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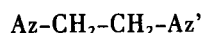
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Twenty symmetrical and asymmetrical 1,2-bisazolyethanes have been obtained from azoles and 1,2-dibromoethane or 1-chloro-2-(pyrazol-1-yl)ethane by phase transfer catalysis (PTC). The  $^1\text{H}$  and  $^{13}\text{C}$  nmr properties are reported and the chemical shifts of the ethylene carbon atoms discussed using an additive model.

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In spite of the interest of 1,2-bisazolyethanes **I**, symmetrical ( $\text{Az} = \text{Az}'$ ) or asymmetrical ( $\text{Az} \neq \text{Az}'$ ), as potential complexing agents that could afford a new family of catalyysts with special characteristics of reactivity [1-4], little attention has been paid to them in the literature.

**I**

$\text{Az} = \text{Azolyl}$  or  $\text{Benzazolyl}$

Only the syntheses of 1,2-bis(benzimidazol-1-yl)ethane by Simonov and Pozharshii [5] and of 1,2-bis(benzotriazol-1-yl)-, 1,2-bis(benzotriazol-2-yl) and 1-(benzotriazol-1-yl)-2-(benzotriazol-2-yl)ethane isomers by Krollpfeiffer *et al.* have been reported [6]. In this latter case no proofs supporting the assignment were afforded.

As a continuation of our work on *N*-polyazolylmethanes [7] we report here the preparation and physicochemical properties of a series of new 1,2-bis(*N*-azolyl)ethanes (Table 1).

With the exception of **3** and **4**, the products studied (Table 1) have been obtained from the corresponding azole or its benzo derivative by alkylation with 1,2-dihaloethane ( $\text{X} = \text{Cl}, \text{Br}$ ), compounds **2-8** and **17-21**, or 1-chloro-2-(pyrazol-1-yl)ethane, compounds **2** and **9-16**, under liquid-liquid or solid-liquid phase transfer catalysis (PTC) [8].

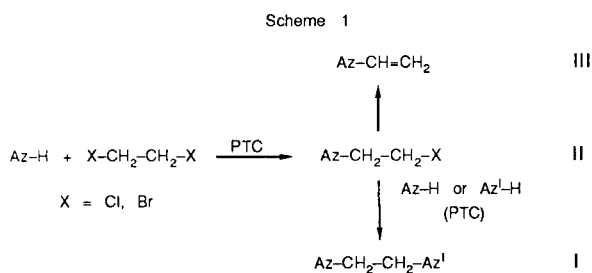


Table 1  
1,2-Bisazolyethanes

Compound Number	IUPAC Names
<b>2</b>	1,2-bis(pyrazol-1-yl)ethane
<b>3</b>	1,2-bis(4-bromopyrazol-1-yl)ethane
<b>4</b>	1,2-bis(4-nitropyrazol-1-yl)ethane
<b>5</b>	1,2-bis(3-nitropyrazol-1-yl)ethane
<b>6</b>	1,2-bis(imidazol-1-yl)ethane
<b>7</b>	1,2-bis(1,2,4-triazol-1-yl)ethane
<b>8</b>	1,2-bis(tetrazol-2-yl)ethane
<b>9</b>	1-(pyrazol-1-yl)-2-(imidazol-1-yl)ethane
<b>10</b>	1-(pyrazol-1-yl)-2-(1,2,4-triazol-1-yl)ethane
<b>11</b>	1-(pyrazol-1-yl)-2-(tetrazol-2-yl)ethane
<b>12</b>	1-(pyrazol-1-yl)-2-(benzimidazol-1-yl)ethane
<b>13</b>	1-(pyrazol-1-yl)-2-(indazol-1-yl)ethane
<b>14</b>	1-(pyrazol-1-yl)-2-(indazol-2-yl)ethane
<b>15</b>	1-(pyrazol-1-yl)-2-(benzotriazol-1-yl)ethane
<b>16</b>	1-(pyrazol-1-yl)-2-(benzotriazol-2-yl)ethane
<b>17</b>	1,2-bis(benzimidazol-1-yl)ethane
<b>18</b>	1,2-bis(indazol-1-yl)ethane
<b>19</b>	1-(indazol-1-yl)-2-(indazol-2-yl)ethane
<b>20</b>	1,2-bis(benzotriazol-1-yl)ethane
<b>21</b>	1-(benzotriazol-1-yl)-2-(benzotriazol-2-yl)ethane

As shown in Scheme 1, depending on the reaction conditions used: stoichiometry of the reactants, nature of the alkylating agent and temperature, it is possible to isolate the *N*-haloethylazoles **II**, the 1,2-bisazolyethanes **I** and the *N*-ethenylazoles **III**.

In fact, even when we isolated **I** or **II** as major products (see Experimental), always some amounts of the other two possible compounds were formed by the PTC technique.

Table 2  
<sup>1</sup>H NMR Chemical Shifts (in ppm) and Coupling Constants (in Hz) of 1,2-Bisazolyethanes

Compound Number	R R'	CH <sub>2</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	Solvent	Observation Frequency
2	pyrazol-1-yl	4.54 (s)	--	7.52 (d) J <sub>3,4</sub> = 1.8	6.10 (t)	6.91 (d) J <sub>4,5</sub> = 2.4	--	--	CDCl <sub>3</sub>	300
3	4-bromopyrazol-1-yl	4.50 (s)	--	7.48 (s)	--	7.05 (s)	--	--	CDCl <sub>3</sub>	90
4	4-nitropyrazol-1-yl	4.20 (s)	--	7.80 (d) J <sub>3,5</sub> = 0.8	--	7.31 (d)	--	--	DMSO-d <sub>6</sub>	90
5	3-nitropyrazol-1-yl	4.73 (s)	--	--	6.96 (d)	7.84 (d) J <sub>4,5</sub> = 2.7	--	--	DMSO-d <sub>6</sub>	90
6	imidazol-1-yl	4.28 (s)	7.26 (bs)	--	7.06 (bs)	6.69 (t) J <sub>2,5</sub> = J <sub>4,5</sub> = 1.3	--	--	CDCl <sub>3</sub>	300
7	triazol-1-yl	4.65 (s)	--	7.92 (s)	--	7.75 (s)	--	--	CDCl <sub>3</sub>	90
8	tetrazol-2-yl	5.35 (s)	--	--	--	7.40 (s)	--	--	CDCl <sub>3</sub>	90
9	pyrazol-1-yl	4.4-4.5 (m)	--	7.59 (d) J <sub>3,4</sub> = 1.8	6.19 (t)	7.03 (d) J <sub>4,5</sub> = 2.4	--	--	CDCl <sub>3</sub>	300
10	imidazol-1-yl	4.4-4.5 (m)	7.17 (bs)	--	7.0 (bs)	6.63 (t) J <sub>2,5</sub> = J <sub>4,5</sub> = 1.4	--	--	CDCl <sub>3</sub>	300
11	pyrazol-1-yl	4.4-4.7 (m)	--	7.52 (dd) J <sub>3,4</sub> = 1.85	6.12 (t)	7.00 (dd) J <sub>4,5</sub> = 2.3	--	--	CDCl <sub>3</sub>	90
12	benzimidazol-1-yl	4.4-4.7 (m)	--	7.92 (s)	--	7.65 (s) J <sub>3,5</sub> = 0.5	--	--	CDCl <sub>3</sub>	300
13	pyrazol-1-yl	4.78 (t) J = 5.9	--	7.54 (d) J <sub>3,4</sub> = 1.8	6.17 (t)	7.12 (d) J <sub>4,5</sub> = 2.4	--	--	CDCl <sub>3</sub>	300
14	tetrazol-2-yl	5.14 (t) J = 5.9	--	--	--	8.51 (s)	--	--	CDCl <sub>3</sub>	300
15	pyrazol-1-yl	4.44 (t) J = 5.5	--	7.56 (d) J <sub>3,4</sub> = 1.8	6.07 (t)	6.80 (d) J <sub>4,5</sub> = 2.4	--	--	CDCl <sub>3</sub>	300
16	benzimidazol-1-yl	4.61 (t) J = 5.5	7.35 (s)	--	7.75 (m)	--	--	--	CDCl <sub>3</sub>	300
17	benzimidazol-1-yl	--	--	--	--	--	--	--	--	--

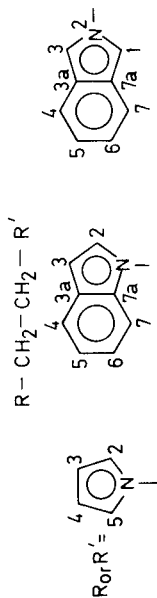
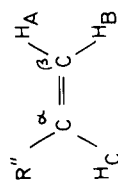


Table 2 (continued)

Compound Number	R R'	CH <sub>2</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	Solvent	Observation Frequency
13	pyrazol-1-yl indazol-1-yl	4.60 (t)	--	7.49 (d)	5.93 (t)	6.78 (d)	--	--	CDCl <sub>3</sub>	300
		J = 5.7	--	J <sub>3,4</sub> = 1.9	J <sub>4,5</sub> = 2.4	J <sub>4,5</sub> = 2.4	--	--		
		4.76 (t)	--	8.01 (bs)	7.05 (m)	7.21 (m)	6.99 (m)	J <sub>6,7</sub> = 8.4		
		J = 5.5			J <sub>4,5</sub> = 8.1					
14	pyrazol-1-yl indazol-2-yl	4.66 (t)	--	7.54 (d)	6.01 (t)	6.81 (d)	--	--	CDCl <sub>3</sub>	300
		J = 5.5	--	J <sub>3,4</sub> = 1.7	J <sub>4,5</sub> = 2.2	--	--	--		
		4.79 (t)	--	7.41 (bs)	7.69 (m)	7.26 (m)	7.52 (m)			
		J = 5.6		J <sub>4,5</sub> = 8.8	J <sub>4,6</sub> = 0.9	J <sub>5,6</sub> = 6.8	J <sub>6,7</sub> = 8.7			
15	pyrazol-1-yl benzotriazol-1-yl	4.72 (t)	--	7.53 (d)	5.98 (t)	6.85 (d)	--	--	CDCl <sub>3</sub>	300
		J = 5.6	--	J <sub>3,4</sub> = 1.8	J <sub>4,5</sub> = 2.2	--	--	--		
		5.08 (t)	--	--	7.99 (m)	7.04 (m)	7.04 (m)	J <sub>6,7</sub> = 7.1		
		J = 5.6		J <sub>3,4</sub> = 1.8	J <sub>4,5</sub> = 7.1					
16	pyrazol-1-yl benzotriazol-2-yl	4.87 (t)	--	7.54 (d)	6.10 (t)	7.07 (d)	--	--	CDCl <sub>3</sub>	90
		J = 6.0	--	J <sub>3,4</sub> = 1.8	J <sub>4,5</sub> = 2.4	--	--	--		
		5.18 (t)	--	--	7.62-7.98	7.62-7.98 (m)	7.62-7.98 (m)			
		J = 6.0		--						
17	benzimidazol-1-yl	4.62 (s)	7.45 (s)	--	7.81 (m)	--	7.27-7.32 (m)	--	CDCl <sub>3</sub>	300
		4.86 (s)	--	7.98 (s)	7.64 (m)	--	6.9-7.14 (m)	--		
		4.86 (s)	--	7.97 (d)	7.55 (m)	6.95 (m)	7.09 (m)	7.22 (m)		
				J <sub>3,7</sub> = 1.1	J <sub>4,5</sub> = 8.1	J <sub>4,6</sub> = 1.2	J <sub>4,7</sub> = 0.9			
				J <sub>5,6</sub> = 6.9	J <sub>5,7</sub> = 0.9	J <sub>6,7</sub> = 8.3				
19	indazol-1-yl	4.93 (m)	--	8.06 (d)*	7.55 (m)**	7.05 (m)	6.69 (m)	7.35 (m)	DMSO-d <sub>6</sub>	300
				J <sub>3,7</sub> = 1.0	J <sub>4,5</sub> = 8.3	J <sub>4,6</sub> = 1.1	J <sub>4,7</sub> = 1.0			
				J <sub>5,6</sub> = 6.6	J <sub>5,7</sub> = 0.9	J <sub>6,7</sub> = 8.4				
				8.07 (d)*	7.70 (m)	7.20 (m)	7.59 (m)			
				J <sub>3,7</sub> = 1.1	J <sub>4,5</sub> = 7.8	J <sub>4,6</sub> = 1.1	J <sub>4,7</sub> = 1.0			
				J <sub>5,6</sub> = 6.6	J <sub>5,7</sub> = 1.2	J <sub>6,7</sub> = 8.5				
20	benzotriazol-1-yl	5.20 (s)	--	--	7.88 (m)	--	7.0-7.30 (m)	6.87 (m)	CDCl <sub>3</sub>	90
		5.33 (m)	--	--	7.97 (m)	--	7.30-7.44 (m)	7.66 (m)		
		5.44 (m)	--	--	J <sub>4,5</sub> = 8.2	--	7.30-7.44 (m)	J <sub>6,7</sub> = 8.2		
21	benzotriazol-1-yl benzotriazol-2-yl	5.44 (m)	--	--	7.81 (m)	--	7.30-7.44 (m)	7.81 (m)	DMSO-d <sub>6</sub>	300
					J <sub>4,5</sub> = 6.5	--	7.30-7.44 (m)	J <sub>6,7</sub> = 6.5		
					J <sub>4,6</sub> = 3.0	--	7.30-7.44 (m)	J <sub>5,7</sub> = 3.0		

[bs] Broad signal. [s] Singlet. [d] Doublet. [dd] Doublet of doublets. [m] Multiplet. [\*] and [\*\*] signals can be reversed.

Table 3  
<sup>1</sup>H NMR Chemical Shifts (in ppm) and Coupling Constants (in Hz) of 1-Ethenylazoles and Benzazoles



Compound Number	R''	H <sub>A</sub>	H <sub>B</sub>	H <sub>C</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	Solvent	Observation Frequency
25	tetrazol-2-yl	6.21 J <sub>AC</sub> = 14.9	5.37 J <sub>BC</sub> = 9.0	7.55 J <sub>AB</sub> = -2.0	--	--	--	8.53 (s)	--	--	CDCl <sub>3</sub>	90
26	benzimidazol-1-yl	5.50 J <sub>AC</sub> = 15.5	5.06 J <sub>BC</sub> = 9.0	7.16 J <sub>AB</sub> = -1.5	8.16 (s)	--	--	--	7.25-7.86 (m) →	--	CDCl <sub>3</sub>	90
27	indazol-1-yl	5.61 J <sub>AC</sub> = 15.4	4.85 J <sub>BC</sub> = 8.9	7.65 J <sub>AB</sub> ~ 0	--	8.25 (s)	--	--	7.11-7.90 (m) →	--	DMSO-d <sub>6</sub>	90
28	indazol-2-yl	6.08 J <sub>AC</sub> = 15.5	5.21 J <sub>BC</sub> = 9.0	7.61 J <sub>AB</sub> ~ 0	--	8.66 (s)	--	--	7.0-7.80 (m) →	--	DMSO-d <sub>6</sub>	90
29	benzotriazol-1-yl	6.05 J <sub>AC</sub> = 15.9	5.36 J <sub>BC</sub> = 9.0	7.82 J <sub>AB</sub> = -1.2	--	--	--	--	7.35-8.27 (m) →	--	DMSO-d <sub>6</sub>	90
30	benzotriazol-2-yl	6.37 J <sub>AC</sub> = 15.6	5.55 J <sub>BC</sub> = 8.8	7.88 J <sub>AB</sub> ~ -1	--	--	7.95 (m)	7.55 (m)	7.55 (m)	7.95 (m)	DMSO-d <sub>6</sub>	90

When comparing these results with those obtained for bisazolylmethanes, it is worth while to note the fact that in the latter series it was not possible to stop the alkylation reaction with dichloromethane at the stage of the *N*-chloromethyl derivative, which can only be obtained by treatment of the *N*-hydroxymethylazole with thionyl chloride [9]. Concerning the regioselectivity of the alkylation reaction in heteroaromatic five-membered rings with several nucleophilic sites, the relative percentages are indicated in Table 6 and are similar in both series. With 1,2-dihaloethane neither 1,2-bis(indazol-2-yl) nor 1,2-bis(benzotriazol-2-yl)ethanes were isolated from indazole and benzotriazole, respectively.

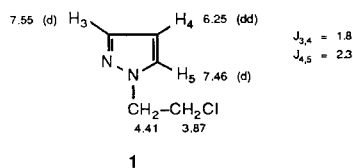
Compounds **3** and **4** were obtained by electrophilic aromatic substitution with bromine and nitric acid respectively on 1,2-bis(pyrazol-1-yl)ethane in quantitative yields.

#### <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopic Properties.

The <sup>1</sup>H nmr data of the various 1,2-bisazolylethanes are reported in Table 2 and the assignment of the signals to the different heterocyclic protons was made using the corresponding bisazolylmethanes [10,11] and *N*-substituted azoles [8] as model compounds.

Protons of the ethylene bridge appear as an A<sub>4</sub> system for symmetrical compounds: **2-8**, **17**, **18** and **20**, the chemical shift being shifted downfield with the increasing number of ring nitrogen atoms in the adjacent azole (*cf.* imidazole, δ<sub>H</sub>: 4.28-2*H*-tetrazole, δ<sub>H</sub>: 5.35; benzimidazole, δ<sub>H</sub>: 4.56-benzotriazole, δ<sub>H</sub>: 5.20) and the benzoannellation effect (*cf.* imidazole, δ<sub>H</sub>: 4.28-benzimidazole, δ<sub>H</sub>: 4.56; pyrazole, δ<sub>H</sub>: 4.54-1*H*-indazole, δ<sub>H</sub>: 4.86).

In 1-chloro-2-(pyrazol-1-yl)ethane **1** the protons AA'XX' of the two CH<sub>2</sub> groups appear in deuteriochloroform at δ<sub>H</sub>: 4.41 (t) and δ<sub>H</sub>: 3.87 (t) ppm with a coupling constant of 6.0 Hz.

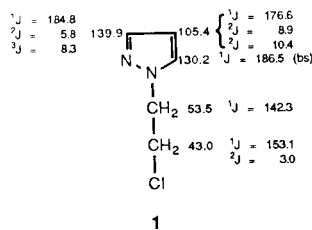


In asymmetrical 1,2-bisazolylethanes the proton signals of the ethylene group range from an AA'XX' system in the case of two azoles with clearly different electronic properties (*cf.* pyrazole σ<sub>p</sub>: 0.19-2*H*-tetrazole σ<sub>p</sub>: 0.59 [12]) to an AA'BB' system when the two azoles are similar (*cf.* pyrazole σ<sub>p</sub>: 0.19-imidazole σ<sub>p</sub>: 0.24 [12]).

The <sup>1</sup>H nmr spectra of 1-ethenylazoles, first-order analyzed, are shown in Table 3. Those of pyrazole, imidazole and 1,2,4-triazole have been previously described [13] and are not included.

The <sup>13</sup>C nmr results for 1,2-bisazolylethanes are reported in Table 4. Only a small variation of the <sup>13</sup>C chemical shifts of one azole residues with the nature of the other azole substituent is observed. The <sup>13</sup>C-<sup>1</sup>H coupling constant values have been occasionally used to distinguish the signals of heterocyclic carbon atoms: **9** (pyrazole-C<sub>5</sub> from imidazole-C<sub>4</sub>); **10** (pyrazole-C<sub>3</sub> from 1,2,4-triazole-C<sub>5</sub>) and **12** (pyrazole-C<sub>3</sub> from benzimidazole-C<sub>2</sub> and pyrazole-C<sub>4</sub> from benzimidazole-C<sub>7</sub>).

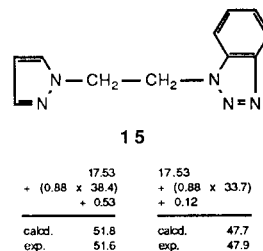
The <sup>13</sup>C chemical shifts and coupling constants of 1-chloro-2-(pyrazol-1-yl)ethane **1** in deuteriochloroform are as follows:



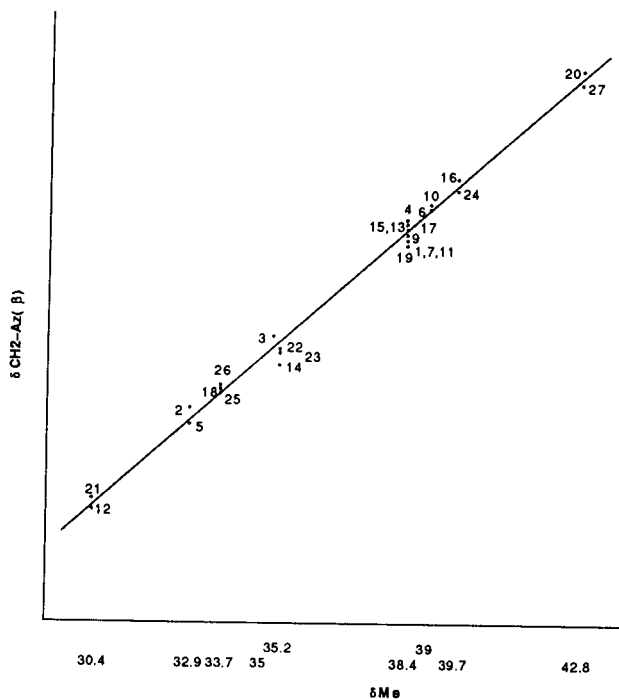
The <sup>13</sup>C chemical shifts of the methylene carbons follow an empirical model (eq 1).

$$\delta \text{CH}_2 = 17.53 + 0.88 \delta \text{CH}_3 + \text{Az} (\beta) \quad (1)$$

where δ CH<sub>3</sub> is the chemical shift of the methyl group of *N*-methylazoles [7] and Az (β) the effect of the azole situated β with regard to the CH<sub>2</sub>. The 27 chemical shifts fitted eq 1 with remarkable accuracy (CC<sup>2</sup> = 0.993). The Az (β) values are: pyrazol-1-yl, 0.53; imidazol-1-yl, 1.03; 1,2,4-triazol-1-yl, -0.30; 1,2,3,4-tetrazol-2-yl, -1.01; benzimidazol-1-yl, -0.02; indazol-1-yl, -0.24; indazol-2-yl, 0.06; benzotriazol-1-yl, 0.12; benzotriazol-2-yl, -0.175. For instance, compound **15** corresponds to:



Finally in Table 5, the <sup>13</sup>C nmr data for *N*-ethenylazoles, except those of pyrazole, imidazole and 1,2,4-triazole registered by Sigalov *et al.* [13] in 1981, are assembled.



## EXPERIMENTAL

Melting points were determined in a capillary tube with a Büchi SMP-20 apparatus and are uncorrected. All the new isolated compounds described in this paper give correct analytical results (C, H, N) for the calculated empirical formulae (Table 8). The  $^1\text{H}$  nmr spectra were obtained with a Varian XL-300 working by the PFT technique with an Aspect 2000 Data System with 16 K memory and a continuous wave Varian EM-390 spectrometers. The  $^{13}\text{C}$  nmr spectra were recorded on a Varian XL-300 (75 MHz), spectral width 16000 Hz, number of data points 65536 (memory size 64 K), acquisition time 2.0s (digital resolution 0.5 Hz per point), pulse width, 5.0  $\mu\text{s}$ , relaxation delay, 1-3 s. Chemical shifts ( $\delta$ ) in ppm and coupling constants (J) in Hz were measured in deuteriochloroform or hexadeuteriodimethylsulfoxide referred to TMS as internal standard. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are accurate to 0.01 ppm and 0.1 ppm, respectively. Coupling constants are accurate to  $\pm 0.2$  Hz for  $^1\text{H}$  nmr and  $\pm 0.5$  Hz for the  $^{13}\text{C}$  nmr. Analytical thin layer chromatography has been performed on silica gel Alugram Sil G/UV $_{254}$  with a layer thickness of 0.25 mm. Column chromatography with silica gel Merck 60 (70-230 mesh, ASTM) with the eluent indicated in each case.

## 1-Chloro-2-(pyrazol-1-yl)ethane (I).

A mixture of pyrazole (4 g, 59 mmoles), 19 ml of 40% aqueous sodium hydroxide, tetrabutylammonium bromide (0.39 g, 1.2 mmoles) and 80 ml of 1,2-dichloroethane was heated (external temperature, 80-82 $^\circ$ ) for 24 hours. After cooling, the organic phase was separated and the aqueous residue extracted with 3 x 70 ml of dichloroethane. All the organic fractions were combined, dried over anhydrous sodium sulfate and the solvent removed under vacuum. The oily product obtained was distilled under reduced pressure giving I with 90% yield, bp 178 $^\circ$ /40 mm.

1,2-Bisazoly-, 1-Azoly-2-benzazoly- and 1,2-Bisbenzazolyethanes: General Phase Transfer Catalysis Procedures.

## Procedure A.

A mixture of azole or benzazole (29 mmoles), 10 ml of 40% aqueous sodium hydroxide, tetrabutylammonium bromide (1.4 mmoles), and 1,2-dibromoethane (14.5 mmoles) in 25 ml of toluene were heated (external

Table 4  
 $^{13}\text{C}$  NMR Chemical Shifts (in ppm) and  $^{13}\text{C}$ - $^1\text{H}$  Coupling Constants (in Hz) of 1,2-Bisazolyethanes

Compound Number	R	R'	$\text{CH}_2$	$\text{C}_2$	$\text{C}_3$	$\text{C}_{3a}$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$	$\text{C}_7$	$\text{C}_{7a}$	Solvent
2	pyrazol-1-yl		51.6 $^1J = 141.9$	--	139.9 $^1J = 184.8$ $^2J = 5.9$ $^3J = 8.3$	--	105.3 $^1J = 176.7$ $^2J = 8.7$ $^3J = 10.4$	130.1 $^1J = 186.9$ (bs) $^2J = 8.3$ (bs) $^3J = 4.4$ (bs)	--	--	--	$\text{CDCl}_3$
3	4-bromopyrazol-1-yl		51.9 $^1J = 142.7$	--	140.9 $^1J = 192.4$ $^3J = 7.0$	--	93.1 $^2J = 7.7$ $^3J = 6.1$	130.4 $^1J = 192.6$ (bs)	--	--	--	$\text{CDCl}_3$
4	4-nitropyrazol-1-yl		51.8 $^1J = 145.6$	--	135.9 $^1J = 197.6$ $^3J = 5.4$	--	135.1 $^2J = 6.0$	131.1 $^1J = 199.2$ (bs)	--	--	--	$\text{DMSO-}d_6$

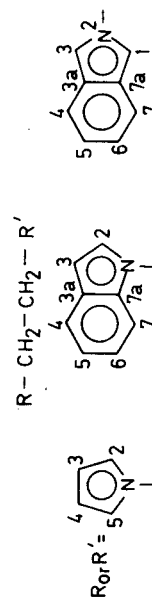


Table 4 (continued)

Compound Number	R R'	CH <sub>2</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3a</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>7a</sub>	Solvent
5	3-nitropyrazol-1-yl	52.2 <sup>1</sup> J = 145.6		155.4	--	102.8 <sup>1</sup> J = 188.0 <sup>2</sup> J = 8.7	134.6 <sup>1</sup> J = 195.5 <sup>2</sup> J = 7.6	--	--	--	DMSO-d <sub>6</sub>
6	imidazol-1-yl	47.9 <sup>1</sup> J = 141.4 <sup>3</sup> J = 9.9 <sup>3</sup> J = 6.8	137.1 <sup>1</sup> J = 206.3	--	--	130.4 <sup>1</sup> J = 189.9	118.5 <sup>1</sup> J = 188.7	--	--	--	CDCl <sub>3</sub>
7	triazol-1-yl	48.4 <sup>1</sup> J = 143.7	--	152.0 <sup>1</sup> J = 208.2 <sup>3</sup> J = 12.2	--	--	<sup>2</sup> J = <sup>3</sup> J = 10.3 144.0 <sup>1</sup> J = 210.9 <sup>3</sup> J = 7.6	--	--	--	CDCl <sub>3</sub>
8	tetrazol-2-yl	51.0 <sup>1</sup> J = 147.0	--	--	--	--	153.4 <sup>1</sup> J = 215.0	--	--	--	CDCl <sub>3</sub>
9	pyrazol-1-yl	52.7 <sup>1</sup> J = 140.9	--	140.6 <sup>1</sup> J = 185.2 <sup>2</sup> J = 5.9 <sup>3</sup> J = 8.3	--	105.9 <sup>1</sup> J = 177.8 <sup>2</sup> J = 8.4 <sup>3</sup> J = 10.5	130.4 <sup>1</sup> J = 186.6 (bm)	--	--	--	CDCl <sub>3</sub>
10	imidazol-1-yl	46.8 <sup>1</sup> J = 142.1	137.2 <sup>1</sup> J = 206.6 <sup>3</sup> J = 10.1 <sup>3</sup> J = 6.8 <sup>3</sup> J = 3.4	--	--	129.7 <sup>1</sup> J = 189.9 <sup>2</sup> J = <sup>3</sup> J = 10.2 <sup>3</sup> J = 3.1	118.7 <sup>1</sup> J = 189.0 <sup>2</sup> J = 16.3 <sup>3</sup> J = 3.1	--	--	--	CDCl <sub>3</sub>
11	pyrazol-1-yl	50.8 <sup>1</sup> J = 142.5	--	140.4 <sup>1</sup> J = 185.3 <sup>2</sup> J = 6.1 <sup>3</sup> J = 8.1	--	105.7 <sup>1</sup> J = 177.4 <sup>2</sup> J = 8.6 <sup>3</sup> J = 10.3	130.3 <sup>1</sup> J = 189.6 (bs)	--	--	--	CDCl <sub>3</sub>
11	triazol-1-yl	49.2 <sup>1</sup> J = 144.1	--	152.2 <sup>1</sup> J = 207.4 <sup>3</sup> J = 11.9	--	--	144.1 <sup>1</sup> J = 210.9 <sup>3</sup> J = 7.5	--	--	--	CDCl <sub>3</sub>
11	pyrazol-1-yl	50.3 <sup>1</sup> J = 142.1	--	140.7 <sup>1</sup> J = 186.3 <sup>2</sup> J = 5.8 <sup>3</sup> J = 9.3	--	106.1 <sup>1</sup> J = 177.0 <sup>2</sup> J = 7.8 <sup>3</sup> J = 11.8	130.0 <sup>1</sup> J = 186.1 (bs)	--	--	--	CDCl <sub>3</sub>
12	tetrazol-2-yl	52.7 <sup>1</sup> J = 144.7	--	--	--	--	153.1 <sup>1</sup> J = 214.9	--	--	--	CDCl <sub>3</sub>
12	pyrazol-1-yl	51.1 <sup>1</sup> J = 141.3	--	140.6 <sup>1</sup> J = 185.4 <sup>2</sup> J = 5.8 <sup>3</sup> J = 8.3	--	106.0 <sup>1</sup> J = 177.6 <sup>2</sup> J = 8.5 <sup>3</sup> J = 10.3	130.3 <sup>1</sup> J = 184.0 (bs)	--	--	--	CDCl <sub>3</sub>
	benzimidazol-1-yl	44.8 <sup>1</sup> J = 141.9	143.1 <sup>1</sup> J = 206.0 <sup>3</sup> J = 3.8	--	143.5 (bm)	120.3 <sup>1</sup> J = 162.4 <sup>2</sup> J = 7.0	122.4 <sup>1</sup> J = 160.0 <sup>2</sup> J = 2.9 <sup>3</sup> J = 5.9	123.2	109.2 <sup>1</sup> J = 160.8 <sup>2</sup> J = 8.2 <sup>3</sup> J = 8.3	133.2 (bm)	

Table 4 (continued)

Compound Number	R R'	CH <sub>2</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3a</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>7a</sub>	Solvent
<b>13</b>	pyrazol-1-yl	51.4	--	139.8	--	105.4	130.0	--	--	--	CDCl <sub>3</sub>
		<sup>1</sup> J = 141.9	--	<sup>1</sup> J = 185.2 <sup>2</sup> J = 6.3 <sup>3</sup> J = 7.9	--	<sup>1</sup> J = 177.1	<sup>1</sup> J = 185.0 (bs)	--	--	--	
<b>14</b>	indazol-1-yl	48.6	--	133.9	123.6	120.6	120.6	126.3	108.5	140.0	CDCl <sub>3</sub>
		<sup>1</sup> J = 140.8	--	<sup>1</sup> J = 189.6 <sup>3</sup> J = 1.9	(bm)	<sup>1</sup> J = 162.1 <sup>3</sup> J = 7.0	<sup>1</sup> J = 162.1 <sup>3</sup> J = 7.0	<sup>1</sup> J = 160.0 <sup>3</sup> J = 7.4	<sup>1</sup> J = 163.5 <sup>3</sup> J = 7.1		
<b>14</b>	pyrazol-1-yl	51.7	--	140.3	--	105.5	130.3	--	--	--	CDCl <sub>3</sub>
		<sup>1</sup> J = 142.4	--	<sup>1</sup> J = 185.1 <sup>2</sup> J = 6.2 <sup>3</sup> J = 8.1	--	<sup>1</sup> J = 177.0 <sup>2</sup> J = 10.0 <sup>2</sup> J = 9.0	<sup>1</sup> J = 187.1 (bs)	--	--	--	
<b>15</b>	indazol-2-yl	53.3	--	124.0	121.7	120.3	121.7	126.2	117.3	149.4	CDCl <sub>3</sub>
		<sup>1</sup> J = 142.7	--	<sup>1</sup> J = 189.8	(bs)	<sup>1</sup> J = 162.6 <sup>3</sup> J = 7.5	<sup>1</sup> J = 160.7 <sup>3</sup> J = 7.3	<sup>1</sup> J = 159.4 <sup>3</sup> J = 7.6	<sup>1</sup> J = 163.2 <sup>3</sup> J = 7.0	<sup>3</sup> J = 7.8	
<b>15</b>	pyrazol-1-yl	51.6	--	140.6	--	105.9	130.2	--	--	--	CDCl <sub>3</sub>
		<sup>1</sup> J = 140.8	--	<sup>1</sup> J = 185.5 <sup>2</sup> J = 5.7 <sup>3</sup> J = 8.0	--	<sup>1</sup> J = 177.5 <sup>2</sup> J = 9.9 <sup>2</sup> J = 8.9	<sup>1</sup> J = 185.0 (bs)	--	--	--	
<b>16</b>	benzotriazol-1-yl	47.9	--	--	145.6	119.7	123.9	127.4	108.9	n.o.	CDCl <sub>3</sub>
		<sup>1</sup> J = 143.1	--	--	--	<sup>1</sup> J = 159.3 <sup>3</sup> J = 7.6	<sup>1</sup> J = 162.0 <sup>3</sup> J = 7.5	<sup>1</sup> J = 161.2 <sup>3</sup> J = 8.8	<sup>1</sup> J = 167.5 <sup>3</sup> J = 7.7		
<b>16</b>	pyrazol-1-yl	51.0	--	140.3	--	105.8	129.8	--	--	--	CDCl <sub>3</sub>
		<sup>1</sup> J = 143.0	--	<sup>1</sup> J = 186.7 <sup>2</sup> J = <sup>3</sup> J = 7.0	--	<sup>1</sup> J = 177.1 <sup>2</sup> J = <sup>3</sup> J = 9.4	<sup>1</sup> J = 189.8 (bs)	--	--	--	
<b>17</b>	benzotriazol-2-yl	56.1	--	--	144.6	118.1	126.6	126.6	118.1	144.6	CDCl <sub>3</sub>
		<sup>1</sup> J = 144.7	--	--	--	<sup>1</sup> J = 167.7 <sup>3</sup> J = 4.8	<sup>1</sup> J = 160.7 <sup>3</sup> J = 8.0	<sup>1</sup> J = 160.7 <sup>3</sup> J = 8.0	<sup>1</sup> J = 167.7 <sup>3</sup> J = 4.8		
<b>17</b>	benzimidazol-1-yl	44.6	142.5	133.7	143.9	121.0	122.8*	123.6*	108.6	133.0	CDCl <sub>3</sub>
		<sup>1</sup> J = 140.8	<sup>1</sup> J = 205.2	--	(bs)	<sup>1</sup> J = 163.6 <sup>3</sup> J = 7.4	<sup>1</sup> J = 160.2 <sup>3</sup> J = 6.8	<sup>1</sup> J = 161.4 <sup>3</sup> J = 7.9	<sup>1</sup> J = 163.4 <sup>3</sup> J = 7.9	(bs)	
<b>18</b>	indazol-1-yl	48.2	--	133.7	123.6	120.3*	120.6*	126.1	108.2	139.7	CDCl <sub>3</sub>
		<sup>1</sup> J = 141.6	--	<sup>1</sup> J = 188.4 <sup>4</sup> J = 2.7	(bs)	<sup>1</sup> J = 161.0 <sup>3</sup> J = 7.4	<sup>1</sup> J = 161.2 <sup>3</sup> J = 8.5	<sup>1</sup> J = 161.5 <sup>3</sup> J = 8.0 <sup>3</sup> J = 1.7	<sup>1</sup> J = 164.1 <sup>3</sup> J = 7.9 <sup>3</sup> J = 1.6	(bs)	
<b>19</b>	indazol-1-yl	48.4	--	133.3	123.3	120.4*	120.8*	125.4**	109.0	139.5	DMSO-d <sub>6</sub>
		<sup>1</sup> J = 142.7	--	<sup>1</sup> J = 189.3 <sup>4</sup> J = 1.7	(bs)	<sup>1</sup> J = 161.3 <sup>3</sup> J = ~7 (a)	<sup>1</sup> J = 160.5 <sup>3</sup> J = 8.0	<sup>1</sup> J = 159.0 <sup>3</sup> J = 8.2	<sup>1</sup> J = 165.6 <sup>3</sup> J = 7.3	(bs)	
<b>19</b>	indazol-2-yl	52.2	--	124.3	121.2	120.4*	120.6*	125.9**	116.8	148.2	DMSO-d <sub>6</sub>
		<sup>1</sup> J = 142.9	--	<sup>1</sup> J = 192.3 <sup>4</sup> J = 2.2	(bs)	<sup>1</sup> J = 161.3 <sup>3</sup> J = ~7 (a)	<sup>1</sup> J = 161.7 <sup>3</sup> J = 8.1	<sup>1</sup> J = 160.7 <sup>3</sup> J = 8.3	<sup>1</sup> J = 161.3 <sup>3</sup> J = 7.3	<sup>3</sup> J = 9.6 <sup>3</sup> J = 2.2	

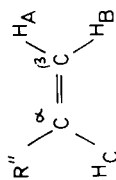


Table 4 (continued)

Compound Number	R	R'	CH <sub>2</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3a</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>7a</sub>	Solvent
20	benzotriazol-1-yl	R'	47.1	--	--	145.0	119.0	123.9	127.2	109.8	132.8	DMSO-d <sub>6</sub>
			<sup>1</sup> J = 144.7	--	(bm)	<sup>1</sup> J = 166.6	<sup>1</sup> J = 162.8	<sup>1</sup> J = 163.1	<sup>1</sup> J = 167.3			
				<sup>3</sup> J = 6.3	<sup>3</sup> J = 6.7	<sup>3</sup> J = 7.5	<sup>3</sup> J = 7.4					
21	benzotriazol-1-yl	R'	47.7	--	--	145.6	119.8	124.0	127.8	107.9	133.3	CDCl <sub>3</sub>
				--	<sup>1</sup> J = 145.0	<sup>1</sup> J = 165.1	<sup>1</sup> J = 162.2	<sup>1</sup> J = 164.1	<sup>1</sup> J = 170.5			
				<sup>3</sup> J = 9.6	<sup>3</sup> J = 7.8	<sup>3</sup> J = 7.6	<sup>3</sup> J = 7.8	<sup>3</sup> J = 8.6				
	benzotriazol-2-yl	R'	55.3	--	--	143.7	117.7	126.5	126.5	117.7	143.7	DMSO-d <sub>6</sub>
			<sup>1</sup> J = 146.0	--	<sup>3</sup> J = 9.3	<sup>1</sup> J = 164.2	<sup>1</sup> J = 161.4	<sup>1</sup> J = 161.4	<sup>1</sup> J = 164.2			
				<sup>3</sup> J = 9.2	<sup>3</sup> J = 8.0	<sup>3</sup> J = 7.4	<sup>3</sup> J = 7.4	<sup>3</sup> J = 8.0				

[bs] Broad signal. [bm] Broad multiplet. [no] Not observed. [\*] and [\*\*] signals can be reversed.

Table 5

<sup>13</sup>C NMR Chemical Shifts (in ppm) and <sup>13</sup>C-<sup>1</sup>H Coupling Constants (in Hz) of 1-Ethenylazoles and Benzazoles

Compound Number	R''	C <sub>α</sub>	C <sub>β</sub>	C <sub>3</sub>	C <sub>3a</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>7a</sub>	Solvent
25	tetrazol-2-yl	129.9	109.1	--	--	--	--	--	--	--	Solvent
		<sup>1</sup> J = 181.1	<sup>1</sup> J = 161.1	--	--	152.7	--	--	--	--	
		<sup>1</sup> J = 162.0	<sup>1</sup> J = 162.0	<sup>3</sup> J = 4.4	<sup>1</sup> J = 214.3	--	--	--	--	--	
26	benzimidazol-2-yl	128.1	102.6	140.6	--	120.6	123.1	123.9	110.4	132.5	CDCl <sub>3</sub>
		<sup>1</sup> J = 177.3	<sup>1</sup> J = 158.2	<sup>1</sup> J = 207.5	<sup>1</sup> J = 162.4	<sup>1</sup> J = 160.2	<sup>1</sup> J = 161.5	<sup>1</sup> J = 163.8			
		<sup>2</sup> J = 3.2	<sup>2</sup> J = 164.8	<sup>3</sup> J = 4.0	<sup>3</sup> J = 7.2	<sup>3</sup> J = 7.6	<sup>3</sup> J = 7.6	<sup>3</sup> J = 7.6			
27	indazol-1-yl	130.1	98.0	--	136.0	121.9	121.3	127.5	109.6	138.2	DMSO-d <sub>6</sub>
		<sup>1</sup> J = 178.7	<sup>1</sup> J = 161.4	<sup>1</sup> J = 192.0	<sup>1</sup> J = 162.4	<sup>1</sup> J = 163.5	<sup>1</sup> J = 161.7	<sup>1</sup> J = 164.8			
		<sup>2</sup> J = 4.0	<sup>2</sup> J = 163.1	<sup>3</sup> J = 1.6	<sup>3</sup> J = 7.7	<sup>3</sup> J = 8.1	<sup>3</sup> J = 8.1	<sup>3</sup> J = 7.8			
28	indazol-2-yl	134.1	104.6	--	123.1	121.1	122.1	127.1	117.3	148.8	DMSO-d <sub>6</sub>
		<sup>1</sup> J = 182.1	<sup>1</sup> J = 160.6	<sup>1</sup> J = 193.3	<sup>1</sup> J = 163.4	<sup>1</sup> J = 161.2	<sup>1</sup> J = 160.0	<sup>1</sup> J = 162.2			
		<sup>2</sup> J = 4.6	<sup>2</sup> J = 163.7	<sup>3</sup> J = 3.0	<sup>3</sup> J = 7.6	<sup>3</sup> J = 7.9	<sup>3</sup> J = 8.2	<sup>3</sup> J = 6.9			

Table 5 (continued)

Compound Number	R''	C <sub>α</sub>	C <sub>β</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3a</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>7a</sub>	Solvent	
29	benzotriazol-1-yl	129.3	104.0	--	--	146.4	120.3	124.5	128.3	110.1	131.4	CDCl <sub>3</sub>	
		<sup>1</sup> J = 179.8	<sup>1</sup> J = 160.0		<sup>1</sup> J = 165.4	<sup>1</sup> J = 163.2	<sup>1</sup> J = 8.6	<sup>1</sup> J = 7.1	<sup>1</sup> J = 6.8	<sup>1</sup> J = 161.2	<sup>1</sup> J = 166.1		
		<sup>2</sup> J = 3.9	<sup>1</sup> J = 164.4		<sup>2</sup> J = 7.1	<sup>2</sup> J = 6.8	<sup>2</sup> J = 4.4	<sup>2</sup> J = 7.1	<sup>2</sup> J = 2.0	<sup>2</sup> J = 7.9	<sup>2</sup> J = 7.1		
30	benzotriazol-2-yl	134.4	108.8	--	--	144.0	118.1	127.6	127.6	118.1	144.0	DMSO-d <sub>6</sub>	
		<sup>1</sup> J = 187.9	<sup>1</sup> J = 161.9		<sup>1</sup> J = 164.3 <sup>b</sup>	<sup>1</sup> J = 164.4	<sup>1</sup> J = 9.3	<sup>1</sup> J = 6.9	<sup>1</sup> J = 7.5	<sup>1</sup> J = 164.4	<sup>1</sup> J = 164.3		<sup>1</sup> J = 9.3
		<sup>2</sup> J = 7.0	<sup>1</sup> J = 165.0		<sup>2</sup> J = 1.8	<sup>2</sup> J = 1.9	<sup>2</sup> J = 5.1	<sup>2</sup> J = 1.8	<sup>2</sup> J = 1.9	<sup>2</sup> J = 7.5	<sup>2</sup> J = 6.9		<sup>2</sup> J = 5.1

[bm] Broad multiplet.

Table 6

Experimental Conditions and Physical Characteristics of 1,2-Bisazolyethanes

Compound Number	Procedure (Reaction Time Hours)	Isolation	Yield	mp or bp (°C)	Rf (CHCl <sub>3</sub> : Ethanol)
2	A (48)	a	80	184/40 mm Hg	0.54 (10:1)
	B (120)	a	85		
5	A (24)	b.1	80	216-220	0.65 (10:1)
6	A (72)	c.1	45	142/144	0.10 (10:1)
7	A (24)	b.1	45	157-159	0.19 (10:1)
	C(48)	b.1	40		
8	A (24)	*	10	*	*
9	B (48)	c.2	45	oil	0.45 (10:1)
10	B (72)	c.3	50	oil	0.46 (10:1)
11	B (48)	c.4	35	66-68	0.53 (10:1)
12	B (48)	c.1 plus b.3	55	166-167	0.68 (10:1)

Table 6 (continued)

Compound Number	Procedure (Reaction Time Hours)	Isolation	Yield	mp or bp (°C)	Rf (CHCl <sub>3</sub> : Ethanol)
13	B (24)	c.1	30	oil	0.67 (10:1)
14	B (24)	c.1	45	69-70	0.61 (10:1)
15	B (24)	c.1	35	77-78	0.83 (10:1)
16	B (24)	c.1	45	89-90	0.69 (10:1)
17	A (24)	b.1	70	216-220 Lit [5]:225-226	0.11 (10:1)
18	A (24)	b.1	15	100-104	0.64 (95:5)
19	A (24)	b.1	20	106-110	0.60 (95:5)
20	A (24)	b.1	10	158-160	0.60 (95:5)
	C (48)	c.1	55	Lit [6]:161	
21	A (24)	b.1	15	125	
	C (48)	c.1	45	Lit [6]:136-137	0.65 (95:5)

[a] Distillation. [b] Crystallization from 1. dichloromethane; 2. dichloromethane-ethanol; 3. *n*-hexane. [c] Column chromatography on silica gel with dichloromethane and dichloromethane-ethanol: 1. (99:1); 2. (98:2); 3. (96:4); 4. (95:5). [\*] This compound was not isolated from the reaction crude and the yield was calculated by pmr spectroscopy.

Table 7

*N*-Ethenylazoles and -benzazoles R-CH = CH<sub>2</sub>

Compound Number	R	bp (°)/mm Hg	Literature Reference
22	pyrazol-1-yl	63/50	[14]
23	imidazol-1-yl	80/10	[15]
24	1,2,4-triazol-1-yl	112-113/50	[16]
25	tetrazol-2-yl	66-68/60	[17]
26	benzimidazol-1-yl	145-147/12	[5]
27	indazol-1-yl	78/4	[14]
28	indazol-2-yl	103/2	[14]
29	benzotriazol-1-yl	104-107/0.5	[6,15,18]
30	benzotriazol-2-yl	84/3	[6]

temperature, 60-80°) for 24-72 hours. After cooling, the aqueous phase was extracted with 3 x 40 ml of dichloromethane and the extracts combined with the organic phase. The solvent was removed from the organic solution and the crude product obtained was purified as indicated in Table 6.

#### Procedure B.

To a mixture of azole or benzazole (29 mmoles), 10 ml of 40% aqueous sodium hydroxide and tetrabutylammonium bromide (1.4 mmoles, 1-chloro-2-(pyrazol-1-yl)ethane (29 mmoles) in 25 ml of toluene was added. After heating at an external temperature of 70-90° for 24-120 hours the work-up of the reaction was as in Procedure A.

#### Procedure C.

A suspension of azole or benzazole (29 mmoles), anhydrous potassium carbonate (29 mmoles), powdered potassium hydroxide (29 mmoles), tetrabutylammonium bromide (1.4 mmoles) and 1,2-dibromoethane (14.5 mmoles) in 50 ml of toluene or xylene, was heated (external temperature ~120°) for 48 hours. The hot reaction mixture was filtered and the

Table 8

Microanalytical Data for 1,2-Bisazolylethanes

Compound Number	Molecular Formulae	Calculated (%)			Found (%)		
		C	H	N	C	H	N
2	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub>	59.24	6.21	34.54	59.03	6.02	34.72
3	C <sub>8</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>4</sub>	30.03	2.52	17.51	29.77	2.41	17.31
4	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> O <sub>4</sub>	38.10	3.20	33.32	38.28	3.08	33.56
5	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> O <sub>4</sub>	38.10	3.20	33.32	38.17	3.00	33.64
6	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub>	59.24	6.21	34.54	59.35	6.28	34.28
7	C <sub>8</sub> H <sub>8</sub> N <sub>6</sub>	43.90	4.91	51.19	43.73	4.88	51.01
9	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub>	59.24	6.21	34.54	58.93	6.13	34.48
10	C <sub>7</sub> H <sub>8</sub> N <sub>5</sub>	51.52	5.56	42.92	51.83	5.42	42.74
11	C <sub>8</sub> H <sub>8</sub> N <sub>6</sub>	43.90	4.91	51.19	44.01	4.88	51.03
12	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>	67.90	5.70	26.40	67.85	5.74	26.12
13	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>	67.90	5.70	26.40	67.94	5.68	26.07
14	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>	67.90	5.70	26.40	67.92	5.55	26.44
15	C <sub>11</sub> H <sub>11</sub> N <sub>5</sub>	61.96	5.20	32.84	61.67	5.24	32.65
16	C <sub>11</sub> H <sub>11</sub> N <sub>5</sub>	61.96	5.20	32.84	61.78	5.28	32.54
18	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub>	73.26	5.38	21.36	73.37	5.24	21.09
19	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub>	73.26	5.38	21.36	73.03	5.60	21.45

residue washed twice with 30 ml of warm toluene or xylene. The solution was dried over anhydrous sodium sulfate and then isolation method indicated in Table 6 was applied in each case.

*N*-Ethenylazoles and benzazoles were formed during the preparation of 1,2-bisazolylyl-, 1-azolylyl-2-benzazolylyl- and 1,2-bisbenzazolylylethanes by the PTC procedures indicated above as secondary products. All of them were isolated as oils in the first fractions eluted by column chromatography from the reaction mixtures with poor yields (~10%) and have been found described in the literature (Table 7). We have found that the yields in ethenyl derivatives increase with the temperature of the reaction mixture.

## 1,2-Bis(4-bromopyrazol-1-yl)ethane (3).

To a solution of 1,2-bis(pyrazol-1-yl)ethane (1.1 g, 6.8 mmoles) in 25 ml of dried chloroform, 1 ml bromine (1.8 mmoles) in 10 ml of anhydrous chloroform was added drop by drop. The reaction mixture was heated under reflux for 2 hours giving after cooling a yellow precipitate of 3-hydrobromide (2.8 g, 86% yield), that was filtered off and washed with ether mp 200-205°.

The hydrobromide of 3 was dissolved in the minimal amount of warm water and neutralized with a saturated solution of aqueous sodium carbonate, precipitating 3 as a white solid, mp 102° (ethanol).

## 1,2-Bis(4-nitropyrazol-1-yl)ethane (4).

1,2-bis(Pyrazol-1-yl)ethane (0.8 g, 5 mmoles) was dissolved in 15 ml of sulfuric acid (82%) and with external cooling, a mixture of 7.5 ml of fuming nitric acid and 7.5 ml of sulfuric acid (82%) was added dropwise (reaction temperature, 0-5°). After stirring during one night at room temperature, the reaction mixture was poured onto ice and a white solid precipitated. Compound 4 was recrystallized from ethanol mp 178° (78% yield).

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