

REACTIONS WITH CYCLIC OXALYL COMPOUNDS, PART 26<sup>1</sup>: THE FISCHER-INDOLE  
 REARRANGEMENT OF STERICALLY HINDERED SYSTEMS, PART 7<sup>2</sup>: DIAZA[n.3.3]  
 PROPELLANES VIA THERMALLY INITIATED FISCHER-INDOLIZATION

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Abstract - The 4,5-bridged pyrrol-2,3-diones 3, obtained from cyclo-  
 condensation reactions of the N,N-disubstituted hydrazones 2 and oxalyl  
 dichloride, can be rearranged into the corresponding diaza[n.3.3]  
 propellanes 4 via a thermally initiated Fischer-indolization process.  
 Their molecular structure is confirmed with aid of an X-ray structure  
 determination of 4a and chemical degradation reactions leading to the  
 tetracyclic indole systems 5.

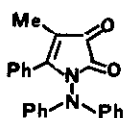
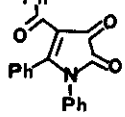
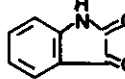
The skeleton of diaza[n.3.3]propellanes is found in alkaloides of the Echitamin-  
 type<sup>3</sup>, in particularly named "Echibolines" by Fritz et al.<sup>4</sup>. A similar compound  
 was described by Gilchrist et al.<sup>5</sup> a few years ago. We found, that diaza[n.3.3]  
 propellanes in principle can be seen as stable intermediates of the Fischer-  
 indolization process, bearing the  $\beta$ -nitrogen still fixed within the molecule.  
 They are prepared by thermolysis of suitable substituted pyrrol-2,3-dione derivatives  
 as reported 10 years ago<sup>2,6</sup>. Now we tried to check the scope and limitations of  
 this particular indolization reaction and to confirm the constitution and steric  
 properties of those propellanes with aid of an X-ray study.

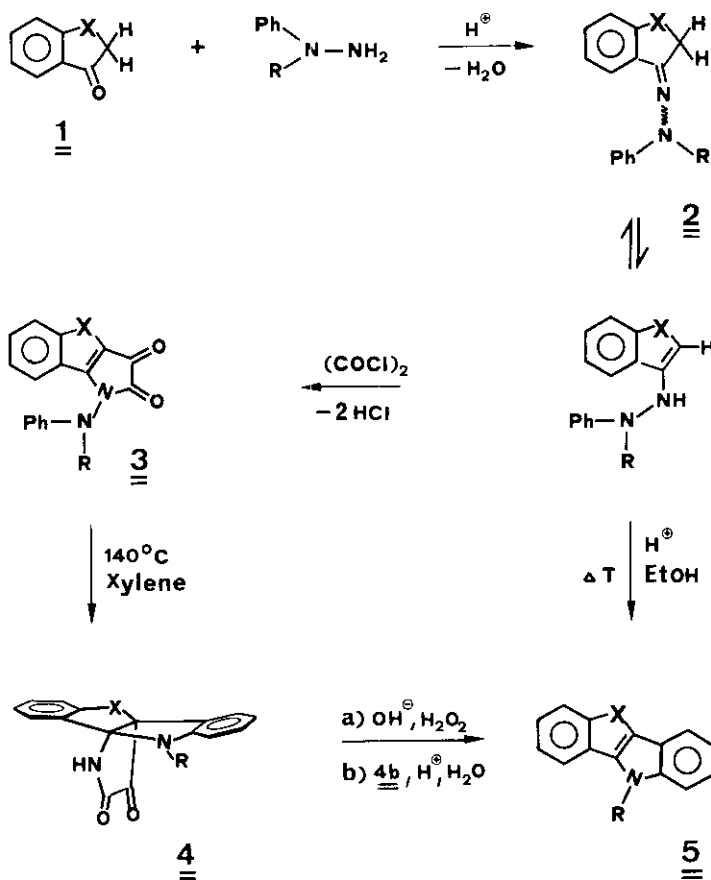
The synthesis starts from the N,N-disubstituted hydrazones 2 of the corresponding  
 bicyclic ketones 1, which are cyclized to the tricyclic pyrroldiones 3 using  
 oxalyl chloride in 40-60% yields (exception 3c : 7% yield). The hydrazones 2 are  
 easily obtained by simple condensation reactions of the ketones 1 and the asym.  
 disubstituted hydrazines (R = Ph or Me): 2c, 2d and 2g are crystalline products  
 (yields 70-90%), 2b and 2e are characterized as liquids, purified by column

chromatography (yields 60-65%), while 2a and 2f without isolation in situ are cyclized as crude liquids to give the corresponding pyrroldiones 3a and 3f respectively. Surprisingly from all hydrazones 2 only 2d<sup>7</sup> and 2g<sup>8</sup> were mentioned in the literature but without giving experimental details. From the ir and <sup>1</sup>H nmr spectroscopic data 2 are found to exist in the hydrazone form of the possible tautomeric equilibrium at 20°C and in solution (CDCl<sub>3</sub>). The downfield shift (δ 8.0 - 8.5 ppm) of the o-proton of the aromatic ring obviously is due to the anisotropic effect of the C=N double bond, which is well known from the corresponding ketones<sup>9</sup>.

The red coloured tricyclic pyrrol-2,3-dione derivatives 3 in general are characterized by their ir spectroscopic data compared with those of various similar derivatives<sup>10</sup> thus indicating their structural analogy: Strong absorption bands in the 1760 - 1770, 1680 - 1700 and 1580 - 1600 cm<sup>-1</sup> region (KBr) are found with all compounds showing this pyrroldione moiety. A <sup>13</sup>C nmr spectrum of 3d was taken as an example and compared with <sup>13</sup>C nmr data of several other analogues. The assignment of the signals from chemical shift values and long range coupling constants again confirm the structural proposal of 3 (see Table 1).<sup>10-12</sup>

Table 1. - <sup>13</sup>C Nmr chemical shifts, signal splitting and coupling constants of ring carbons of several pyrrol-2,3-diones (in d<sub>6</sub>-DMSO) :

Compound	C-2	C-3	C-4	C-5
<u>3d</u>	162.9 (s)	172.5 (t, 4Hz)	114.2 (t, 6Hz)	150.5 (m)
	156.0 (s)	177.5 (q, 4Hz)	106.7 (q, 7Hz)	160.6 (m)
	157.0 (s)	178.4 (s)	112.6 (s)	173.2 (t, 4Hz) <sup>13</sup>
	159.3 (s)	184.4 (d)	117.7 (m)	150.7 (m)



	R	X
a	Ph	-(CH <sub>2</sub> ) <sub>3</sub> -
b	Ph	-s-CH <sub>2</sub> -
c	Ph	-o-CH <sub>2</sub> -
d	Me	-CH <sub>2</sub> -
e	Me	-(CH <sub>2</sub> ) <sub>2</sub> -
f	Me	-(CH <sub>2</sub> ) <sub>3</sub> -
g	Me	-s-CH <sub>2</sub> -

The pyrrol-2,3-diones 3 (except 3d) are rearranged into the corresponding yellow coloured diazaproPELLanes 4 by simple heating in boiling xylene (30-45 min). After cooling down to room temperature pure 4 precipitate from the reaction mixture. Elucidation of the molecular skeletons of 4 is based on an X-ray structure determination of 4a. (Figure 1).

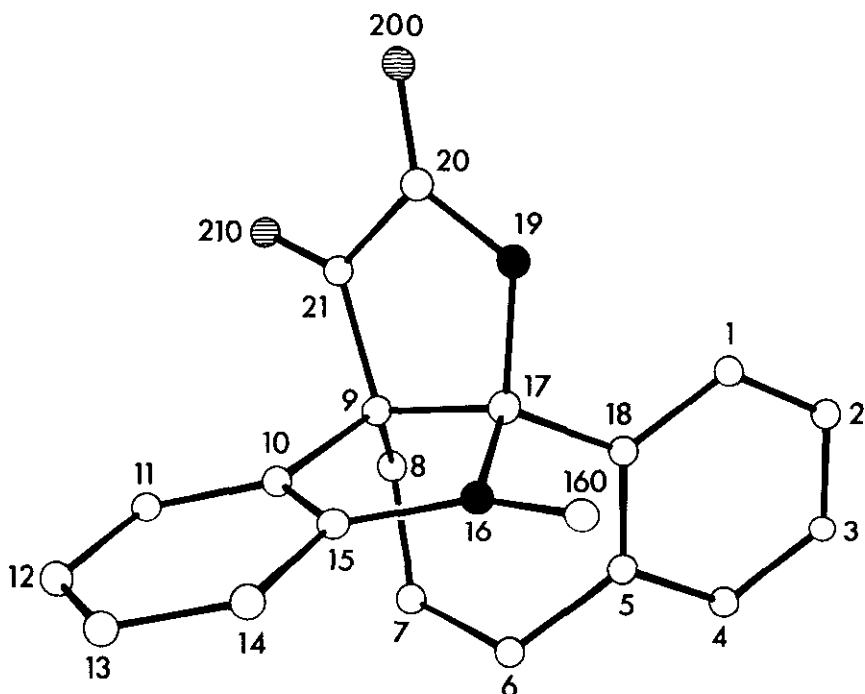


Figure 1. Molecule of 4a with the numbering of the atoms corresponding to Tables 2 and 3; solid circles are nitrogens, hatched circles are oxygens, and open circles are carbons.

4a crystallizes monoclinically in space group  $P 2_1/n$  (Nr. 14) with  $a = 1211.3(4)$ ,  $b = 1332.7(4)$ ,  $c = 1009.4(3)$  pm and  $\beta = 95.97(2)^\circ$ . The calculated crystal density of  $1.313 \text{ g.cm}^{-3}$  indicates that 4 molecules form the unit cell. All atomic parameters, bond lengths and angles can be depicted from Tables 3 and 4, the numbering of atoms from Figure 1. Most bond lengths are within the expected regions, the central  $c(17) - C(9)$  bond is slightly lengthened ( $158.4 \text{ pm}$ )<sup>14</sup>. A Newman projection along this bond (Figure 2) shows the interplanar angles and the deviations of planarity in the ring systems forming the propeller. In the crystal the molecules are associated via  $N(19) - H \dots O(200)$  hydrogen bridge bindings as shown from the stereo view of the unit cell (Figure 3). The heavy atom - heavy atom distance of  $282 \text{ pm}$  shows the expected value.<sup>15</sup>

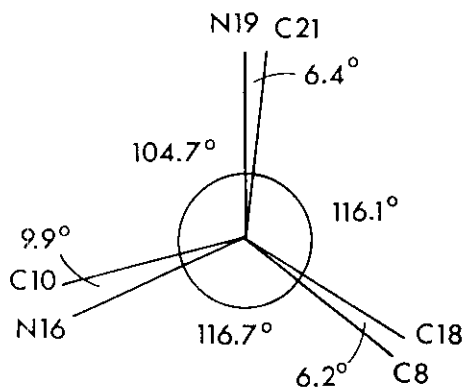


Figure 2. - Newman-Projection of 4a along C(17)-C(9).

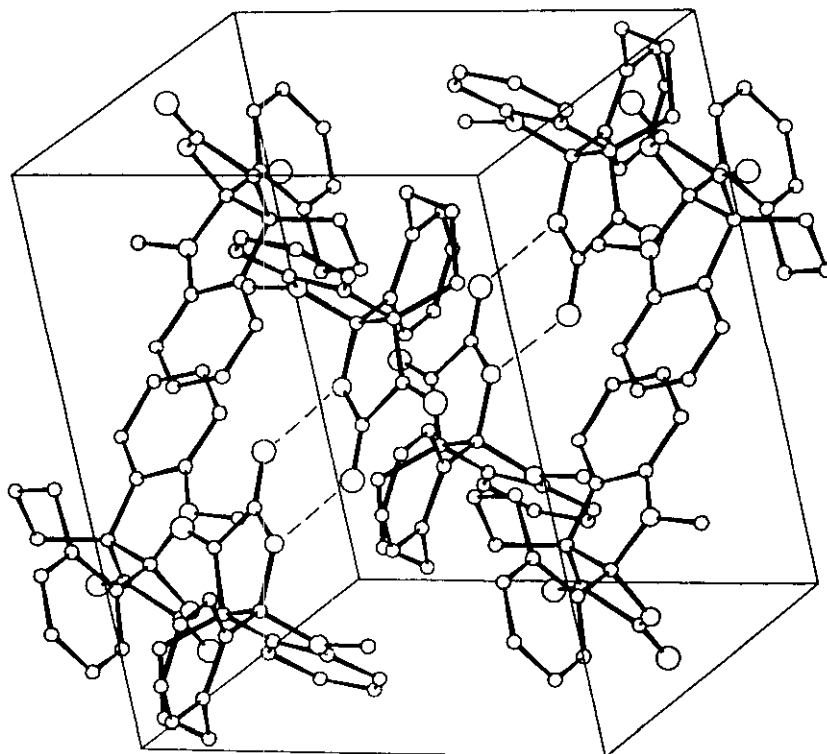
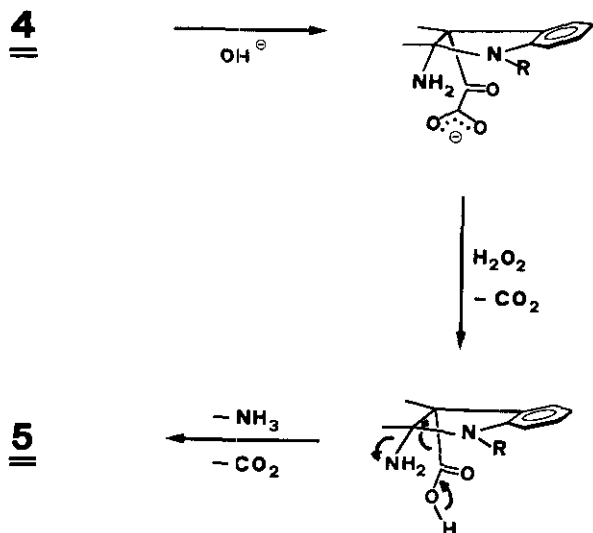


Figure 3. - Stereographic projection of the unit cell.

Based on this X-ray structure determination of 4a the assignment of all ir,  $^1\text{H}$ -nmr and  $^{13}\text{C}$ -nmr spectroscopic data of the diazapropellanes 4 is easy and clearly shows the structural analogy of all compounds 4 : In particular, the ir absorption bands of 4a-g are nearly identical (3200-3050, 1760-1765 und 1710-1720  $\text{cm}^{-1}$ ), in the  $^{13}\text{C}$  Nmr spectrum of 4a signals at  $\delta$  61 and 88 ppm (central  $\text{sp}^3$  - carbons), 162 ppm (Lactam-carbonyl) and 200 ppm (C=O) are in good agreement with the corresponding data of a quite similar diazapropellane (62.5, 89.4, 157.5 and 194.1 ppm).<sup>2</sup>

Concerning the reaction mechanism of the rearrangement 3 + 4 a close connexion to the mechanism of the thermically initiated Fischer - Indole synthesis is evident.<sup>16</sup> To prove if in fact a [3,3] sigmatropic shift is involved in the new C-C bond formation, KIE - experiments should be helpful.<sup>17</sup>

Hydrolysis of the diazapropellanes 4. - As expected from earlier results<sup>2,10b</sup>, hydrolysis of 4 with alkaline  $\text{H}_2\text{O}_2$  under opening of the pyrroledione ring and subsequent loss of the NH-CO-CO - moiety gives the tetracyclic indole derivatives 5 in moderate yields (30% - 50%), which in an independent way can easily be synthesized from  $\text{H}^+$  - catalysed Fischer indole synthesis of the corresponding hydrazones 2. 5b is obtained too by acidic ethanolysis of 4b in 90% yield. 5d<sup>18</sup>, 5e<sup>19</sup>, 5f<sup>20</sup> and 5g<sup>18</sup> were known from the literatures, therefore the structural assignment of all indole derivatives based on melting points, elemental analyses, ir and  $^1\text{H}$ -nmr spectroscopic data was easy (see Experimental section). The reaction pathway 4 + 5 should include a primary attack at the aminal moiety, opening of the  $\alpha$ -oxo-lactam function and oxidative decarboxylation to an anthranilic acid type intermediate, which then with loss of  $\text{CO}_2$  and  $\text{NH}_3$  in a fragmentational process finally stabilizes to the indole system. This reaction mechanism partially agrees with the well known synthesis of anthranilic acid derivatives from the corresponding isatines.<sup>21</sup>



EXPERIMENTAL

Melting points were determined on a Tottoli melting point apparatus and are uncorrected. CHN - elemental analyses were performed on a Carlo Erba Elemental Analyzer Model 1106, Ir spectra were recorded on a Perkin-Elmer Model 298.  $^1\text{H}$  and  $^{13}\text{C}$  Nmr spectra were obtained either on a Varian EM 360 or Varian XL-200 spectrometer with TMS as an internal standard. The single crystal X-ray analysis was carried out with a Syntex P3 four-circle diffractometer.

Thiochroman-4-on-N,N-diphenylhydrazone (2b)

To a solution of 1.64 g (10 mmole) 1b in 10 ml dry ethanol 1.84 g (10 mmole) N,N-diphenylhydrazine, 0.01 ml acetic acid and 3.5 g active molecular sieve  $3/4 \text{ \AA}$  are added. After 48h at room temperature the molecular sieve is removed and the solution evaporated. The crude oily residue was then purified with aid of MPLC-chromatography (silicagel 60, 1 atm., eluent  $\text{CHCl}_3$ ) :  $\delta$  2.8 (m, 4H),

6.8-7.4 (m, 13H), 8.5 ppm (dd, 1H). Anal. Calc. for  $C_{21}H_{18}N_2S$  : C 76.32, H 5.50, N 8.84; Found : C 76.57, H 5.60, N 8.45.

Chroman-4-on-N,N-diphenylhydrazone (2c)

A solution of 1.84 g (10 mmole) N,N-diphenylhydrazine and 1.48 g (10 mmole) 1c in 10 ml ethanol and 0.01 ml acetic acid is stirred for 20h at room temperature. The so formed crystalline product is separated by suction and recrystallized from a small amount of ethanol to give 2.67 g (85%) yellow needles, mp 133°C. -  $^1H$  Nmr ( $CDCl_3$ ) :  $\delta$  2.4 (t, 2H), 4.1 (t, 2H), 6.8-7.5 (m, 13H), 8.4 (dd, 1H). Anal. Calc. for  $C_{21}H_{18}N_2O$  : C 80.22, H 5.78, N 8.92; Found : C 80.35, H 5.77, N 8.84.

Indan-1-on-N-methyl-N-phenylhydrazone (2d)

1.22 g (10.0 mmole) N-methyl-N-phenylhydrazine, 1.32 (10.0 mmole) 1d and 0.01 ml acetic acid are dissolved in 10 ml ethanol and 3 g active molecular sieve  $3/4 \text{ \AA}$  are added. After 48h the filtered solution is evaporated and the residue purified by MPLC chromatography (silicagel 60, 1 atm., eluent  $CHCl_3$ ) to yield 1.6 g (68%) of a yellow oil. -  $^1H$  Nmr ( $CDCl_3$ ) :  $\delta$  2.8 (t, 2H), 2.9 (t, 2H), 3.2 (s, 3H), 6.8 - 7.5 (m, 8H), 8.0 (dd, 1H). Anal. Calc. for  $C_{16}H_{16}N_2$  : c 81.35, H 6.78, N 11.86; Found : C 81.15, H 6.75, N 11.98.

1-Tetralon-N-methyl-N-phenylhydrazone (2e)

A quite similar procedure as described above using 1.22 g (10 mmole) N-methyl-N-phenylhydrazine and 1.46 g (10 mmole) 1e yields 1.62 g (65%) of 2e. -  $^1H$  Nmr ( $CDCl_3$ ) : 2.0 (m, 2H), 2.9 (m, 2H), 3.2 (s, 3H), 6.8-7.5 (m, 8H), 8.4 (dd, 1H). Anal. Calc. for  $C_{17}H_{18}N_2$  : C 81.55, H 7.26, N 11.19; Found : C 81.58, H 7.36, N 11.34.

Thiochroman-4-on-N-methyl-N-phenylhydrazone (2g)

A mixture of 1.64 g (10 mmole) 1g, 1.22 g (10 mmole) N-methyl-N-phenylhydrazine, 0.01 ml acetic acid and 3.5 g active molecular sieve in 10 ml ethanol reacts for 48h at 20°C. The crude precipitate together with the molecular sieve is filtered, dissolved in a small amount of hot ethanol, filtered again and after cooling 2.0 g (70%) of yellow coloured 2g can be isolated, mp 71°C. -  $^1H$  Nmr ( $CDCl_3$ ) :  $\delta$  3.0 (m, 4H), 3.2 (s, 3H), 6.8-7.4 (m, 8H), 8.4 (dd, 1H). - Anal. Calc. for  $C_{16}H_{16}N_2S$  : C 71.60, H 6.02, N 10.44, S 11.95; Found : C 71.84, H 5.84, N 10.47, S 11.75.



1-Diphenylamino-4H,5H,6H-benzo[6,7]cyclohepta[1,2]pyrrol-2,3-dione (3a)

A solution of 1.6 g (10 mmole) 1a, 1.84 g (10 mmole) N,N-diphenylhydrazine and 0.01 ml acetic acid in 20 ml ethanol is stirred for 10h. After addition of 3.5 g active molecular sieve  $3/4 \text{ \AA}$  the mixture is held at  $20^{\circ}\text{C}$  for 20h. Then the molecular sieve is removed, the ethanol evaporated and the viscous oily residue dried over KOH in vacuo. To 3.1 g of this yellow oil, dissolved in 100 ml of dry ether, a solution of 0.9 ml oxalyldichloride in 20 ml dry ether is slowly added dropwise with stirring. After 11h at room temperature the precipitated crude product is triturated with excess of  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  solution is filtered from little insoluble material and evaporated to dryness. The residue is treated with dry ether and recrystallized from dry ethanol to yield 1.95 g (50%) red crystals, mp  $167^{\circ}\text{C}$ . - Ir(KBr) : 1765, 1695, 1600  $\text{cm}^{-1}$ . - Anal. Calc. for  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2$  : C 78.92, H 5.31, N 7.37; Found : C 79.20, H 5.59, N 7.41.

1-Diphenylamino-4H-1-benzothiopyrano[4,3-b]pyrrol-2,3-dione (3b)

To a solution of 1.65 g 2b in 50 ml dry ether 0.6 ml (7.0 mmole) of oxalyldichloride, diluted with 20 ml dry ether, are added slowly with stirring. After 20h at room temperature the precipitate is separated by suction and recrystallized from abs. ethanol yielding 0.67 g (60%) of red coloured crystals, mp  $145^{\circ}\text{C}$ . - Ir(KBr) : 1765, 1685, 1585  $\text{cm}^{-1}$ . - Anal. Calc. for  $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  : C 71.85, H 4.20, N 7.29, S 8.33; Found : C 71.84, H 4.29, N 7.15, S 8.20.

1-Diphenylamino-4H-1-benzopyrano[4,3-b]pyrrol-2,3-dione (3c)

Under  $\text{N}_2$ -atmosphere a solution of 0.6 ml (7.0 mmole) of oxalyl dichloride in 20 ml dry ether is slowly added dropwise to 1.57 g (5 mmole) 2c, dissolved in 50 ml dry ether, the so formed, deeply red coloured precipitate is separated by suction after 5h and washed with excess of dry ether extensively. The yield is 0.13 g (7%), mp  $169^{\circ}\text{C}$  (decomp.). - Ir(KBr) : 1765, 1685, 1595  $\text{cm}^{-1}$ . - Anal. Calc. for  $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_3$  : C 75.00, H 4.35, N 7.61; Found : C 74.89, H 4.20, N 7.58.

1-Methylphenylamino-3,4-dihydro-2H-indeno[1,2-b]pyrrol-2,3-dione (3d)

Dropwise addition of 1.2 ml (14 mmole) oxalyldichloride, dissolved in 20 ml of dry ether, to a solution of 2.36 g (10 mmole) 2d, in 100 ml of dry ether with stirring for 15h yields 2.15 g (74%) of red crystals, recrystallized from dry ethanol, mp  $167^{\circ}\text{C}$ . - Ir(KBr) : 1765, 1685, 1605  $\text{cm}^{-1}$ . -  $^{13}\text{C}$  Nmr spectrum ( $d_6\text{DMSO}$ ) :

$\delta$  172.5 (t), 162.9 (s), 150.5 (m), 148.5 (t), 114.2 (t), 40.1 (q), 30.7 (t). - Anal. Calc. for  $C_{18}H_{14}N_2O_2$  : C 74.46, H 4.87, N 9.65; Found : C 74.33, H 5.03, N 9.40.

1-Methylphenylamino-2,3,4,5-tetrahydro-benz[g]indol-2,3-dione (3e)

An identical experimental procedure as described above for 3d leads to isolation of 1.0 g (35%) of red crystals, mp  $158^\circ C$  (from ethanol). Ir(KBr) : 1765, 1700,  $1610\text{ cm}^{-1}$ . - Anal. Calc. for  $C_{19}H_{16}N_2O_2$  : C 74.97, H 5.31, N 9.21; Found : C 74.93, H 5.33, N 9.08.

1-Methylphenylamino-4H,5H,6H-benzo[6,7]cyclohepta[1,2-b]pyrrol-2,3-dione (3f)

The identical experimental procedure as described for the synthesis of 3a (see above) is used with 1.6 g (10 mmole) 1a, 1.22 g (10 mmole) N-methyl-N-phenylhydrazine and 0.9 mol (10.5 mmole) oxalyldichloride finally to get 1.9 g (54%) 3f, mp  $173^\circ C$ . - Ir(KBr) : 1760, 1695,  $1605\text{ cm}^{-1}$ . - Anal. Calc. for  $C_{20}H_{18}N_2O_2$  : C 75.44, H 5.71, N 8.80; Found : C 75.69, H 5.64, N 8.72.

1-Methylphenylamino-4H-1-benzothiopyrano[4,3-b]pyrrol-2,3-dione (3g)

A solution of 1.2 ml (14 mmole) oxalyldichloride in 20 ml dry ether is added dropwise to 2.68 g (10 mmole) 2g, dissolved in 100 ml dry ether. Stirring for 20h gives a red precipitate which crystallizes from dry ethanol. The yield is 1.38 g (43%), mp  $138^\circ C$ . - Ir(KBr) : 1765, 1695,  $1595\text{ cm}^{-1}$ . - Anal. Calc. for  $C_{18}H_{14}N_2O_2S$  : C 67.05, H 4.39, N 8.69, S 9.94; Found : C 66.84, H 4.57, N 8.53, S 9.75.

Synthesis of the Diazapropellanes 4 : General Procedure

A suspension of the appropriate amount of 3 in dry xylene (5-10 ml) is heated under reflux for 30-45 min. The corresponding propellane 4 either separates from the hot solution or is obtained after evaporating of the solvent by treating with dry ether and is recrystallized from ethanol. Further experimental details see Table 2.

14,15-Dioxo-12-phenyl-5H,6H,7H-7a,12a-iminoethano-1-benz[6,7]cyclohept[1,2-b]indole(4a)

IR(KBr) : 3200-3050, 1765, 1720  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $d_6$ -DMSO) :  $\delta$  1.4 (m, 6H), 6.7-7.6 (m, 13H), 11.4 (s, 1H).

13,14-Dioxo-11-phenyl-6,11-dihydro-6a,11a-iminoethano-1-benzothiopyrano[4,3-b]indole (4b)

IR(KBr) : 3200-3050, 1760, 1715  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $d_6$ -DMSO) :  $\delta$  2.8 (m, 2H), 6.3-7.7 (m, 13H), 11.4 (s, 1H).

13,14-Dioxo-11-methyl-6,11-dihydro-6a,11a-iminoethanobenzo[a]carbazole(4e)

IR(KBr) : 3200-3050, 1760, 1720  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $d_6$ -DMSO) :  $\delta$  2.5 (m, 4H), 2.7 (s, 3H), 6.4-7.6 (m, 8H), 11.3 (s, 1H).

14,15-Dioxo-12-methyl-5H,6H,7H-7a,12a-iminoethano-1-benzo[6,7]-cyclohept[1,2-b]indole(4f)

IR(KBr) : 3200-3050, 1760, 1710  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $d_6$ -DMSO) :  $\delta$  1.4 (m, 6H), 2.3 (s, 3H), 6.5-7.4 (m, 8H), 11.4 (s, 1H). -  $^{13}\text{C-Nmr}$  ( $d_6$ -DMSO) : quarternary carbons at  $\delta$  200, 162, 152, 140, 137, 127, 89, 61 ppm.

13,14-Dioxo-11-methyl-6,11-dihydro-6a,11a-iminoethano-1-benzothiopyrano[4,3-b]indole (4g)

IR(KBr) : 3200-3050, 1760, 1725  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $d_6$ -DMSO) :  $\delta$  2.5 (s, 3H), 2.9 (m, 2H), 6.4-8.0 (m, 8H), 11.4 (s, 1H).

X-Ray Analysis Data for 4a. - The crystallographic analysis of a yellow crystal (0.3x0.3x0.3 mm) was performed on a Syntex P3 four-circle diffractometer with  $\text{MoK}\alpha$  radiation in the  $\omega$ -scan mode for  $2\theta_{\text{max}} = 55^\circ$ . The structure was solved on the basis of 2838 reflections ( $F > 3\sigma(F)$ ) by direct methods using SHELXTL 83 on the Eclipse S/250 computer. The final  $R_{\text{aniso}}$ -value was 0.043. Further details of structure determination are deposited at the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (FRG). These data are available with quotation of the registry number CSD-52661, the authors, and the reference to this publication.

Table 2. - Experimental and analytical data of 4

	A	yield	B	mp.		Elemental analysis			
						C	H	N	S
<u>4a</u>	0.2 g	<u>3a</u> 0.125 g 63%	Ethanol	246°C	$C_{25}H_{20}N_2O_2$ (380.37)	Calc. 78.92	5.31	7.37	
						Found 78.69	5.25	7.37	
<u>4b</u>	0.2 g	<u>3b</u> 0.100 g 50%	Ethanol	240°C	$C_{23}H_{16}N_2O_2S$ (384.47)	Calc. 71.85	4.20	7.29	8.24
						Found 71.95	4.26	7.28	8.51
<u>4e</u>	0.25g	<u>3e</u> 0.180 g 72%	Ethanol	245°C	$C_{19}H_{16}N_2O_2$ (304.37)	Calc. 74.97	5.31	9.21	
						Found 74.85	5.37	9.01	
<u>4f</u>	0.5 g	<u>3f</u> 0.330 g 66%	Ethanol	240°C	$C_{20}H_{18}N_2O_2$ (318.40)	Calc. 75.44	5.71	8.80	
						Found 75.50	5.72	8.73	
<u>4g</u>	0.3 g	<u>3g</u> 0.210 g 70%	Ethanol	220°C	$C_{18}H_{14}N_2O_2S$ (322.40)	Calc. 67.05	4.39	8.69	9.93
						Found 67.12	4.60	8.44	9.66

A: amount of pyrroldione 3

B: recrystallized from

Table 3. - Final atomic coordinates and thermal parameters of 4a

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C(1)	0.0729(2)	0.8715(2)	0.8519(2)	0.047(1)	0.050(1)	0.048(1)	-0.004(1)	0.011(1)	0.001(1)
C(2)	0.0760(2)	0.8598(2)	0.9904(3)	0.060(2)	0.084(2)	0.052(2)	-0.018(2)	0.014(1)	0.004(2)
C(3)	0.1081(2)	0.7840(3)	0.0593(3)	0.051(2)	0.115(3)	0.040(1)	0.006(2)	0.008(1)	0.002(2)
C(4)	0.1396(2)	0.7005(2)	0.9920(3)	0.045(1)	0.080(2)	0.048(1)	0.020(1)	0.004(1)	-0.001(1)
C(5)	0.1400(2)	0.7003(2)	0.8549(2)	0.036(1)	0.050(1)	0.045(1)	0.010(1)	0.001(1)	-0.004(1)
C(6)	0.1842(2)	0.5103(2)	0.7876(3)	0.063(2)	0.039(1)	0.058(2)	0.013(1)	-0.007(1)	0.006(1)
C(7)	0.2984(2)	0.6285(2)	0.7401(3)	0.057(2)	0.056(2)	0.056(2)	0.006(1)	-0.003(1)	0.023(1)
C(8)	0.3110(2)	0.7313(2)	0.5771(2)	0.032(1)	0.055(1)	0.054(1)	-0.000(1)	0.002(1)	0.007(1)
C(9)	0.2141(2)	0.7618(2)	0.5755(2)	0.032(1)	0.034(1)	0.045(1)	0.004(1)	0.008(1)	0.005(1)
C(10)	0.1790(2)	0.6839(2)	0.4700(2)	0.043(1)	0.035(1)	0.037(1)	0.005(1)	0.006(1)	0.007(1)
C(11)	0.2425(2)	0.6360(2)	0.3825(2)	0.054(1)	0.050(1)	0.046(1)	0.008(1)	0.015(1)	0.014(1)
C(12)	0.1920(2)	0.5655(2)	0.2948(2)	0.087(2)	0.050(1)	0.042(1)	-0.001(1)	0.017(1)	0.019(1)
C(13)	0.0802(2)	0.5464(2)	0.2933(2)	0.086(2)	0.045(1)	0.043(1)	-0.005(1)	0.002(1)	0.004(1)
C(14)	0.0151(2)	0.5931(2)	0.3801(2)	0.057(1)	0.043(1)	0.045(1)	0.001(1)	-0.002(1)	-0.002(1)
C(15)	0.0664(2)	0.6617(2)	0.4703(2)	0.045(1)	0.033(1)	0.037(1)	0.006(1)	0.003(1)	0.005(1)
N(16)	0.0226(1)	0.7108(1)	0.5738(2)	0.032(1)	0.039(1)	0.043(1)	-0.002(1)	0.004(1)	-0.001(1)
C(17)	0.1001(2)	0.7866(2)	0.6323(2)	0.033(1)	0.030(1)	0.039(1)	0.004(1)	0.006(1)	0.003(1)
C(18)	0.1041(2)	0.7878(2)	0.7834(2)	0.031(1)	0.040(1)	0.040(1)	0.002(1)	0.005(1)	-0.003(1)
N(19)	0.0693(1)	0.8864(1)	0.5733(2)	0.041(1)	0.033(1)	0.043(1)	0.008(1)	0.011(1)	0.005(1)
C(20)	0.1398(2)	0.9253(2)	0.4940(2)	0.041(1)	0.036(1)	0.048(1)	0.005(1)	0.011(1)	0.004(1)
C(21)	0.2414(2)	0.8572(2)	0.5029(2)	0.039(1)	0.039(1)	0.057(1)	0.005(1)	0.013(1)	0.002(1)
C(160)	-0.0934(1)	0.7148(2)	0.5915(3)	0.034(1)	0.054(1)	0.066(2)	0.000(1)	0.007(1)	-0.003(1)
O(200)	0.1285(1)	0.0029(1)	0.4286(2)	0.055(1)	0.045(1)	0.072(1)	0.024(1)	0.025(1)	0.011(1)
O(210)	0.3264(1)	0.8777(1)	0.4582(2)	0.048(1)	0.062(1)	0.115(1)	0.026(1)	0.038(1)	0.006(1)

Table 3. - Bond lengths and bond angles of 4a.

[Pm]															
C(1) - C(2)	139.5(4)	C(6) - C(7)	152.9(4)	C(10) - C(15)	139.5(3)	N(16) - C(160)	143.6(3)	C(1) - C(18)	138.7(3)	C(7) - C(8)	152.6(4)	C(11) - C(12)	138.9(3)	C(17) - C(18)	152.1(3)
C(2) - C(3)	137.4(4)	C(8) - C(9)	153.1(3)	C(12) - C(13)	137.6(4)	C(17) - N(19)	148.9(3)	C(3) - C(4)	137.9(4)	C(9) - C(10)	151.8(3)	C(13) - C(14)	138.7(4)	N(19) - C(20)	133.5(2)
C(4) - C(5)	138.5(3)	C(9) - C(17)	158.4(3)	C(14) - C(15)	139.0(3)	C(20) - C(21)	152.4(3)	C(5) - C(6)	150.5(3)	C(9) - C(21)	152.1(3)	C(15) - N(16)	138.5(3)	C(20) - O(200)	122.6(3)
C(5) - C(18)	141.5(3)	C(10) - C(11)	138.5(3)	N(16) - C(17)	146.1(3)	C(21) - O(210)	119.7(3)								

[°]											
C(2) - C(1) - C(18)	120.4(2)	C(9) - C(10) - C(11)	129.0(2)	N(16) - C(17) - C(9)	104.9(2)						
C(1) - C(2) - C(3)	119.9(3)	C(9) - C(10) - C(15)	110.2(2)	N(16) - C(17) - C(18)	111.4(2)						
C(2) - C(3) - C(4)	120.1(2)	C(11) - C(10) - C(15)	120.8(2)	N(16) - C(17) - N(19)	109.4(2)						
C(3) - C(4) - C(5)	121.6(3)	C(10) - C(11) - C(12)	118.7(2)	C(9) - C(17) - C(18)	115.3(2)						
C(4) - C(5) - C(6)	119.4(2)	C(11) - C(12) - C(13)	120.0(2)	C(9) - C(17) - N(19)	103.5(2)						
C(4) - C(5) - C(18)	118.5(2)	C(12) - C(13) - C(14)	122.3(2)	C(18) - C(17) - N(19)	111.9(2)						
C(6) - C(5) - C(18)	122.1(2)	C(13) - C(14) - C(15)	117.6(2)	C(1) - C(18) - C(5)	119.6(2)						
C(5) - C(6) - C(7)	113.0(2)	C(14) - C(15) - C(10)	120.5(2)	C(1) - C(18) - C(17)	121.8(2)						
C(6) - C(7) - C(8)	114.0(2)	C(14) - C(15) - N(16)	128.6(2)	C(5) - C(18) - C(17)	118.6(2)						
C(7) - C(8) - C(9)	114.5(2)	C(10) - C(15) - N(16)	110.7(2)	C(17) - N(19) - C(20)	115.9(2)						
C(8) - C(9) - C(10)	115.4(2)	C(15) - N(16) - C(17)	110.5(2)	N(19) - C(20) - C(21)	107.2(2)						
C(8) - C(9) - C(17)	116.7(2)	C(15) - N(16) - C(160)	124.6(2)	N(19) - C(20) - O(200)	127.4(2)						
C(8) - C(9) - C(21)	110.8(2)	C(17) - N(16) - C(160)	121.3(2)	C(21) - C(20) - O(200)	125.3(2)						
C(10) - C(9) - C(17)	101.8(2)			C(9) - C(21) - C(20)	108.2(2)						
C(10) - C(9) - C(21)	107.0(2)			C(9) - C(21) - O(210)	127.6(2)						
C(17) - C(9) - C(21)	104.0(2)			C(20) - C(21) - O(210)	124.2(2)						

Synthesis of the Indoles 5.a) Alkaline - oxidative hydrolysis of diazapropepanes 4. - General Procedure. -

5 ml of H<sub>2</sub>O<sub>2</sub> (30%) are added in small portions to a solution of 0.1 g of 4 in 10 ml 2N NaOH and 5 ml ethanol with stirring. After 12h at room temperature a precipitate is formed, which is recrystallized from ethanol/charcoal.

12-Phenyl-5,6,7,12-tetrahydro-benzo[6,7]cyclohept[1,2-b]indole (5a)

From 4a, yield 0.02 g (25%), mp 96°C. - Ir(KBr) : 1600 cm<sup>-1</sup>. - <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : δ 2.2-2.9 (m, 6H), 6.5-7.9 (m, 13H). - Anal. Calc. for C<sub>23</sub>H<sub>19</sub>N : C 89.27, H 6.20, N 4.53; Found : C 89.53, H 5.94, N 4.45.

11-Phenyl-6,7-dihydro-benz[b]indolo[2,3-d]thiopyrane (5b)

From 4b, yield 0.04 g (50%), mp 113°C. - <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : δ 4.1 (s, 2H), 6.5-7.6 (m, 13H). - Anal. Calc. for C<sub>21</sub>H<sub>15</sub>NS : C 80.47, H 4.83, N 4.47, S 10.23; Found : C 80.52, H 4.85, N 4.44, S 10.33.

11-Methyl-5,6-dihydro-benzo[a]carbazole (5e)

From 4e, yield 0.04 g (52%), mp. 133°C. - Uv-vis (MeOH) : 318 ( $\epsilon$ 9621), 245 ( $\epsilon$ 11442), 212 ( $\epsilon$ 12925). -  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) :  $\delta$  2.9 (m, 4H), 3.9 (s, 3H), 6.7-7.9 (m, 8H). - Anal. Calc. for  $\text{C}_{17}\text{H}_{15}\text{N}$  : C 87.50, H 6.48, N 6.00; Found : C 87.72, H 6.72, N 6.11.

12-Methyl-5,6,7,12-tetrahydro-benzo[6,7]cyclohept[1,2-b]indole (5f)

From 4f, yield 0.03 g (39%), mp 121°C. -  $\text{Ir}(\text{KBr})$  : 1570  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) :  $\delta$  2.2-2.9 (m, 6H), 3.8 (s, 3H), 6.7-7.7 (m, 8H). - Anal. Calc. for  $\text{C}_{18}\text{H}_{17}\text{N}$  : C 87.40, H 6.94, N 5.66; Found : C 87.57, H 6.86, N 5.56.

11-Methyl-6,7-dihydro-benz[b]indolo[2,3-d]thiopyrane (5g)

From 4g, yield 0.04 g (51%), mp 95°C. -  $\text{Ir}(\text{KBr})$  : 1570  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) :  $\delta$  3.8 (s, 3H), 4.0 (s, 2H), 6.9-7.5 (m, 8H). - Anal. Calc. for  $\text{C}_{16}\text{H}_{13}\text{NS}$  : C 76.45, H 5.22, N 5.57, S 12.76; Found : C 76.62, H 5.28, N 5.55, S 12.68.

b) Synthesis of 5b from  $\text{H}^+$ -catalyzed hydrolysis of 4b

Refluxing of 0.15 g (0.39 mmole) of the propellane 4b in a mixture of 50 ml ethanol and 5 ml 2N HCl for 28h and subsequent evaporating of the solvent yields 0.11 g (90%) 5b, recrystallized from ethanol/charcoal.

c) Synthesis of the indoles 5 via Fischer-indolization. - General procedure. -

The appropriate amount of the hydrazones 2 is refluxed in 10 ml ethanol/3ml HCl conc. for 15-45 min. After cooling the corresponding indole 5 separates and is recrystallized from ethanol/charcoal.

5b: 0.45 g 2b give 0.24 g (56%) indole 5b, reaction time 45 min.

5e<sup>19</sup>: 0.70 g 2e give 0.50 g (77%) 5e, reaction time 20 min.

5g<sup>18</sup>: 0.50 g 2g give 0.37 g (79%) 5g, reaction time 20 min.

5-Methyl-5,6-dihydro-indeno[1,2-b]indole (5d)<sup>18</sup>

0.50 g 2d after 15 min yield 0.27 g (58%) 5d, mp 153°C. -  $\text{Ir}(\text{KBr})$  : 1610  $\text{cm}^{-1}$ . -  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) : 3.5 (s, 2H), 3.9 (s, 3H), 7.0-7.7 (m, 8H). - Anal. Calc. for  $\text{C}_{16}\text{H}_{13}\text{N}$  : C 87.62, H 5.99, N 6.39; Found : C 87.87, H 5.08, N 6.61.

5a: A solution of 0.9 g (5.62 mmole) 1a and 1.04 g (5.64 mmole) N,N-diphenylhydrazine in 10 ml ethanol and 0.5 ml H<sub>2</sub>SO<sub>4</sub> conc. refluxes for 10h. Most of the ethanol is evaporated then the oily residue crystallizes from scratching. Yield 0.4 g (22%) from ethanol/charcoal.

5f<sup>20</sup>: After refluxing of 1.6 g (10 mmole) 1f and 1.22 g (10 mmole) N-methyl-N-phenylhydrazine in 10 ml ethanol and 5 ml HCl conc. for 8h and evaporation to dryness, the oily residue crystallizes from ethanol/charcoal. Yield 1.45 g (59%).

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