereas with sodium azide in aqueous ethanol a mixture of the azide (**37**) and tetrazole (**38**) was obtained. The azide is the more stable isomer since it is formed from the tetrazole by sublimation or in hot *N,N*-dimethylformamide. Alternatively, the azide (**37**) could be converted into the tetrazole (**38**) in the presence of



sodium methylate, inducing the formation of the sodium salt (**39**), which gives the pure tetrazole (**38**) upon acidification. The azide undergoes cycloaddition with acetylacetone, *i.e.* with its enol form, and the product **40** was obtained. Its structure follows from nmr data and is in accordance with our previous observations (29,30).



Finally, some cyclizations were performed with 3-amino-1*H*-pyrazolo[3,4-*b*]pyridine (**2**). The compound reacted thermally either with acetylacetone or ethyl acetoacetate and in the presence of polyphosphoric acid to give the pyridopyrazolopyrimidines **41** and **43**. When hydrogenated in the presence of palladized carbon they are transformed into the corresponding tetrahydro derivatives **42** and **44**. These results are comparable to observations made during reduction of some heterocyclic systems with bridgehead nitrogen where the pyridine part of the molecule is reduced preferentially (31).

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. All nmr spectra were obtained on a JEOL JNM C60-HL spectrometer and mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6L instrument.

3-Diazopyrazolo[3,4-*b*]pyridine (**1**).

A suspension of 3-amino-1*H*-pyrazolo[3,4-*b*]pyridine (**2**) (32) (0.5 g.) in methanol (5 ml.) was cooled to 0°, aqueous fluoroboric acid (1 ml. of 50%) and ether (10 ml.) were added and the precipitate filtered. The salt was dissolved in methanol (60 ml.) and this solution was added dropwise into a stirred and externally cooled solution (0°) of methanol (20 ml.), aqueous fluoroboric acid (0.5 ml. of 50%) and isoamyl nitrite (3 ml.). After half of the solution was added (1 hour), additional isoamyl nitrite (1 ml.) was added and the addition of the amine salt solution was continued for 1.5 hour. During addition the solution should be only yellow or slightly orange coloured, otherwise the rate of addition is too fast. After addition was complete the solution was left to stand on ice for 1 hour and then evaporated *in vacuo* at 20° to about 10 ml. After addition of ether (10 ml.) the crystals were filtered and washed with diethyl ether, m.p. 170-195° dec. (yield 57%); ms: $M^+ - HBF_4$ = 145 (45%); nmr (DMSO-d_6): τ = 1.28 (dd, H_6),

1.38 (dd, H_4), 2.42 (dd, H_5), 0.0 (s, NH); $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.4, $J_{5,6}$ = 4.0 Hz.

The so obtained diazonium salt (1 g.) was suspended in water (10 ml.) and neutralized with sodium bicarbonate to *p*H 6-7. The mixture was extracted several times with chloroform and the obtained product crystallized from a mixture of chloroform and petroleum ether, m.p. 150-152° dec. with explosion (yield 80%); ms: M^+ = 145 (44%); nmr (deuteriochloroform): τ = 1.35 (dd, H_6), 1.84 (dd, H_4), 2.67 (dd, H_5), $J_{4,5}$ = 8.0, $J_{5,6}$ = 4.0, $J_{4,6}$ = 1.6 Hz.

Anal. Calcd. for $C_6H_3N_5$: C, 49.65; H, 2.08; N, 48.26. Found: C, 49.66; H, 2.04; N, 48.35.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and 3-amino-1*H*-pyrazolo[3,4-*b*]pyridine.

A. Diazotization of 3-Amino-1*H*-pyrazolo[3,4-*b*]pyridine.

A solution of 3-amino-1*H*-pyrazolo[3,4-*b*]pyridine (**2**) (1.0 g.) in water (10 ml.) and concentrated hydrochloric acid (2 ml.) was cooled to 0° and diazotized with a solution of sodium nitrite (0.62 g.) in water (2 ml.). After standing on ice for 40 minutes the reaction mixture was diluted with water (15 ml.) and neutralized with solid sodium bicarbonate to *p*H 6. The separated product was filtered and sublimed at 130-140°. The sublimate (150 mg.) was identified as 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine (**5**). The residue (250 mg.) was the triazene (**3**). Extraction of the filtrate with chloroform afforded a mixture of 3-diazopyrazolo[3,4-*b*]-pyridine (**1**), 1*H*-pyrazolo[3,4-*b*]pyridine (**4**) and a small amount of 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine (**5**). The diazo compound was obtained pure after crystallization of the mixture from a mixture of chloroform and petroleum ether, yield 60 mg. The parent compound was obtained pure after evaporation of the solvent and sublimation at 90°/10 mm.

B.

A solution of 3-aminopyrazolopyridine (**2**) (134 mg.) and 3-diazopyrazolo[3,4-*b*]pyridine (**1**) (145 mg.) in cold ethanol (5 ml.) was left to stand at 0° for 1 hour. The separated product was filtered and washed with ethanol and then crystallized from a mixture of aqueous ethanol and dimethyl sulfoxide. The triazene (**3**) (80 mg.) had m.p. 252-254°; ms: m/e = 251 (M^+- 28) (5%); nmr (DMSO-d_6, 130°): τ = 1.48 (dd, H_6 and H_6'), 1.67 (dd, H_4 and H_4'), 2.84 (dd, H_5 and H_5'), $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.5, $J_{5,6}$ = 4.5 Hz.

Anal. Calcd. for $C_{12}H_9N_9$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.85; H, 3.53; N, 44.81.

The filtrate was evaporated to dryness and the residue sublimed at 100°/10 mm. The sublimate was identified as 1*H*-pyrazolo-[3,4-*b*]pyridine (**4**) (20 mg.). Sublimation was continued at 130-140°/10 mm and the product obtained was identified as 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine (**5**).

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and 1,3-Dicarbonyl Compounds.

A cooled solution of 3-diazopyrazolo[3,4-*b*]pyridine (145 mg., 1 mmole) in ethanol (4 ml.) was treated at 0° with 1 mmole of the corresponding 1,3-dicarbonyl compound and the reaction mixture was stirred at 0° for 4-5 hours, the product was filtered and washed with ethanol. In the case of ethyl acetoacetate, after 30 minutes the reaction mixture was diluted with water (4 ml.), the product filtered and washed with ethanol. If necessary, the product can be crystallized from ethanol, or aqueous ethanol, or a mixture of ethanol and *N,N*-dimethylformamide. The condensation products (**6-12**) are presented in Table I.

Cyclization of the Condensation Products into Fused 1,2,4-Triazine Derivatives.

One mmole of the corresponding hydrazone was suspended in ethanol (7 to 10 ml.) and the reaction mixture was heated under reflux for 1 hour. In the presence of few drops of hydrochloric acid the cyclization can be accomplished in 5-10 minutes. The solvent was evaporated *in vacuo* and the residue washed with diethyl ether. In this manner the following compounds were synthesized.

3-Acetyl-4-methylpyrido[3′,2′:4,5]pyrazolo[3,2-*c*]-1,2,4-triazine (**13**).

Compound **13** was obtained from **6** in 50% yield, m.p. 174-175°; ms: M^+ = 227 (10%); nmr (DMSO-d_6): τ = 0.95 (m, H_8, H_{10}), 2.4 (dd, H_9), 6.83 (s, COMe), 7.1 (s, Me), $J_{8,9}$ = 4.4, $J_{9,10}$ = 8.0 Hz.

Anal. Calcd. for $C_{11}H_9N_5O$: C, 58.14; H, 3.99; N, 30.82. Found: C, 57.82; H, 4.14; N, 30.49.

3-Benzoyl-4-methylpyrido[3′,2′:4,5]pyrazolo[3,2-*c*]-1,2,4-triazine (**14**).

Compound **14** was obtained from **7** in 66% yield, m.p. 180-182°; ms: M^+ = 289 (100%); nmr (DMSO-d_6): τ = 0.87 (m, H_8, H_{10}), 1.9-2.35 (m, C_6H_5), 2.35 (dd, H_9), 6.97 (s, Me), $J_{8,9}$ = 4.0, $J_{9,10}$ = 8.0 Hz.

Anal. Calcd. for $C_{16}H_{11}N_5O$: C, 66.42; H, 3.83; N, 24.21. Found: C, 66.61; H, 4.17; N, 24.52.

3-Carbethoxy-4-methylpyrido[3′,2′:4,5]pyrazolo[3,2-*c*]-1,2,4-triazine (**15**).

Compound **15** was obtained from **8** in 58% yield, m.p. 142-143°; ms: M^+ = 257 (100%): nmr (DMSO-d_6): τ = 0.9 (m, H_8, H_{10}), 2.36 (dd, H_9), 5.45 (q, $COOCH_2Me$), 6.8 (s, Me), 8.55 (t, $COOCH_2CH_3$), $J_{8,9}$ = 4.5, $J_{9,10}$ = 8.0, J_{Et} = 7.0 Hz.

Anal. Calcd. for $C_{12}H_{11}N_5O$: C, 56.02; H, 4.31; N, 27.23. Found: C, 56.05; H, 4.48; N, 27.16.

8,9,10,11-Tetrahydropyrido[3′,2′:4,5]pyrazolo[3,2-*c*]benzo[*e*]-1,2,4-triazine (**16**, R = H).

Compound **16** (R = H) was obtained upon heating the hydrazone **10** for 10 minutes in *N,N*-dimethylformamide in 55% yield, m.p. 207-211° (with conversion into the aromatic compound **17** (R = H); ms: M^+ = 239 (100%); nmr (DMSO-d_6): τ = 1.0 (m, H_3, H_5), 2.46 (dd, H_4); 6.35 (t, 11-CH_2), 7.1 (m, 9- and 10-CH_2), $J_{3,4}$ = 4.4, $J_{4,5}$ = 8.0 Hz.

Anal. Calcd. for $C_{12}H_9N_5O$: C, 60.24; H, 3.79; N, 29.28. Found: C, 60.60; H, 3.47; N, 29.32.

8-Hydroxypyrido[3′,2′:4,5]pyrazolo[3,2-*c*]benzo[*e*]-1,2,4-triazine (**17**, R = H).

The above compound (**16**, R = H) (239 mg.) when heated at 210-220° for 10 minutes and then sublimed at 230-240°/10 mm afforded the aromatized tetracycle in 58% yield, m.p. 252-257° (from toluene and *N,N*-dimethylformamide); ms: M^+ = 237 (100%); nmr (DMSO-d_6): τ = 0.9 (dd, H_5), 1.72 (dd, H_3), 3.17 (dd, H_4), 2.0 (deg. dd, H_{10}), 2.45 (dd, H_{11}), 2.75 (dd, H_9); $J_{3,4}$ = 4.6, $J_{4,5}$ = 8.0, $J_{3,5}$ = 2.0, $J_{9,10}$ = $J_{10,11}$ = 7.5, $J_{9,11}$ = 1.0 Hz.

Anal. Calcd. for $C_{12}H_7N_5O$: C, 60.75; H, 2.97; N, 29.53. Found: C, 60.92; H, 3.25; N, 29.46.

10,10-Dimethyl-8,9,10,11-tetrahydropyrido[3′,2′:4,5]pyrazolo-[3,2-*c*]benzo[*e*]-1,2,4-triazine (**16**, R = Me).

A suspension of the hydrazone (**11**) (285 mg.) in poly-

phosphoric acid (2 g.) was heated at 60-70° for 1 hour. The reaction mixture was diluted with iced water, neutralized with ammonia and the separated product filtered and crystallized from ethanol and dimethyl sulfoxide, m.p. 282-284° (67% yield); ms: M^+ = 267 (100%); nmr (DMSO-d_6, 120°): τ = 1.0 (m, H_3, H_5), 2.43 (dd, H_4), 6.38 (s, 11-CH_2), 7.16 (s, 9-CH_2), 8.74 (s, Me), $J_{3,4}$ = 4.6, $J_{4,5}$ = 8.0 Hz.

Anal. Calcd. for $C_{14}H_{13}N_5O$: C, 62.91; H, 4.90; N, 26.20. Found: C, 62.81; H, 5.08; N, 26.00.

8-Hydroxy-9,10-dimethylpyrido[3',2':4,5]pyrazolo[3,2-*c*]benzo[*e*]-1,2,4-triazine (**17**, R = Me).

The corresponding hydrazone (**11**) (285 mg.) in concentrated sulfuric acid (2 ml.) was heated at 100° for 3 hours. The cooled reaction mixture was poured on ice (15 g.) and neutralized with concentrated ammonia. The separated product was filtered, washed with water and crystallized from ethanol and *N,N*-dimethylformamide, m.p. 292-296°; yield 55%; ms: M^+ = 265 (100%); nmr (DMSO-d_6, 110°): τ = 1.1 (m, H_3, H_5), 2.16 (s, H_{11}), 2.52 (dd, H_4), 7.46 (s, 10-Me), 7.67 (s, 9-Me), $J_{3,4}$ = 4.6, $J_{4,5}$ = 8.0 Hz.

Anal. Calcd. for $C_{14}H_{11}N_5O$: C, 63.38; H, 4.18; N, 26.40. Found: C, 63.41; H, 4.09; N, 26.65.

Pyrido[3',2':4,5]pyrazolo[3,2-*c*]indeno[3,2-*e*]-1,2,4-triazin-8-one (**18**).

Compound **18** was obtained from the hydrazone (**12**) either by heating it at 250-260° for 4 hours or in hot concentrated sulfuric acid or polyphosphoric acid in 60-65% yield, m.p. 338-342° (from ethanol and *N,N*-dimethylformamide); ms: M^+ 273 (7%); nmr (DMSO-d_6, 150°): τ = 0.9 (dd, H_3), 1.0 (dd, H_5), 1.48 (m, H_{12}), 2.12 (m, H_9, H_{10}, H_{11}), 2.38 (dd, H_4), $J_{3,4}$ = 4.3, $J_{4,5}$ = 8.0, $J_{3,5}$ = 1.9 Hz.

Anal. Calcd. for $C_{15}H_7N_5O$: C, 65.93; H, 2.58; N, 25.63. Found: C, 65.60; H, 3.00; N, 25.39.

Pyrido[3',2':4,5]pyrazolo[3,2-*c*]naphtho[2,1-*e*]-1,2,4-triazine (**20**).

A solution of **1** (145 mg.) in ethanol (4 ml.) was treated at 0° under stirring with 2-naphthol (144 mg.). The separated azo compound (**19**) was filtered and crystallized from ethanol and *N,N*-dimethylformamide, m.p. 263-266° (with conversion to the cyclic product) (yield 75%); ms: M^+ = 289 (100%).

Anal. Calcd. for $C_{16}H_{11}N_5O$: C, 66.42; H, 3.83; N, 24.21. Found: C, 66.43; H, 3.81; N, 24.18.

The azo compound (**19**) (290 mg.) and concentrated sulfuric acid (2 ml.) were heated at 120° for 2 hours. Upon cooling, the reaction mixture was poured on ice (10 g.), the separated product filtered and crystallized from a mixture of ethanol and *N,N*-dimethylformamide, m.p. 269-272° (56% yield); ms: M^+ = 271 (100%); nmr (DMSO-d_6, 150°): τ = 0.47 (m, H_4), 0.95 (m, H_7, H_9), 1.33 (dd, H_{13}, H_{14}), 1.65-2.25 (m, H_1, H_2, H_3), 2.42 (dd, H_8), $J_{7,8}$ = 7.6, $J_{8,9}$ = 4.2 Hz.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and Ethyl Cyclopentanone-2-carboxylate.

A solution of (**1**) (145 mg.) and ethyl cyclopentanone-2-carboxylate (130 mg.) in ethanol (4 ml.) was left at 0° for 4 hours. After addition of 2 drops of concentrated hydrochloric acid, the mixture was left at 0° for further 24 hours. The yellow precipitate was filtered and crystallized from ethanol (yield 23%). It was the hydrochloride salt, and for obtaining the free base (**21**), the salt (1 mmole) was suspended in ethanol (5 ml. of 50%) and neutralized with sodium bicarbonate to *p*H 6-7. The product was filtered and crystallized from a small quantity of ethanol, m.p. 130-132°; ms: M^+ = 347 (9%); nmr (DMSO-d_6): τ = 1.1 (dd, H_4), 1.33 (dd, H_6), 2.77 (dd, H_5), 7.43 and 8.2 (m, -$(CH_2)_3$-), 5.68 and 5.86 (q, two COOCH_2CH$_3$), 8.62 and 8.79 (t, two COOCH$_2$CH_3), $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.8, $J_{5,6}$ = 4.5, J_{Et} = 7.0 Hz.

Anal. Calcd. for $C_{16}H_{21}N_5O_4$: C, 55.32; H, 6.09; N, 20.16. Found: C, 55.03; H, 5.97; N, 20.27.

Formation of Triazenes and Diazosulfides.

To a stirred solution of **1** (145 mg.) in cold ethanol (4 ml.) a solution of the corresponding amine or thiol (1.1 mmoles) was added at 0°. After 30 minutes (in the case of 2-aminopyridine after 4 days at room temperature) the separated product was filtered and crystallized. The obtained products (**22-27**) are listed in Table II.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and 6-Hydrazinotetrazolo[1,5-*b*]pyridazine.

6-Hydrazinotetrazolo[1,5-*b*]pyridazine (**28**) (302 mg.) was dissolved in hot methanol (140 ml.) and the solution cooled to 0°. To the stirred solution 3-diazopyrazolo[3,4-*b*]pyridine (**1**) (290 mg.) was added portionwise. After addition was complete (30 minutes) the reaction mixture was stirred at room temperature for 1 hour and then left for 24 hours. The solvent was evaporated *in vacuo*, the residue dissolved in methanol (25 ml.) and the compounds were separated by tlc on Merck-PSC-Fertigplatten, Kieselgel 60 F 254, 2 mm, using chloroform and methanol, 20:1, as mobile phase. For elution methanol was used.

There were obtained: 6-azidotetrazolo[1,5-*b*]pyridazine (**29**) (R_f = 0.65, 190 mg.), m.p. 126-129°, identical with an authentic specimen; 1*H*-pyrazolo[3,4-*b*]pyridine (**4**) (R_f = 0.47, 20 mg.), identical with an authentic specimen; 3-amino-1*H*-pyrazolo[3,4-*b*]pyridine (**2**) (R_f = 0.2, 226 mg.), identical with an authentic specimen. The product with R_f = 0.57 (13 mg.) was found to be a mixture of 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine (**5**) and tetrazolo[1,5-*b*]pyridazine (**30**). This mixture was separated by tlc, using chloroform and methanol, 5:1, as solvent and the corresponding R_f values were then, R_{f_1} = 0.63, R_{f_2} = 0.54.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and hydrazine Hydrate.

Into a dry ice cooled solution of hydrazine hydrate (75 mg., 1.5 moles of 100%) in methanol (5 ml.) 3-diazopyrazolo[3,4-*b*]-pyridine (145 mg.) was added and the mixture was left at 0° for 6 hours. The solvent was evaporated *in vacuo* and the residue was crystallized from ethanol to give 3-azidopyrazolo[3,4-*b*]pyridine (**5**) (80 mg.). The insoluble part (3 mg.) was identified as the triazene (**3**). The filtrate, after separation of the azide, was chromatographed by tlc and the presence of a small amount of pyrazolo[3,4-*b*]pyridine was established.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and Phenylhydrazine.

A solution of phenylhydrazine (108 mg.) in methanol (6 ml.) was cooled to -20° and under stirring 3-diazopyrazolo[3,4-*b*]-pyridine (**1**) (145 mg.) was added portionwise. After standing at -20° for 15 minutes the mixture was analyzed by gas chromatography and benzene and aniline were identified as components of the reaction mixture. The reaction mixture was treated with methanol (6 ml.), heated to boil and the product filtered. It was identified as the tetrazene (**31**) (90 mg.). The filtrate was evaporated to dryness, methanol (1.5 ml., or 4 ml. of ether) was added, the mixture was cooled to 0° and the separated product filtered (60 mg.). It was identified as 3-azido-1*H*-pyrazolo[3,4-*b*]-pyridine (**5**). The filtrate was again evaporated to dryness and the residue sublimed at 90-100°/1 mm to give 1*H*-pyrazolo[3,4-*b*]-pyridine (**4**) (4 mg.), and at 120-140°/1 mm, some 3-azido-1*H*-

pyrazolo[3,4-*b*]pyridine (**2**) (3 mg.) was ascertained by tlc. The presence of phenylazide was proved by nmr spectroscopic examination of the reaction mixture, before and after addition of some authentic phenylazide.

The tetrazene (**31**) had m.p. 173-175° dec.; ms: m/e = 225 ($M^+ - N_2$) (24%).

Anal. Calcd. for $C_{12}H_{11}N_7$: C, 56.91; H, 4.38; N, 38.72. Found: C, 57.03; H, 4.56; N, 38.63.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and 2-Hydrazinopyridine.

The reaction was performed in a similar manner as that with phenylhydrazine, using 218 mg. of the hydrazine and 290 mg. of the diazo compound. The reaction mixture was filtered to give 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine (**5**) (120 mg.) and the filtrate was submitted to tlc on Kieselgel PSC-Fertigplatten F-254, 2 mm, methanol and chloroform, 1:40, as the mobile phase. After elution with methanol the following compounds were identified: tetrazolo[1,5-*a*]pyridine (**32**) (54 mg., R_f = 0.59); 3-azido-1*H*-pyrazolo[3,4-*b*]pyridine (**5**) (75 mg., R_f = 0.38); 2-aminopyridine (80 mg., R_f = 0.28); and 3-aminopyrazolo[3,4-*b*]pyridine (**2**) (70 mg., R_f = 0.09). All compounds were identified on the basis of melting points and spectroscopic identification after comparison with authentic specimens.

Decomposition of the Triazene (**24**) with Hydrobromic Acid.

A mixture of hydrobromic acid (2.5 ml. of 48%) and the triazene (**24**) (239 mg.) was heated at 60-70° for 1 hour. The cold solution was diluted with water (10 ml.) and neutralized with sodium bicarbonate to *p*H 7. The separated product was filtered and crystallized from water. It was identified as 3-bromo-1*H*-pyrazolo[3,4-*b*]pyridine, m.p. 170-171° (yield 100 mg.); ms: M^+ = 197 (100%); nmr (DMSO-d_6): τ = 1.30 (dd, H_6), 1.85 (dd, H_4), 2.68 (dd, H_5), $J_{4,5}$ = 8.4, $J_{4,6}$ = 1.6, $J_{5,6}$ = 4.6 Hz.

Anal. Calcd. for $C_6H_5BrN_3$: C, 36.39; H, 2.04; N, 21.22. Found: C, 36.36; H, 2.36; N, 20.96.

The filtrate was extracted with chloroform (3 x 10 ml.), and the solution evaporated. In the residue, 2-bromopyridine (50 mg.) was identified by gas chromatography.

Photochemical Transformations of 3-Diazopyrazolo[3,4-*b*]pyridine.

A. In Methanol.

A solution of **1** (100 mg.) in methanol (15 ml.) was irradiated in a Rayonet photoreactor with light of λ = 254 nm for 4 hours. The solvent was evaporated to dryness and the residue was sublimed at 90-95°. 1*H*-Pyrazolo[3,4-*b*]pyridine (**4**) was obtained in 50% yield, m.p. 97-99°; ms: M^+ = 119 (100%); nmr (deuteriochloroform): τ = 1.35 (dd, H_6), 1.88 (dd, H_4), 1.89 (s, H_3), 2.86 (dd, H_5), $J_{4,5}$ = 7.7, $J_{4,6}$ = 1.5, $J_{5,6}$ = 4.4 Hz.

Anal. Calcd. for $C_6H_5N_3$: C, 60.49; H, 4.23; N, 35.28. Found: C, 60.37; H, 3.95; N, 35.03.

The same transformation, if performed thermally, is accomplished in 10 hours.

B. In Benzene.

The same reaction was performed in benzene for 60 hours. Upon filtration, the filtrate was evaporated to dryness *in vacuo* and the residue was crystallized from benzene to give 3-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine in 65% yield, m.p. 168-171°; ms: M^+ = 195 (100%); nmr (DMSO-d_6): τ = 1.40 (m, H_4 and H_6), 1.95 (m, H_2, and H_6), 2.4-2.85 (m, H_5 and H_3', H_4' and H_5').

Anal. Calcd. for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.53. Found: C, 73.68; H, 4.67; N, 21.79.

If the reaction was performed thermally in boiling benzene, after 34 hours the same compound was obtained in 53% yield.

Cycloaddition of 1*H*-Pyrazolo[3,4-*b*]pyridine-3-diazonium Tetrafluoroborate to 2,3-Dimethylbutadiene. Formation of **33**.

A solution of *cis*-2,3-dimethylbutadiene (123 mg.) in acetonitrile (4 ml.) was cooled to 0° and treated with 1*H*-pyrazolo-[3,4-*b*]pyridine-3-diazonium tetrafluoroborate (233 mg.). The reaction mixture was left to stand at 0° for three hours, the solvent was evaporated *in vacuo* and the residue crystallized from methanol and ether, m.p. 236-239° (yield 28%); ms: m/e = 225 ($M^+ - HBF_4$) (100%); nmr (DMSO-d_6): τ = -0.63 (s, H_6'), 0.22 (s, H_3'), 1.05 (dd, H_6), 1.18 (dd, H_4), 2.37 (dd, H_5), 7.3 (s, Me), $J_{4,5}$ = 8.4; $J_{4,6}$ = 1.6; $J_{5,6}$ = 4.5 Hz.

Anal. Calcd. for $C_{12}H_{12}BF_4N_5$: C, 46.04; H, 3.86; N, 22.37. Found: C, 45.83; H, 4.12; N, 22.42.

Reaction between 3-Diazopyrazolo[3,4-*b*]pyridine and 2,5-Dimethylfuran. Formation of **36**.

A solution of 2,5-dimethylfuran (144 mg.) in methanol (3 ml.) was cooled to 0° and 3-diazopyrazolo[3,4-*b*]pyridine (**1**) (145 mg.) was added. Upon standing 1 hour at room temperature the solvent was evaporated *in vacuo*, the residue treated with ethanol (3 ml.) and the reaction mixture heated under reflux for 1 hour. On cooling, the separated product was filtered and crystallized from ethanol and *N,N*-dimethylformamide, m.p. 270-273° (42% yield); ms: M^+ = 241 (55%); nmr (DMSO-d_6): τ = 1.37 (dd, H_6), 1.52 (dd, H_4), 2.72 (dd, H_5), 3.32 (s, H_4'), 7.41 (s, Me), $J_{4,5}$ = 8.1, $J_{5,6}$ = 4.6, $J_{4,6}$ = 1.6 Hz.

Anal. Calcd. for $C_{12}H_{11}N_5O$: C, 59.74; H, 4.60; N, 29.03. Found: C, 59.51; H, 4.67; N, 28.85.

3-Azido-1*H*-pyrazolo[3,4-*b*]pyridine (**37**).

A solution of hydroxylamine hydrochloride (83 mg.) in ethanol (4 ml. of 50%) was treated at 0° with **1** (145 mg.) and the reaction mixture was left at 0° for three hours. Upon neutralization with sodium bicarbonate to *p*H 6-7, the separated product was filtered and crystallized from ethanol, m.p. 178-180° dec., (50% yield); ms: M^+ = 160 (35%); nmr (DMSO-d_6): τ = 1.50 (dd, H_6), 2.0 (dd, H_4), 2.89 (dd, H_5), $J_{4,5}$ = 8.0, $J_{4,6}$ = 1.6, $J_{5,6}$ = 5.0 Hz.

Anal. Calcd. for $C_6H_4N_6$: C, 45.00; H, 2.52; N, 52.48. Found: C, 45.18; H, 2.92; N, 52.09.

If 3-diazopyrazolo[3,4-*b*]pyridine was treated with an equimolar amount of sodium azide in 50% ethanol at 0° for 30 minutes, after neutralization a product was obtained which was a mixture of the above azide and the corresponding tetrazolo compound (**38**).

5*H*-Tetrazolo[1',5':1,5]pyrazolo[3,4-*b*]pyridine (**38**).

3-Azidopyrazolo[3,4-*b*]pyridine (**37**) (160 mg.) was suspended in methanolic sodium methylate (prepared from 23 mg. of sodium and 4 ml. of methanol) and the mixture was left at room temperature until a complete solution occured (2-3 hours, alternatively the mixture can be heated under reflux for several minutes). The solvent was evaporated *in vacuo* and the residue was crystallized from a mixture of methanol and ether, m.p. about 100° (yield 80%); nmr (DMSO-d_6): τ = 1.58 (dd, H_7), 1.72 (dd, H_9), 3.18 (dd, H_8), $J_{7,8}$ = 4.5, $J_{7,9}$ = 2.0, $J_{8,9}$ = 7.8 Hz.

The crude, hygroscopic sodium salt (**39**) was dissolved in water (4 ml.) and the solution neutralized with 2*N* hydrochloric acid (or 2*N* acetic acid) at 5° to *p*H 6-7. The separated product was filtered and washed with ethanol, m.p. 178-180° dec. (yield 94%). Over 130°, the compound is transformed into the azide form (**37**), ms: M^+ = 160 (35%; nmr (DMSO-d_6): τ = 0.95 (dd, H_9), 1.44

(dd, H_7), 2.76 (dd, H_8), $J_{7,8}$ = 6.0, $J_{7,9}$ = 1.4, $J_{8,9}$ = 7.5 Hz.

Anal. Calcd. for $C_6H_4N_6$: C, 45.00; H, 2.52; N, 52.48. Found: C, 45.31; H, 2.50; N, 52.20.

The tetrazolo compound (**38**) can be transformed into the azido isomer (**37**) by heating it in *N,N*-dimethylformamide to boiling and slowly pouring the solution in cold water. Alternatively, the azide is obtained also by sublimation of the tetrazole at 130-140°.

4-Acetyl-5-methyl-1-(pyrazolo[3,4-*b*]pyridin-3′-yl)-1,2,3-triazole (**40**).

A mixture of the azide (**37**) (160 mg.), acetylacetone (150 mg.), ethanol (6 ml.) and triethylamine (0.5 ml.) was heated under reflux for 15 hours. The solvent was evaporated *in vacuo* and the residue was crystallized from ethanol, m.p. 235-237°; ms: M^+ = 242 (30%); nmr (DMSO-d_6): τ = 1.16 (dd, H_6), 1.49 (dd, H_4), 2.54 (dd, H_5), 7.18 (s, COMe), 7.30 (s, Me), $J_{4,5}$ = 8.4, $J_{5,6}$ = 4.5, $J_{4,6}$ = 1.6 Hz.

Anal. Calcd. for $C_{11}H_{10}N_6O$: C, 54.54; H, 4.16; N, 34.70. Found: C, 54.41; H, 4.04; N, 34.60.

2,4-Dimethylpyrido[3′,2′:4,5]pyrazolo[2,3-*a*]pyrimidine (**41**).

3-Amino-1*H*-pyrazolo[3,4-*b*]pyridine (**28**) (0.5 g.) and acetylacetone (0.5 g.) were mixed with polyphosphoric acid (4 g. of 83%). The reaction mixture was heated at 70° for 2 hours and then at 100-120° for 2 hours. Upon cooling, water (15 ml.) was added and the mixture was neutralized with solid sodium bicarbonate to *p*H 7. Upon extraction with chloroform (4 times with 10 ml.) and evaporation of the solvent the product was crystallized from ethanol, m.p. 189-190° (yield 65%); ms: M^+ = 198 (100%); nmr (deuteriochloroform): τ = 1.02 (dd, H_8), 1.35 (dd, H_{10}), 2.78 (dd, H_9), 2.92 (q, H_3), 7.02 (d, 4-Me), 7.25 (s, 2-Me), $J_{8,9}$ = 4.6, $J_{9,10}$ = 8.4, $J_{8,10}$ = 1.8, $J_{3,4\text{-Me}}$ = 0.8 Hz.

Anal. Calcd. for $C_{11}H_{10}N_4$: C, 66.65; H, 5.09; N, 28.27. Found: C, 66.70; H, 4.99; N, 28.21.

2,4-Dimethyl-7,8,9,10-tetrahydropyrido[3′,2′:4,5]pyrazolo[2,3-*a*]-pyrimidine (**42**).

The above compound (**41**) (0.8 g.) was dissolved in methanol (200 ml.), palladized carbon (0.6 g. of 10%) was added and the reaction mixture was hydrogenated in a Parr hydrogenator at 3 atmospheres for 36 hours. Upon filtration, the filtrate was evaporated to dryness and the residue crystallized from chloroform and petroleum ether and then sublimed at 120-130°/10 mm, m.p. 155-157° (yield 38%); ms: M^+ = 202 (68%); nmr (deuteriochloroform): τ = 3.73 (broad s, H_3), 6.6 (m, 8-CH_2), 7.18 (t, 10-CH_2), 7.45 (broad s, 4-Me), 7.53 (s, 2-Me), 8.0 (m, 9-CH_2), $J_{8,9}$ = $J_{9,10}$ = 6.0 Hz.

Anal. Calcd. for $C_{11}H_{14}N_4$: C, 65.32; H, 6.98; N, 27.70. Found: C, 65.18; H, 7.07; N, 27.40.

2-Methylpyrido[3′,2′:4,5]pyrazolo[2,3-*a*]pyrimid-4(1*H*)one (**43**).

The amino compound (**2**) (1.5 g.), ethyl acetoacetate (3 ml.) and polyphosphoric acid (12 g.) were heated at 90-100° for 2 hours. The cold reaction mixture was diluted with water (50 ml.) and neutralized with solid sodium bicarbonate to *p*H 6. The product was filtered, washed with ethanol and crystallized from *N,N*-dimethylformamide, m.p. over 330° (yield 41%); ms: M^+ = 200 (100%); nmr (DMSO-d_6, 150°): τ = 1.38 (dd, H_8), 1.63 (dd, H_{10}), 3.02 (dd, H_9), 4.10 (s, H_3), 7.55 (s, Me), $J_{8,9}$ = 5.0, $J_{9,10}$ = 8.2, $J_{8,10}$ = 1.7 Hz.

Anal. Calcd. for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 59.85; H, 4.29; N, 27.78.

2-Methyl-7,8,9,10-tetrahydropyrido[3′,2′:4,5]pyrazolo[2,3-*a*]-pyrimidin-4(1*H*)one (**44**).

It was obtained from the above compound (**43**) by hydrogenation over palladized carbon in 5 days as described for the 2,4-dimethyl analog, m.p. 318-321° (yield 48%); ms: M^+ = 204 (7%); nmr (DMSO-d_6, 100°): τ = 4.78 (s, H_3), 6.85 (m, 8-CH_2), 7.55 (t, 10-CH_2), 7.83 (s, Me), 8.18 (m, 9-CH_2), $J_{8,9}$ = $J_{9,10}$ = 5.0 Hz.

Anal. Calcd. for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.50; H, 5.77; N, 26.98.

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