1,3-Dipolar Cycloaddition of 2-Diazoalkanes to Pyridazin-3(2*H*)-one Derivatives. The Formation of 3*H*-Pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one and 3*H*-Pyrazolo[3,4-*d*]pyridazin-7(6*H*)-one Derivatives

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1,3-Dipolar cycloadditions of diazoalkanes to pyridazin-3(2*H*)-ones **1-7** and pyridazin-3(2*H*)-thiones **8** and **9** are regioselective producing **3H**-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-ones **15-19**, **27-29** and **34-38** as the major products. In some instances, the isomeric 3*H*-pyrazolo[3,4-*d*]pyridazin-7(6*H*)-ones, such as **20** and **23** were isolated as the minor products. From **3** and **6** the primary 3a,7a-dihydro cycloadducts **25** and **26**, and rearranged 1,2-dihydro intermediate **31** were isolated. From **10** and 1-diazoindane the isomeric exo- and endo-spiro products **39** and **40** were formed.

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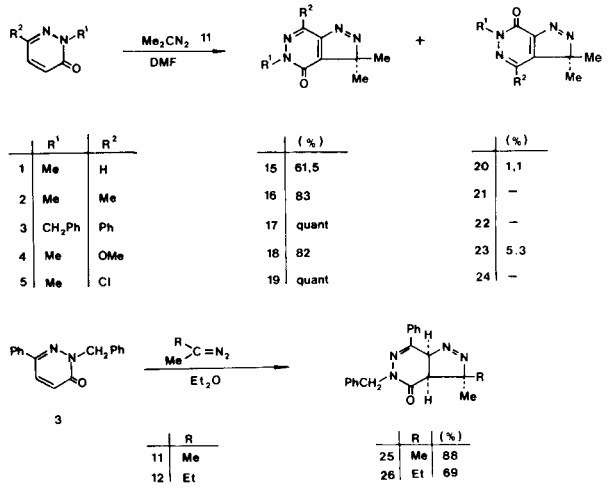
It has been reported that 1,3-dipolar cycloadditions of diazoalkanes to pyridazine derivatives afford pyrazolo[3,4-*d*]pyridazines [1,2], while with 2-methyl-6-phenylpyridazin-3(2*H*)-one the formation of a mixture of 1,2-diazepine derivative, 4-isopropyl substituted pyridazine derivative and diazabicyclo[4.1.0]heptenone derivative has been found [3].

Due to this ambiguity and on the basis of our experience in a series of bicyclic azolo- and azinopyridazines in which pyrazoloazolo- and pyrazoloazinopyridazines are formed regiospecifically [4-15], we decided to study this reaction in pyridazin-3(2*H*)-one series in more detail.

In this paper we report the cycloadditions of diazoalkanes to a series of pyridazin-3(2*H*)-ones in various solvents. The following compounds were selected for this study: 2-methylpyridazin-3(2*H*)-one (**1**), 2,6-dimethylpyridazin-3(2*H*)-one (**2**), 2-benzyl-6-phenylpyridazin-3(2*H*)-one (**3**), 6-methoxy-2-methylpyridazin-3(2*H*)-one (**4**), 6-chloro-2-methylpyridazin-3(2*H*)-one (**5**), 6-phenylpyridazin-3(2*H*)-one (**6**), 6-methylpyridazin-3(2*H*)-one hydrate (**7**), 2-methyl-6-phenylpyridazin-3(2*H*)-thione (**8**), 2-benzyl-6-phenylpyridazin-3(2*H*)-thione (**9**), and 2-methyl-6-phenylpyridazin-3(2*H*)-one (**10**) as dipolarophiles and 2-diazopropane (**11**), 2-diazobutane (**12**), 1-diazo-1-phenylethane (**13**), and 1-diazoindane (**14**) as 1,3-dipoles. The cycloaddition of 2-diazopropane (**11**) to pyridazin-3(2*H*)-one derivatives **1-5** in DMF was found to be regiospecific and the corresponding 3,3-dimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-ones **15-19** were formed as the only or the major products in high yields. However, in the case of **1** and **4** also minor amounts of regioisomers, derivatives of pyrazolo[3,4-*d*]pyridazin-7(6*H*)-one, **20** and **23** were formed in 1.1% and 5.3% yield, respectively. We observed that the reaction rate is strongly dependent on the substituents at position 6. For example, with **5** the reaction was finished in 20 minutes while with **2** the reagent was decomposed before the cycloaddition was finished, and approximately 17% of the starting material was recovered. In some instances, when, instead of DMF, diethyl ether was used as less polar solvent also the primary cycloadducts were isolated due to their low solubility. For example, when **3** was treated with **11** or **12**, the corresponding 3a,7a-dihydro derivatives **25** and **26** were precipitated in analytically pure form from the reaction mixture in 88% and 69% yield, respectively.



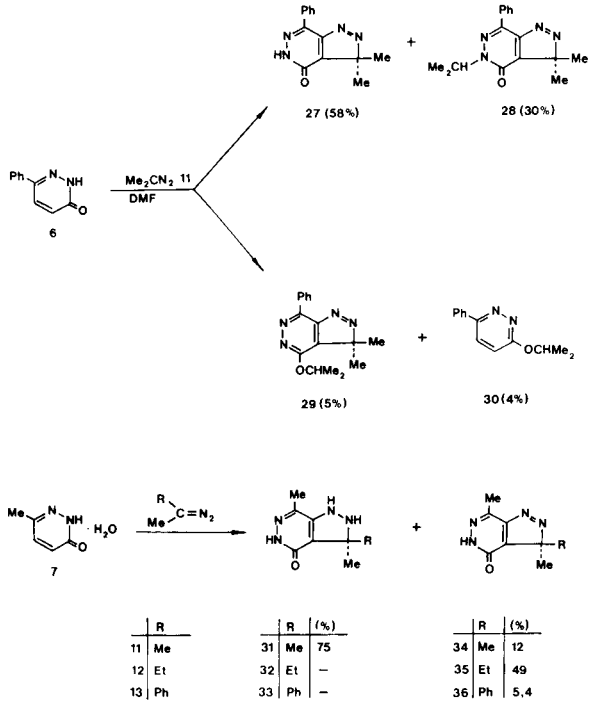
	R^1	R^2	(%)	(%)
1	Me	H	15 61,5	20 1,1
2	Me	Me	16 83	21 –
3	CH_2Ph	Ph	17 quant	22 –
4	Me	OMe	18 82	23 5.3
5	Me	Cl	19 quant	24 –

	R
11	Me
12	Et

	R	(%)
25	Me	88
26	Et	69

More complicated is the cycloaddition of diazoalkanes to 6-substituted pyridazin-3(2*H*)-ones, such as **6** and **7**, due to *N*- and *O*-alkylation taking place in pyridazine part of the molecule. When **6** was treated with **11** in DMF, four compounds were formed and isolated, 3,3-dimethyl-7-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**27**), its *N*- and *O*-alkylated, *i.e.* 5-isopropyl- **28** and 4-isopropyl-**29**, derivatives, and *O*-alkylated starting compound, *i.e.* 3-isopropyloxypyridazine derivative **30**, in 58%, 30%, and 4% yields, respectively. Compound **29** was formed from **27** by *O*-alkylation, since **16** does not react with **11** under the same reaction conditions. The compound **7** gave with **11** two products 3,3,7-trimethyl-1,2-dihydro-3*H*-pyrazolo-[3,4-*d*]pyridazin-4(5*H*)-one (**31**) in 75% yield, which was, in spite of its instability, isolated because of its insolubility in the reaction mixture, and dehydrogenated compound **34**

in 12% yield. With diazoalkane **12**, only dehydrogenated product **35** was obtained in 49% yield. The reaction of **7** with phenyl substituted diazoalkane **13** was very slow to give **36** in very low yield (only 5.4%). The 1,2-dihydro intermediates **32** and **33** were not isolated, since they are soluble in the reaction mixture.



Pyridazine-3(2*H*)-thiones **8** and **9** were found to be the most reactive dipolarophiles in this series. In both cases the cycloaddition with **11** was finished in several minutes to give cycloadducts **37** and **38** in 56% and 36% yield, respectively. The compound **37** was obtained also from **41**, the structure of which was confirmed by X-ray analysis [15].

In the reaction of **10** with 1-diazoindane (**14**) in a molar ratio 1:2.5 in DMF the primary cycloadduct could be detected only by tlc. However, it is extremely unstable and was decomposed into a mixture of exo-3-methyl-5-phenyl-2-oxo-3,4-diazabicyclo[4.1.0]hept-4-ene-7-spiro-1′-indane (**39**) and its endo isomer **40** in 23% and 25% yield, respectively. Besides these two products 1-indanone and 1-indanone azine as side products, and unreacted **10** in 2%, 31%, and 50% yield respectively, were isolated.

Table 1

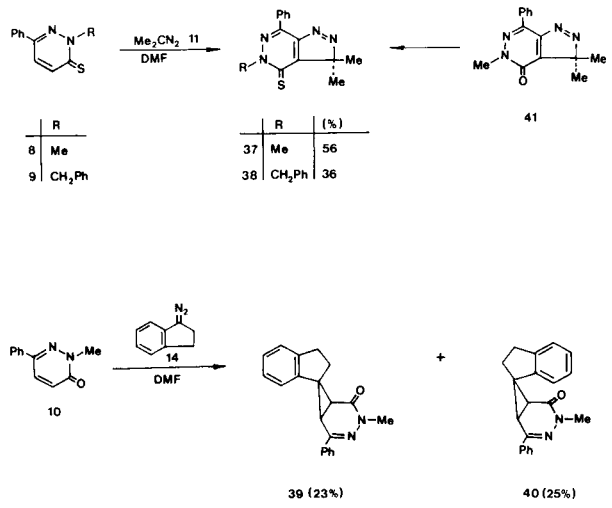
^{1}H Chemical shifts of pyrazolo[3,4-*d*]pyridazin-4(5*H*)-ones and -7(6*H*)-ones [δ|ppm|] in Deuteriochloroform [TMS]

Compound	3,3-diMe	R_1	R_2
15	1.68	3.90 (Me)	8.61 (H)
34	1.67	12.3 (H)	2.82 (Me)
18	1.68	3.77 (Me)	4.10 (OMe)
19	1.69	3.85 (Me)	– (Cl)
20	1.59	3.93 (Me)	7.96 (H)
23	1.62	3.80 (Me)	4.05 (OMe)

Table 2

^{1}H Chemical Shifts of R^2 δH [ppm] in Deuteriochloroform/TMS

Substituent X	R	R^1	R^2	Compound				
O	Me	Me	H	**1**, 7.82			**15**, 8.61 [+0.79]	**20**, 7.96 [+0.14]
O	Me	CH_2Ph	Ph	**3**, 7.1-7.8	**25**, 7.0-7.45 [–0.21] and 7.85-8.2 [+0.6]	–	–	–
O	Me	CH_2Ph	Ph	**3**, 7.1-7.8	**26**, 7.1-7.6 [-0.1] and 7.95-8.35 [+0.6]			
O	Me	H	Ph	**6**, 7.2-7.8	–	–	**27**, 7.35-7.65 [0] and 8.1-8.35 [+0.75]	–
O	Me	H	Me	**7**, 2.21	–	**31**, 2.09 [-0.12]	**34**, 2.82 [+0.61]	–
O	Et	H	Me	**7**, 2.21	–	–	**35**, 2.83 [+0.62]	
O	Ph	H	Me	**7**, 2.21	–	–	**36**, 2.81 [+0.60]	
O	Me	Me	Me	**2**, 2.30	–	–	**16**, 2.83 [+0.53]	–
S	Me	Me	Ph	**8**, 7.3-7.9	–	–	**37**, 7.4-7.65 [-0.05] and 8.35-8.6 [+0.95]	–
S	Me	CH_2Ph	Ph	**8**, 7.3-7.9	–	–	**38**, 7.15-7.6 [-0.1] and 8.3-8.55 [+0.95]	–



Tabe 3

^{13}C Chemical Shifts of Pyridazin-3(2*H*)-ones ($\delta^{13}C$ [ppm] in Deuteriochloroform/TMS

Compound		R_1	R_2	C_3	C_4	C_5
C_6						
1	40.0 (Me)	- (H)	160.7	129.3	131.6	136.1
2	39.8 (Me)	20.6 (Me)	159.9	129.4	133.3	144.1
3	55.5(CH_2Ph)	(Ph) [a]	159.5	130.0	130.2	144.3
4	39.3 (Me)	54.2 (OMe)	159.3	132.5	126.4	152.9
5	40.1 (Me)	- (Cl)	159.2	131.6	133.7	137.1

[a] See experimental.

Structural Assignments.

The 1,3-dipolar cycloaddition of diazoalkanes to 4,5-unsubstituted pyridazin-3(2*H*)-ones is in general regioselective, and in most cases regiospecific. In bicyclic azolo- and azinopyridazines with a bridgehead nitrogen atom we have shown by chemical transformations [4-15] and in some instances by X-ray analysis [16,17] that the newly formed pyrazole ring is [4,3-*d*] fused. For products of cycloaddition of diazomethane to 2-methylpyridazin-3(2*H*)-one it has been shown by an independent synthesis that pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (~80%) and pyrazolo-[3,4-*d*]pyridazin-7(6*H*)-one (~10%) derivatives are formed [2]. X-ray analysis of the cycloadduct of 2-methyl-6-phenyl-pyridazin-3-(2*H*)-one with 2-diazopropane has shown to be 7-phenyl-3,3,5-trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one [15].

In this study, ^1H and ^{13}C nmr spectrometry turned out to be suitable methods for structure determination and differentiation between isomeric pyrazolo[3,4-*d*]pyridazin-4(5*H*)-ones and isomeric -7(6*H*)-ones. The chemical shifts for geminal methyl groups at position 3 in ^1H nmr spectra of 5-unsubstituted and 5-substituted 3*H*-pyrazolo-[3,4-*d*]pyridazin-4(5*H*)-ones are of constant values, independent on the substituents at position 7. They are in average for $\Delta\delta \cong -0.1$ ppm higher than in the isomeric 3*H*-pyrazolo[3,4-*d*]pyridazin-7(6*H*)-ones (Table 1). The most significant feature is anisotropic effect of the azo group of pyrazole ring, the consequence of which is a downfield shift of protons of substituents at position 7 in -4(5*H*)-one in comparison to protons at position 6 of the corresponding starting pyridazin-3(2*H*)-one derivatives (Table 2). In compounds **25**, **26**, **27**, **37** and **38** with R^2 = Ph are the *ortho* protons of the phenyl group in pyrazolo-pyridazines shifted downfield in comparison to the monocyclic pyridazin-3(2*H*)-ones and they appear as two well separated multiplets. The lower multiplet in 3a,7a-dihydro derivatives in **25** and **26** is shifted downfield for $\Delta\delta \cong 0.6$ ppm, in compounds **15** and **27** for $\Delta\delta \cong 0.75$-0.8 ppm and in **37** and **38** for $\Delta\delta \cong 0.95$ ppm. Similarly, in isopropyloxy derivative **29** the lower multiplet is shifted downfield for $\Delta\delta \cong 0.065$ ppm in comparison to that in the compound **30**. However, on this basis we can not differenciate between the isomeric compounds **18** and **23**, since the chemi-

Table 4

^{13}C Chemical Shifts of 3*H*-Pyrazolo[3,4-*d*]pyridazin-4(5*H*)-ones ($\delta^{13}C$ [ppm] in Deuteriochloroform/TMS)

Compound	3,3-diMe	C_3	C_4	C_7	C_{3a}	C_{7a}	5-Me
15	19.3	94.6	157.9 [-2.8]	130.6 [-5.5]	144.2 [+14.9]	151.7 [+20.1]	39.7 [-0.3]
16	19.4	95.0	157.9 [-2.0]	139.6 [-4.5]	144.0 [+14.6]	151.6 [+18.3]	39.3 [-0.5]
18	19.3	95.4	156.9 [-2.4]	147.2 [-5.7]	147.9 [+15.4]	144.4 [+18.0]	38.6 [-0.7]
19	19.3	96.9	157.1 [-2.1]	131.0 [-6.1]	146.6 [+15.0]	149.3 [+15.6]	39.7 [-0.4]

Table 5

^{13}C Chemical Shifts of 3*H*-Pyrazolo[3,4-*d*]pyridazin-4(6*H*)-ones ($\delta^{13}C$ [ppm] in Deuteriochloroform/TMS)

Compound	3,3-diMe	C_3	C_7	C_4	C_{7a}	C_{7a}	5-Me
20	20.6	93.0	156.1 [-4.6]	129.5 [-6.6]	147.0 [+17.7]	151.8 [+20.2]	40.4 [+0.4]
23	19.4	94.2	155.4 [-3.9]	148.8 [-4.1]	149.1 [+16.6]	144.8 [+18.4]	39.2 [-0.1]

cal shifts for methoxy groups are very similar. Here, the shift reagent, $Eu(fod)_3$, was applied. Addition of 20 mg and 40 mg of $Eu(fod)_3$ to a solution of 75 mg of **18** in 0.5 ml of deuteriochloroform is accompanied with the shifts of the 3,3-diMe singlet from δ = 1.63 ppm to δ = 1.67 ppm and δ = 1.81 ppm, respectively, and the 5-Me singlet from δ = 3.68 ppm to δ = 3.75 ppm and δ = 4.13 ppm, respectively, while 7-OMe singlet moves from δ = 4.11 ppm to δ = 4.13 ppm. In the compound **23**, under the same conditions, the 3,3-diMe singlet is shifted from δ = 1.58 ppm to δ = 1.60 ppm and δ = 1.66 ppm, respectively, and the 6-Me singlet from δ = 3.73 ppm to δ = 3.80 ppm and δ = 4.03 ppm, respectively. These data are in agreement with the proposed structures.

3a,7a-Dihydro compounds **25** and **26** show a typical AX type of spectra for H_{3a} and H_{7a} with a coupling constant J $\cong$ 12 Hz, and two singlets for geminal methyl groups at position 3 for compound **25** and two sets of signals for 3-methyl and 3-ethyl group for compound **26** corresponding to two diastereoisomeric pairs of enantiomers, in ratio 3:2, in favor of the isomers with exo oriented ethyl group.

The structural assignments of **39** and **40** was made on the basis of their ^{1}H nmr spectra. The chemical shift for 2'-CH_2 group in indane ring and proton at position 7'' in benzene ring of the indane part of the molecule are strongly dependent on the orientation of the indane moiety against pyridazine part of the molecule. In isomer **39** the 2'-CH_2 group is shifted upfield for $\Delta\delta$ = 0.51 ppm in comparison to that in the isomer **40**. On the other hand, $H_{7''}$ in **40** is shifted for $\Delta\delta$ = 0.25 ppm upfield in comparison to the corresponding proton in **39**.

The structures were confirmed also by ^{13}C nmr spectra. The chemical shifts of the starting pyridazin-3(2*H*)-ones **1**, **2**, **3** and **5** were determined by analogy with derivatives of 2-substituted pyridazin-3(2*H*)-one and 6-methylpyridazin-3(2*H*)-one [18], for **4** by analogy with 6-hydroxypyridazin-3(2*H*)-one [19] and for others on the basis of multiplicity of lines. They are summarized in Table 3. The chemical shifts for 3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-ones **15**, **16**, **18** and **19** and 3*H*-pyrazolo[3,4-*d*]pyridazin-7(6*H*)-ones **20** and **23** are summarized in Tables 4 and 5. The values in brackets are chemical shift differences between the carbon atoms in bicyclic systems and the corresponding carbon atoms in the monocyclic pyridazines. For -4(5*H*)-ones are these differences the largest for C_4 ($\Delta\delta$ = +14.5 to +15.5 ppm) and C_5 ($\Delta\delta$ = +15.6 to +21.0 ppm) and smaller for C_3 ($\Delta\delta$ = −2.0 to −2.8 ppm) and C_6 ($\Delta\delta$ = −4.3 to −6.6 ppm) in comparison to the corresponding starting pyridazin-3(2*H*)-ones, while these difference in -7(6*H*)-ones are for C_4 $\Delta\delta$ = +16.6 to 17.7 ppm, C_5 $\Delta\delta$ = +18.4 to 20.2 ppm, C_3 $\Delta\delta$ = −3.9 to 4.6 ppm, and C_6 $\Delta\delta$ = −4.1 to −6.6 ppm.

EXPERIMENTAL

Melting points were taken on Kofler micro hot stage. All ^{1}H nmr spectra were obtained on a JEOL C-60-HL, ^{13}C nmr spectra on a JEOL 90Q FT spectrometer, mass spectra on a CEC 21-110B or Hitachi-Perkin-Elmer RMU-6L spectrometers and micro analyses for C, H, and N on a Perkin-Elmer Analyser 240 C. For tlc DC Fertigplatten Kieselgel 60 F_{254}, E. Merck, for column chromatography Kieselgel 60, 0.063-0.200 mm, E. Merck, and for flash chromatography Kieselgel 60, 0.040-0.063 mm, E. Merck, were used.

The following compounds were prepared according to the procedures described in the literature: 2-diazopropane (**11**) [20], 2-diazobutane (**12**) [21], 1-diazoindane (**14**) [23], 1-diazo-1-phenylethane (**13**) [29], 2-methylpyridazin-3(2*H*)-one (**1**) [24], 2,6-dimethylpyridazin-3(2*H*)-one (**2**) [25], 2-benzyl-6-phenylpyridazin-3(2*H*)-one (**3**) [24], 6-methoxy-2-methylpyridazin-3(2*H*)-one (**4**) [26], 6-chloro-2-methylpyridazin-3(2*H*)-one (**5**) [26], 6-phenylpyridazin-3(2*H*)-one (**6**) [27], 6-methylpyridazin-3(2*H*)-one hydrate (**7**) [28], 2-methyl-6-phenylpyridazine-3(2*H*)-thione (**8**) [24], 2-methyl-6-phenylpyridazin-3(2*H*)-one (**10**) [24], and 7-phenyl-3,3,5-trimethyl-3*H*-pyrazolo-[3,4-*d*]pyridazin-4(5*H*)-one (**41**) [15].

2-Benzyl-6-phenylpyridazine-3(2*H*)-thione (**9**).

A mixture of 2-benzyl-6-phenylpyridazin-3(2*H*)-one (5.9 g) and phosphorous pentasulphide (5 g) in xylene (27 ml) was heated under reflux for two hours. The reaction mixture was filtered hot. The solid residue was extracted with hot xylene (10 ml) and filtered. The combined filtrates were evaporated *in vacuo*. Ethanol (150 ml) and activated charcoal (1 g) were added to the residue, the mixture was heated under reflux for 10 minutes and filtered. The filtrate was evaporated to one-third *in vacuo*. The crystals were, after cooling, collected by filtration to give **9** (3.37 g, 54%), mp 113-115° (from ethanol); ^{1}H nmr (deuteriochloroform): δ 5.90 (s, CH_2Ph), 7.22 (d, H_4), 7.76 (d, H_5), 7.1-7.9 (m, 6-Ph, CH_2*Ph*), J_{H_4,H_5} = 9.0 Hz.

Anal. Calcd. for $C_{17}H_{14}N_2S$: C, 73.25; H, 5.07; N, 10.06. Found: C, 73.20; H, 5.07; N, 10.10.

3,3,5-Trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**15**) and 3,3,6-Trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-7(6*H*)-one (**20**).

To a solution of **1** (1.92 g, 0.0163 mole) in DMF (15 ml) a solution of **11**, prepared from acetone hydrazone (9 g) in diethyl ether (60 ml), was added and the reaction mixture was left for 12 hours at room temperature. The volatile components were evaporated *in vacuo* and the dry residue was crystallized from water to give analitically pure **15** (1.61 g, 56%). The filtrate was evaporated *in vacuo*, and the dry residue was separated by tlc (DC-Fertigplatten Kieselgel 60 F254, E. Merck, Darmstadt, and diethyl ether as eluent) to give **15** (160 mg), **20** (33 mg) and unreacted material **1** (250 mg). The combined yield of **15** was 1.77 g, (62%), mp 100-101° (water); ^{1}H nmr (deuteriochloroform): δ 1.68 (s, 3,3-diMe), 3.90 (s, 5-Me), 8.61 (s, H_7); ^{13}C nmr (deuteriochloroform): δ 157.9 (br s, C_4), 151.7 (d, C_{7a}, $^2J_{CH}$ = 6 Hz), 144.2 (m, C_{3a}), 130.6 (d, C_7, $^1J_{CH}$ = 194 Hz), 94.6 (hept, C_3, $^2J_{CMe}$ = 4.5 Hz), 39.7 (q, 5-Me, $^1J_{CH}$ = 142 Hz), 19.3 (qq, 3,3-diMe, $^1J_{CH}$ = 132.5 Hz, $^3J_{CMe}$ = 5.0 Hz).

Anal. Calcd. for $C_8H_{10}N_4O$: C, 53.92; H, 5.66; N, 31.44. Found: C, 54.06; H, 5.65; N, 31.28.

Compound **20** was obtained in 1.1% yield (33 mg) mp 187-189° (diisopropyl ether); ^{1}H nmr (deuteriochloroform): δ 1.59 (s, 3,3-diMe), 3.93 (s, 6-Me), 7.96 (s, H_4); ^{13}C nmr (deuteriochloroform): δ 156.1 (s, C_7), 151.8 (m, C_{3a}), 147.0 (d, C_{7a}, $^3J_{CH}$ = 6.0 Hz), 129.5 (d, C_4, $^1J_{CH}$ = 191 Hz), 93.0 (hept, C_3, $^2J_{CMe}$ = 4.5 Hz), 40.4 (q, 6-Me, $^1J_{CH}$ = 142 Hz), 20.6 (qq, 3,3-diMe, $^3J_{CMe}$ = 4.5 Hz).

Anal. Calcd. for $C_8H_{10}N_4O$: C, 53.92; H, 5.66; N, 31.44. Found: C, 54.07; H, 5.75; N, 31.20.

3,3,5,7-Tetramethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**16**).

To a solution of **2** (620 mg, 0.005 mole) in DMF (10 ml) a solution of **11**, prepared from acetone hydrazone (3.0 g) in diethyl ether (20 ml), was added and the mixture was left for 12 hours at room temperature. The volatile components were evaporated *in vacuo* to give 950 mg of the crude product, which is a mixture of **16** and unreacted starting material. After recrystallization from water pure **16** (520 mg, 54%) was obtained, mp 116°; ^{1}H nmr (deuteriochloroform): δ 1.67 (s, 3,3-diMe), 2.83 (s, 7-Me), 3.85 (s, 5-Me); ^{13}C nmr (deuteriochloroform): δ 157.9 (br s, C_4), 151.6 (q, C_{7a}, $^3J_{CMe}$ = 2.5 Hz), 144.0 (hept, C_{3a}, $^3J_{CMe}$ = 3.5 Hz), 139.6 (q, C_7, $^2J_{CMe}$ = 7.0 Hz), 95.0 (hept, C_3, $^2J_{CMe}$ = 4.5 Hz), 39.3 (q, 5-Me, $^1J_{CH}$ = 142 Hz), 19.4 (qq, 3,3-diMe, $^1J_{CH}$ = 132 Hz, $^3J_{CMe}$ = 5.0 Hz), 17.2 (q, 7-Me, $^1J_{CH}$ = 130.5 Hz).

Anal. Calcd. for $C_9H_{12}N_4O$: C, 56.24; H, 6.29; N, 29.15. Found: C, 56.15; H, 6.35; N, 29.18.

5-Benzyl-3,3-dimethyl-7-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**17**).

To a solution of **3** (1.31 g, 0.005 mole) in DMF (10 ml) a solution of **11**, prepared from acetone hydrazone (3.0 g) in diethyl ether (20 ml), was added and the mixture was left for 12 hours at room temperature. The solvent was evaporated *in vacuo* to give **17** (1.65 g, quant) (1.10 g, 67% after recrystallization form diisopropyl ether), mp 108-110°; ^{1}H nmr (deuteriochloroform): δ 1.64 (s, 6H, 3,3-diMe), 5.37 (s, 2H, CH_2Ph), 7.10-7.50 (m, $H_{3'}$, $H_{4'}$, $H_{5'}$, CH_2*Ph*), 8.10-8.40 (m, $H_{2'}$, $H_{6'}$).

Anal. Calcd. for $C_{20}H_{18}N_4O0.5\ H_2O$: C, 70.78; H, 5.64; N, 16.51. Found: C, 70.58; H, 5.37; N, 16.36.

7-Methoxy-3,3,5-trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**18**) and 4-Methoxy-3,3,6-trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-7(6*H*)-one (**23**).

To a solution of **4** (700 mg, 0.005 mole) in DMF (5 ml) a solution of **11**, prepared from acetone hydrazone (3.0 g) in diethyl ether (20 ml), was added and the mixture was left for 12 hours at room temperature. The solvent was evaporated *in vacuo* to one-third, the precipitate was collected by filtration to give **18** (576 mg). The filtrate was evaporated *in vacuo* and the dry residue was crystallized from a mixture of ethanol and water, 2:1, to give further amount of **18** (210 mg). The filtrate was evaporated *in vacuo* and the dry residue was separated by flash chromatography (Kieselgel 60, 0.040-0.063 mm, E. Merck, Darmstadt, and diethyl ether as eluent) to give, after evaporation of the solvent, **18** (65 mg) as the first component, and **23** (55 mg) as the second component.

Compound **18** was obtained in a combined yield of 851 mg (82%) mp 153-155° (ethanol); ^{1}H nmr (deuteriochloroform): δ 1.68 (s, 3,3-diMe), 3.77 (s, 5-Me), 4.10 (s, OMe); ^{13}C nmr (deuteriochloroform): δ 156.9 (q, C_4, $^3J_{CMe}$ = 2.0 Hz), 147.9 (hept, C_{3a}, $^3J_{CMe}$ = 3.0 Hz), 147.2 (q, C_7, $^3J_{COMe}$ = 3.5 Hz), 144.4 (s, C_{7a}), 95.4 (hept, C_3, $^2J_{CMe}$ = 4.5 Hz), 54.8 (q, OMe, $^1J_{CH}$ = 148 Hz), 38.6 (q, 5-Me, $^1J_{CH}$ = 141 Hz), 19.3 (qq, 3,3-diMe, $^1J_{CH}$ = 132.5 Hz, $^3J_{CMe}$ = 5.0 Hz).

Anal. Calcd. for $C_9H_{12}N_4O_2$: C, 51.92; H, 5.81; N, 26.91. Found: C, 51.78; H, 5.85; N, 27.18.

Compound **23** was obtained in 5.3% yield (55 mg) mp 172-173° (diisopropyl ether); ^{1}H nmr (deuteriochloroform): δ 155.4 (m, C_7), 149.1 (s, C_{7a}), 148.8 (q, C_4, $^3J_{COMe}$ = 4.0 Hz), 144.8 (hept, C_{3a}, $^3J_{CMe}$ = 3.5 Hz), 94.2 (hept, C_3, $^2J_{CMe}$ = 4.5 Hz), 54.9 (q, OMe, $^1J_{CH}$ = 148 Hz), 39.2 (q, 6-Me, $^1J_{CH}$ = 142 Hz), 19.4 (qq, 3,3-diMe, $^1J_{CH}$ = 132 Hz, $^3J_{CMe}$ = 5.0 Hz).

Anal. Calcd. for $C_9H_{12}N_4O_2$: C, 51.92; H, 5.81; N, 26.91. Found: C, 51.99; H, 5.86; N, 26.87.

7-Chloro-3,3,5-trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**19**).

To a solution of **5** (722 mg, 0.005 mole) in DMF (10 ml) a solution of **11**, prepared from acetone hydrazone (3.0 g) in diethyl ether (20 ml), was added and the mixture was left for 48 hours at room temperature. Recrystallization from diisopropyl ether gave **19** (770 mg, 72%), mp 117-118°; ^{1}H nmr (deuteriochloroform): δ 1.69 (s, 3,3-diMe), 3.85 (s, 5-Me); ^{13}C nmr (deuteriochloroform): δ 157.1 (br s, C_3), 149.3 (s, C_{7a}), 146.6 (hept, C_{3a}, $^3J_{CMe}$ = 3.5 Hz), 131.0 (s, C_7), 96.9 (hept, C_3, $^2J_{CMe}$ = 4.5 Hz), 39.7 (q, 5-Me, $^1J_{CH}$ = 143 Hz), 19.3 (qq, 3,3-diMe, $^1J_{CH}$ = 132 Hz, $^3J_{CMe}$ = 5.0 Hz).

Anal. Calcd. for $C_8H_9ClN_4O$: C, 45.19; H, 4.27; N, 26.35. Found: C, 45.41; H, 4.22; N, 26.50.

5-Benzyl-3,3-dimethyl-7-phenyl-3a,7a-dihydro-3*H*-pyrazolo[3,4-*d*]-pyridazin-4(5*H*)-one (**25**).

To a solution of **3** (524 mg, 0.002 mole) in diethyl ether (30 ml) a solution of **11**, prepared from acetone hydrazone (1.2 g) in diethyl ether (8 ml), was added and the mixture was left for one hour at room temperature and then for 12 hours at −30°. The precipitate was collected by filtration to give **25** (585 mg, 88%), mp 109-113° dec; ^{1}H nmr (deuteriochloroform): δ 0.96 (s, 3H, 3-Me_{endo}), 1.68 (s, 3-Me_{exo}), 2.61 (d, H_{3a}), 4.89 and 4.94 (two s, CH_2Ph), 5.98 (d, H_{7a}), 7.00-7.45 (m, $H_{3'}$, $H_{4'}$, $H_{5'}$ and CH_2*Ph*), 7.85-8.20 (m, $H_{2'}$, $H_{6'}$), $J_{3a,7a}$ = 11.8 Hz.

Anal. Calcd. for $C_{20}H_{20}N_4O$: C, 72.27; H, 6.06; N, 16.85. Found: C, 72.55; H, 6.14; N, 16.53.

5-Benzyl-3-ethyl-3-methyl-7-phenyl-3a,7a-dihydro-3*H*-pyrazolo-[3,4-*d*]pyridazin-4(5*H*)-one (**26**).

To a solution of **3** (524 mg, 0.002 mole) in diethyl ether (30 ml) a solution of **12**, prepared from 2-butanone hydrazone (1.34 g), in diethyl ether (8 ml) was added. The reaction mixture was left for one hour at room temperature and then for 12 hours at −30°. The precipitate was collected by filtration to give **26** (475 mg, 69%), mp 100-102° dec; ^{1}H nmr (deuteriochloroform): δ (A) 0.98 (t, CH_2*Me), 1.00 (s, 3-*Me_{endo}), 2.04 (q, CH_2Me), 2.75 (d, H_{3a}), 4.94 (s, CH_2Ph), 6.04 (d, H_{7a}), 7.10-7.60 (m) and 7.95-8.35 (CH_2*Ph*, Ph), $J_{3a,7a}$ = 12.5 Hz. (B) 0.74 (t, 3H, CH_2Me), 1.67 (s, 3H, 3-Me_{exo}), 2.09 (q, 2H, CH_2Me), 2.65 (d, 1H, H_{3a}), 4.97 (s, 2H, CH_2Ph), 6.01 (d, 1H, H_{7a}), 7.10-7.60 (m) and 7.95-8.35 (m) (10H, CH_2*Ph*, Ph), $J_{3a,7a}$ = 12.5 Hz.

Anal. Calcd. for $C_{21}H_{22}N_4O$: C, 72.81; H, 6.40; N, 16.17. Found: C, 72.51; H, 6.40; N, 15.90.

3,3-Dimethyl-4-isopropyloxy-7-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazine (**29**), 6-Isopropyloxy-3-phenylpyridazine (**30**), 3,3-Dimethyl-

5-isopropyl-7-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**28**) and 3,3-Dimethyl-7-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**27**).

To a solution of **6** (1.157 g, 0.00672 mole) in DMF, a solution of **11**, prepared from acetone hydrazone (8.0 g), in diethyl ether (55 ml), was added and the mixture was left for 12 hours at room temperature. The volatile components were evaporated *in vacuo*. The dry residue was suspended in boiling benzene, cooled to room temperature, the solid collected by filtration and washed with benzene to give pure **27** (815 mg, 51%). The filtrate was evaporated *in vacuo* to give a mixture of four components, which were separated by flash chromatography.

The elution of the first component with benzene gave, after evaporation of the solvent, **29** (100 mg, 5%), bp 175, 2 torr); ^{1}H nmr (deuteriochloroform): δ 1.51 (d, CH*Me*$_2$), 1.66 (s, 3,3-diMe), 5.75 (hept, C*H*Me$_2$), 7.40-7.65 (m, H$_{3'}$, H$_{4'}$, H$_{5'}$), 8.50-8.75 (m, H$_{2'}$, H$_{6'}$), J_{CHMe_2} = 6.0 Hz.

Anal. Calcd. for $C_{16}H_{18}N_4O$: C, 68.06; H, 6.43; N, 19.84. Found: C, 68.34; H, 6.45; N, 19.59.

The elution of the second component with benzene gave, after evaporation of the solvent, **30** (65 mg, 4%), mp 98-100° sublimes 115°, 2 torr); ^{1}H nmr (deuteriochloroform): δ 1.44 (d, CH*Me*$_2$), 5.62 (hept, C*H*Me$_2$), 6.90 (d) and 7.71 (d) (H$_4$ and H$_5$), 7.30-7.55 (m, H$_{3'}$, H$_{4'}$, H$_{5'}$), 7.85-8.10 (m, 2H, H$_{2'}$, H$_{6'}$), J_{CHMe_2} = 6.4 Hz, J_{H_4,H_5} = 9.1 Hz.

Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.87; H, 6.66; N, 12.95.

The elution of the third component with a mixture of benzene and diethyl ether, 10:1, gave, after evaporation of the solvent, **28** (570 mg, 30%), mp 113-115° (sublimes 170°, 2 torr); ^{1}H nmr (carbon tetrachloride): δ 1.45 (d, C*H*Me$_2$), 1.64 (s, 3,3-diMe), 5.29 (hept, C*H*Me$_2$), 7.15-7.50 (m, H$_{3'}$, H$_{4'}$, J$_{5'}$), 8.20-8.45 (m, H$_{2'}$, H$_{6'}$), J_{CHMe_2} = 6.4 Hz; ^{13}C nmr (deuteriochloroform): δ 157.0 (s, C$_4$), 149.7 (s, C$_{7a}$), 144.6 (hept, C$_{3a}$, $^3J_{CMe}$ = 3.0 Hz), 139.2 (t, C$_7$, $^3J_{CH}$ = 4.0 Hz), 133.1, 129.6, 128.6, 128.0 (Ph), 94.3 (hept, C$_3$, $^2J_{CMe}$ = 4.5 Hz), 49.4 (d hept, C*H*Me$_2$, $^1J_{CH}$ = 144 Hz, $^2J_{CMe}$ = 3.5 Hz), 21.4 (m, CHMe$_2$, $^1J_{CH}$ = 128 Hz, $^3J_{CMe}$ = $^2J_{CH}$ = 4.0 Hz), 19.3 (qq, 3,3-diMe, $^1J_{CH}$ = 132 Hz, $^3J_{CMe}$ = 4.5 Hz).

Anal. Calcd. for $C_{16}H_{18}N_4O$: C, 68.06; H, 6.43; N, 19.84. Found: C, 67.77; H, 6.52; N, 19.48.

The elution of the fourth component with a mixture of benzene and diethyl ether, 10:1, gave after evaporation of the solvent, **27** (115 mg, 7%, combined yield 930 mg, 58%), mp 230-231° (ethanol); ^{1}H nmr (DMSO-d$_6$): δ 1.60 (s, 3,3-diMe), 7.35-7.65 (m, H$_{3'}$, H$_{4'}$, H$_{5'}$), 8.10-8.35 (m, H$_{2'}$, H$_{6'}$), 13.5 (br s, NH); ^{13}C nmr (DMSO-d$_6$): δ 158.5 (s, C$_4$), 150.5 (s, C$_{7a}$), 145.5 (hept, C$_{3a}$, $^3J_{CMe}$ = 140.3 (t, C$_7$, $^3J_{CH}$ = 4.0 Hz), 133.2, 129.8, 128.9, 128.2 (Ph), 94.0 (hept, C$_3$, $^2J_{CMe}$ = 4.5 Hz), 19.1 (qq, 3,3-diMe, $^1J_{CH}$ = 132 Hz, $^3J_{CMe}$ = 5.0 Hz).

Anal. Calcd. for $C_{13}H_{12}N_4O$: C, 64.99; H, 5.03; N, 23.32. Found: C, 64.63; H, 5.02; N, 22.97.

3,3,7-Trimethyl-1,2-dihydro-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**31**) and 3,3,7-Trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**34**).

To a solution of **7** (1.28 g, 0.01 mole) in DMF (10 ml) a solution of **11**, prepared from acetone hydrazone (6.0 g), was added and the mixture was stirred for 24 hours at room temperature. The precipitate formed during this time was collected by filtration to give **31** (1.35 g, 75%), mp 190° dec (ethanol); ms: m/e 180 (M$^+$, 13.5%), 165 (M-Me, 100%); ^{1}H nmr (DMSO-d$_6$): 1.34 (s, 3,3-diMe), 2.09 (s, 7-Me), 4.4 (br s, NH).

Anal. Calcd. for $C_8H_{12}N_4O$: C, 53.32; H, 6.71; N, 31.09. Found: C, 53.28; H, 6.82; N, 30.95.

The filtrate was evaporated *in vacuo* and the dry residue was recrystallized from ethanol to give **34** (210 mg, 12%), mp 226-230°; ^{1}H nmr (deuteriochloroform): δ 1.67 (s, 3,3-diMe), 2.82 (s, 7-Me), 12.3 (br s, NH).

Anal. Calcd. for $C_8H_{10}N_4O$: C, 53.92; H, 5.66; N, 31.44. Found: C, 53.94; H, 5.70; N, 31.60.

3,7-Dimethyl-3-ethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**35**).

To a stirred solution of **7** (1.28 g, 0.01 mole) in DMF (10 ml) a solution of **12**, prepared from butanone hydrazone (6.7 g) in diethyl ether (40 ml), was added and stirring was continued for 30 minutes. The mixture was then left in refrigerator for 3 days. Diethyl ether was evaporated *in vacuo*. The crystals formed in DMF solution after 12 hours were separated by filtration to give **35** (0.94 g, 49%), mp 198° (ethanol); ^{1}H nmr (deuteriochloroform): δ 0.56 (t, 3-CH$_2$,*Me*), 1.65 (s, 3-Me), 2.37 (m, 3-C*H*$_2$Me), 2.83 (s, 7-Me), 12.6 (br s, NH), J_{CH_2Me} = 7.5 Hz.

Anal. Calcd. for $C_9H_{12}N_4O$: C, 56.24; H, 6.29; N, 29.15. Found: C, 56.12; H, 6.41; N, 29.19.

3,7-Dimethyl-3-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one (**36**).

To a solution of **7** (1.92 g, 0.015 mole) in DMF (15 ml) a solution of **13**, prepared from acetophenone hydrazone (8.1 g) in diethyl ether (80 ml) was added and the mixture was left for three weeks at room temperature. The unreacted **7** (1.28 g) was removed by filtration, the filtrate was evaporated *in vacuo*, diethyl ether (30 ml) was added to the residue, the mixture was heated for several minutes under reflux. The solid was separated by filtration and recrystallized from ethanol to give **36** (195 mg, 5.4%), mp 188-190°; ^{1}H nmr (deuteriochloroform): δ 1.97 (s, 3-Me), 2.81 (s, 7-Me), 7.05-7.60 (m, Ph), 12.6 (br s, NH); ^{13}C nmr (deuteriochloroform): δ 160.0 (s, C$_4$), 152.6 (q, C$_{7a}$, $^3J_{CMe}$ = 2.5 Hz), 143.7 (q, C$_{3a}$, $^3J_{CMe}$ = 3.0 Hz), 141.7 (q, C$_7$, $^2J_{CMe}$ = 7.0 Hz), 134.2, 129.0, 128.8, 127.0 (Ph), 101.3 (br q, C$_3$, $^2J_{CMe}$ = 3.5 Hz), 21.4 (q, 3-Me, $^1J_{CH}$ = 133.5 Hz), 17.2 (q, 7-Me, $^1J_{CH}$ = 130 Hz).

Anal. Calcd. for $C_{13}H_{12}N_4O$: C, 64.99; H, 5.03; N, 23.32. Found: C, 64.84; H, 5.08; N, 23.22.

7-Phenyl-3,3,5-trimethyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-thione (**37**).

A) From **8**: To a solution of **8** (404 mg, 0.002 mole) in DMF (20 ml) refrigerated to −30°, a solution of **11**, prepared from acetone hydrazone (1.2 g) in diethyl ether (8 ml) refrigerated to −30°, was added. The mixture was allowed to warm slowly to room temperature and then left for two hours at room temperature. The volatile components were evaporated *in vacuo*, water (20 ml) was added to the residue and the solid separated by filtration to give **37** (300 mg, 56%), mp 182-183° (ethanol); ^{1}H nmr (deuteriochloroform): δ 1.76 (s, 3,3-diMe), 4.29 (s, 5-Me), 7.40-7.65 (m, H$_{3'}$, H$_{4'}$, H$_{5'}$), 8.35-8.60 (m, H$_{2'}$, H$_{6'}$).

Anal. Calcd. for $C_{14}H_{14}N_4S$: C, 62.20; H, 5.22; N, 20.72. Found: C, 62.34; H, 5.22; N, 20.67.

B) From **41**: A mixture of **41** (508 mg, 0.002 mole) and phosphorus pentasulphide (0.5 g) in xylene (5 ml) was heated under reflux for two hours. The boiling mixture was filtered and the fil-

trate evaporated *in vacuo*. The dry residue (506 mg, 97%) was recrystallized from ethanol to give **37** (390 mg, 72%), mp 176-180°. The ir and ^{1}H nmr spectra were identical with those obtained from the sample described under A.

5-Benzyl-3,3-dimethyl-7-phenyl-3*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-thione (**38**).

To a solution of **9** (556 mg, 0.002 mole) in DMF (10 ml) refrigerated to −30°, a solution of **11**, prepared from acetone hydrazone (1.2 g) refrigerated to −30°, was added. The reaction mixture was allowed to warm slowly to room temperature. The volatile components were evaporated *in vacuo*, ethanol (10 ml) was added to the oily residue and left for several hours at room temperature. The crystals were then separated by filtration to give **38** (250 mg, 36%), mp 133-134° (ethanol); ^{1}H nmr (deuteriochloroform): δ 1.74 (s, 3,3-diMe), 5.98 (s, C*H*$_2$Ph), 7.15-7.60 (m, H$_{3'}$, H$_{4'}$, H$_{5'}$, CH$_2$*Ph*), 8.30-8.55 (m, H$_{2'}$, H$_{6'}$).

Anal. Calcd. for $C_{20}H_{18}N_4S$: C, 69.34; H, 5.24; N, 16.17. Found: C, 69.59; H, 5.27; N, 16.20.

exo-3-Methyl-5-phenyl-2-oxo-3,4-diazabicyclo[4.1.0]hept-4-ene-7-spiro-1′-indane (**39**) and endo-3-Methyl-5-phenyl-2-oxo-3,4-diazabicyclo[4.1.0]hept-4-ene-7-spiro-1′-indane (**40**).

To a solution of **10** (1054 mg, 0.00566 mole) in DMF (12 ml) a solution of **14**, prepared from indan-1-one hydrazone (2.07 g, 0.0142 mole), in diethyl ether (50 ml) was added. The reaction mixture was left in refrigerator for 24 hours at +5°. The solvents were evaporated *in vacuo*, ethanol (25 ml) was added to the residue and the mixture was heated under reflux for several minutes. After cooling to room temperature, indan-1-one azine (635 mg) was filtered off and the filtrate evaporated *in vacuo*. The residue was separated by flash chromatography (Kieselgel 60, 0.040-0.063 mm, E. Merck, Darmstadt). Elution with benzene (500 ml), followed with a mixture of benzene and diethyl ether, 100:1, 500 ml), 75:1 (1500 ml), 10:1 (750 ml) and finally with diethyl ether (750 ml), gave, after evaporation of solvents *in vacuo* the following compounds:

1. Indan-1-one had mp 38-40° (40 mg). The ir and ^{1}H nmr spectra were identical with those of an authentic sample.

2. exo-3-Methyl-5-phenyl-2-oxo-3,4-diazabicyclo[4.1.0]hept-4-ene-7-spiro-1′-indane (**39**) had mp 215-218° (ethanol) (395 mg, 23%); ^{1}H nmr (deuteriochloroform): δ 1.82 (dt, 2′-CH$_2$), 2.65 (d) and 2.82 (d) (H$_1$ and H$_6$), 2.99 (t, 3′-CH$_2$), 3.46 (s, 3-Me), 6.60-6.80 (m, H$_{7'}$), 7.00-7.70 (m, H$_{4'}$, H$_{5'}$, H$_{6'}$, Ph), $J_{CH_2CH_2}$ = 8.0 Hz, $J_{2'\text{-}CH_2}$ = Hz, $J_{2'\text{-}CH_2}$ = 2 Hz.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.46; H, 6.16; N, 9.31.

3. endo-3-Methyl-5-phenyl-2-oxo-3,4-diazabicyclo[4.1.0]hept-4-en-7-spiro-1′-indane (**40**) had mp 197-198° (ethanol) (425 mg, 25%); ^{1}H nmr (deuteriochloroform): δ 2.33 (t, 2′-CH$_2$), 2.58 (s) and 2.80 (d) (H$_1$ and H$_6$), 3.01 (t, 3′-CH$_2$), 3.51 (s, 3-Me), 6.35-6.55 (m, H$_{7'}$), 6.80-7.70 (m, H$_{4'}$, H$_{5'}$, H$_6$, Ph), $J_{CH_2CH_2}$ = 6.4 Hz, J_{H_1,H_6} = 8.0 Hz.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.41; H, 6.16; N, 9.23.

4. Starting compound **10** was obtained in 47% (490 mg). The ir and ^{1}H nmr spectra were identical with those of an authentic sample.

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REFERENCES AND NOTES

[1] R. R. King, *J. Org. Chem.*, **47**, 5397 (1982).

[2] F. Farina, M. V. Martin, F. Sanchez and A. Tito, *Heterocycles*, **18**, 175 (1982).

[3] M. Franck-Neumann and G. Leclerc, *Tetrahedron Letters*, 1063 (1969).

[4] B. Stanovnik, M. Tišler, I. Leban and L. Golič, J. Chem. Soc., Chem. Commun., 268 (1984).

[5] B. Stanovnik, B. Furlan, A. Sarka, M. Tišler and M. Žličar, *Heterocycles*, **22**, 2479 (1984).

[6] B. Stanovnik, B. Božnar, B. Koren, S. Petriček and M. Tišler, *Heterocycles*, **23**, 1 (1985).

[7] B. Furlan, B. Stanovnik and M. Tišler, *Synthesis*, **78** (1986).

[8] B. Stanovnik, B. Furlan, M. Kupper, L. Malež, A. Štimac, M. Tišler and M. Žličar, *J. Heterocyclic Chem.*, **25**, 393 (1988).

[9] M. Merslavič, A. Petrič, D. Rozman, B. Stanovnik and M. Tišler, *J. Heterocyclic Chem.*, **26**, 445 (1989).

[10] M. Merslavič, A. Petrič, B. Stanovnik and M. Tišler, *J. Heterocyclic Chem.*, **26**, 581 (1989).

[11] M. Merslavič, B. Stanovnik and M. Tišler, *J. Heterocyclic Chem.*, **26**, 585 (1989).

[12] S. J. Buckland, B. Halton and B. Stanovnik, *Tetrahedron Letters*, **27**, 1309 (1986).

[13] S. J. Buckland, B. Halton and B. Stanovnik, *Aust. J. Chem.*, **40**, 2037 (1987).

[14] For a review see: B. Stanovnik, 1,3-Dipolar Cycloadditions of Diazoalkanes to Pyridazines and Condensed Pyridazines, *Actual Chim. Ther.*, 16e serie, 219 (1987).

[15] A. Štimac, B. Stanovnik, M. Tišler and L. Golič, *Tetrahedron*, **46**, 6915 (1990).

[16] I. Leban, L. Golič, B. Stanovnik and M. Tišler, *Acta Cryst.*, **C43**, 1814 (1987).

[17] I. Leban, L. Golič, B. Stanovnik and M. Tišler, *Acta Cryst.*, **C44**, 193 (1988).

[18] H. McNab, *J. Chem. Soc., Perkin Trans. I*, 1203 (1983).

[19] H. P. Fritz, J. Riedel, H. Martin and K. Francke, *Chem. Ber.*, **93**, 1433 (1960).

[20] S. D. Andrews, A. C. Day, P. Raymond and M. C. Whiting, *Org. Synth.*, **50**, 27 (1970).

[21] 2-Diazopropane was prepared according to the same procedure as described in literature for 2-diazopropane [20] from 2-butanone hydrazone [22].

[22] G. J. Karabatsos and C. E. Osborne, *Tetrahedron*, **24**, 3361 (1968).

[23] R. A. Moss and J. D. Funk, *J. Chem. Soc. (C)*, 2026 (1967).

[24] G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, 3789 (1959).

[25] R. F. Homer, H. Gregory and L. Wiggins, *J. Chem. Soc.*, 2191 (1948).

[26] K. Eichenberger, A. Staehelin and J. Druey, *Helv. Chim. Acta*, **37**, 837 (1954).

[27] I. Crossland and L. K. Rasmusen, *Acta Chem. Scand.*, **19**, 1652 (1965).

[28] W. G. Overend and L. F. Wiggins, *J. Chem. Soc.*, 239 (1947).

[29] H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).