Synthesis of Bis(indazolyl)alkanes from 1-Hydroxyalkylindazoles

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Thermal reactions of 1-(hydroxymethyl)indazole and 1-(hydroxymethyl)-3-methylindazole with indazole and 3-methylindazole, performed in the presence or absence of Lewis acids, yield symmetrical and unsymmetrical bis(indazolyl)methanes. An isomerization process is proposed as a mechanism for this reaction by comparison of these results with those obtained in the presence of *p*-toluenesulfonic acid and other 1-(hydroxyalkyl)indazoles.

1-(Hydroxymethyl)indazoles and pyrazoles, readily obtained by reaction of the corresponding azole with formaldehyde,[1-3] are suitable starting materials for the preparation of Mannich bases,[1] chelating agents,[4] and amino acids.[5] Recently, Katritzky et al.[6] have proposed, using a similar methodology, benzotriazole as an important synthetic auxilliary.

Considering the easy obtention of these 1-hydroxymethyl derivatives, and the fact that some bis(indazol-1-yl)methane was formed[1] in the preparation of 1-(hydroxymethyl)indazole, we found it of interest to use 1-(hydroxymethyl)indazoles as precursors in the synthesis of bis(indazolyl)methanes. These types of compounds, useful as metal ligands,[7] were previously prepared by alkylation of indazole either with methylene bromide under pressure[8] or with methylene chloride under phase-transfer catalysis (PTC) conditions.[9]

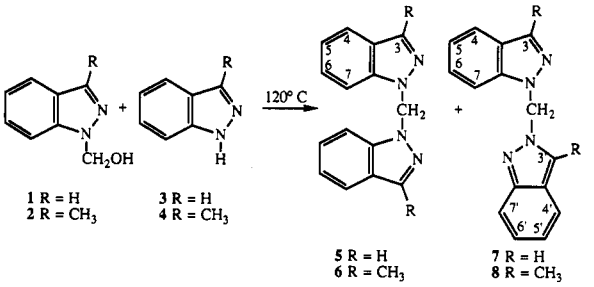
Results and Discussion

Thermal reactions took place in the absence of solvent at 120 °C, between 1-(hydroxymethyl)indazoles **1** and **2** and the corresponding indazole **3** and **4**. The influence of the Lewis acids was examined taking into account our previous results in the reaction of azoles and aromatic aldehydes.[10,11] The ratios of the isomeric reaction products were estimated from the ^{1}H NMR spectra of the reaction crudes. The results found in the case of **1** and **2** are depicted in Scheme I.

The obtention of 1,2′-isomer **7** as the major product is in contrast with the results described for the alkylation of indazole with methylene chloride by PTC,[9b] and those obtained by Katritzky et al. for benzotriazole and aldehydes other than formaldehyde in the presence of thionyl chloride,[12] where the 1,1′-isomer was always the major product. Lewis acids did not affect markedly the course of the reaction of **1** and **3**, and similar product ratios are obtained.

In order to understand these unusual results, the reaction of **1** with **3** was performed in toluene with *p*-toluenesulfonic acid (TsOH) as catalyst, a typical condition for aminal formation. After 2 h under reflux, compound **7** was detected, by TLC analysis, as the major product. However, longer reaction time (5 h) produced an irreversible isomerization to the most stable compound **5**. This isomerization process was evidenced when isolated **7** was treated for 1 h under both reaction conditions. Only under TsOH catalysis was it quantitatively converted into compound **5**, while by heating at 120 °C only 10% of compound **5** was detected in the ^{1}H NMR spectrum of the reaction mixture. Isomerization of compound **8** required 8 h at 120 °C for 30% conversion into **6**.

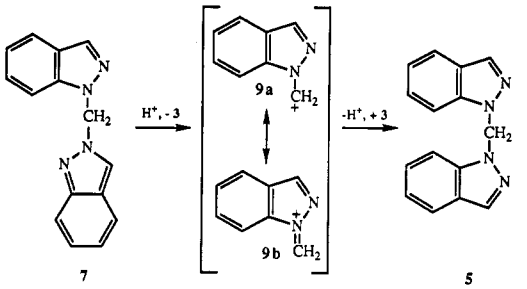
Scheme I



Reaction	Lewis acid	Isomer ratio 1,1′: 1,2′
1 + 3	-	(5 : 7) 1 : 1.3
	$ZnCl_2$	1 : 1
	$NiCl_2$	1 : 1.8
2 + 4	$NiCl_2$	(6 : 8) a

a: The isomer ratio could not be determined by ^{1}H NMR because of the overlapping of the signals.

Scheme II



These results clearly suggest that both types of reactions take place through the mechanism shown in Scheme II,

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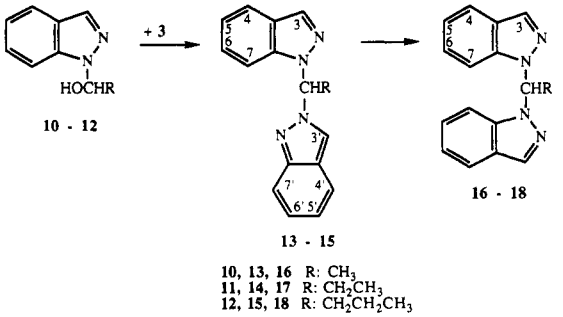
Scheme III



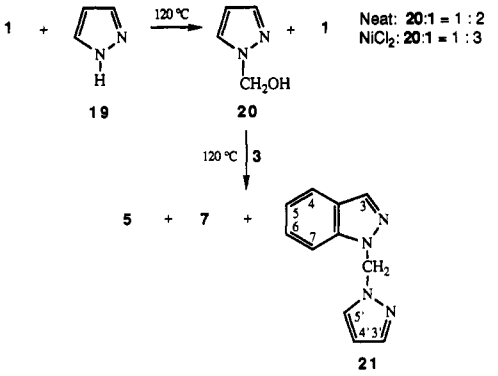
similar to that previously described for aminals.[13] This mechanism is closely related to the dissociation–recombination process reported by Katritzky et al.[14] for the isomerization of 1-(α-aminoalkyl)benzotriazoles and related derivatives. In fact, this later process would take place in the thermal isomerization of the isolated 1,2′-derivatives.

Compound **7** can be considered to be the kinetic product which is formed by the attack of the nitrogen atom in position 2 of the of neutral 1*H*-indazole to 1-(hydroxymethyl)indazole. During the thermal reaction compound **7** slowly isomerizes under indazole (pK_a = 13.86) catalysis to give compound **5** as minor product. However, in the presence of TsOH (pK_a = −6.5), this isomerization process is faster and compound **5** is the major product. The reaction was extended to other 1-(hydroxyalkyl)indazoles **10–12**, and their time course of changes were monitored by ^1H NMR to study the influence of the chain in the proposed mechanism. In all cases, under thermal and acidic conditions, the 1,2′-derivatives **13–15** are initially formed, but they quickly isomerize to the 1,1′-derivatives **16–18** which become the major products (Scheme III).

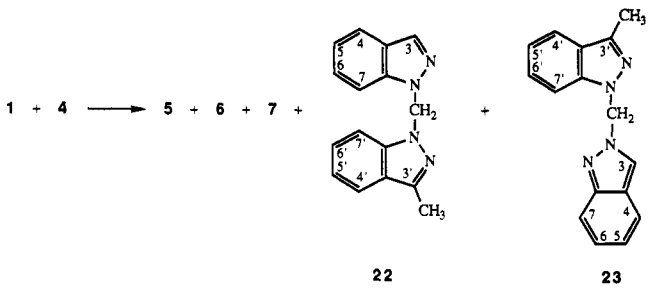
The results obtained always confirmed the proposed isomerization mechanism. The following remarks are worthy of note: (i) the chain (R in Scheme III) stabilizes the canonical form **9a**, (ii) the isomerization is faster in compounds with shorter chain lengths, (iii) a thermal degradation of the 1-(hydroxyalkyl)indazole is observed, mainly in those derivatives with shorter chain length, and (iv) these features could also explain the regiospecificity found by us in the reaction of benzaldehydes and indazole, in which only bis(indazol-1-yl)phenylmethanes were detected.[10,11] In this case the phenyl group produces a strong stabilization of the canonical form **9a** and, as a consequence, an acceleration of the isomerization process.

Thermal cross-over experiments of **1** with pyrazole **19** were also carried out, and no bis(azolyl)methane formation was observed. However, when 1-(hydroxymethyl)pyrazole (**20**) was heated in the presence of **3**, the unsymmetrical compound **21** was obtained together with compounds **5** and **7** (Scheme IV). In the experiments performed with **1** and **4** the symmetrical and unsymmetrical compounds shown in Scheme V were obtained. Although further thermal cross-over experiments are under investigation, it can be mentioned now that an intermolecular dissociation–recombination process is involved in these reactions.

Scheme IV



Scheme V



Finally, considering the results presented in this work, it can be concluded that 1-hydroxyalkyl derivatives from indazoles are suitable and versatile starting materials for the preparation of bis(indazolyl)alkanes. Under thermal conditions it is possible to obtain and isolate 1,2′-isomers as major products by stopping the reaction at the first stages. In fact, compound **8** was isolated in 40% vs 17% yield of **6** after 1 h of reaction. The reaction under TsOH catalysis is an efficient route to prepare 1-bis(indazol-1-yl)alkanes regiospecifically.

Experimental Section

Melting points were obtained on a Gallenkamp MFB-595 and are uncorrected. Elemental analyses were performed with a Perkin-Elmer 240 apparatus. Mass spectra were determined on a VG-12-250 spectrometer at 70 eV. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC-200 (200, 50.3 MHz) under standard conditions. Since the 1-(hydroxyalkyl)indazoles **10–12** partially decompose in $CDCl_3$ solution to indazole and the corresponding aldehyde, their NMR data have been taken from the mixtures. TLC chromatography was performed on DC-Alufolien/Kieselgel 60 F_{254} (Merck, 0.2 mm) and column chromatography through silica gel Merck 60 (70–230 mesh).

Products were purchased from commercial sources. $ZnCl_2$ and $NiCl_2$ were stored in a vacuum desiccator prior to use. The following compounds were prepared by described procedures: 3-methylindazole,[15] 1-(hydroxymethyl)indazole,[1] and 1-(hydroxymethyl)pyrazole.[3] Isolated yields and physical constants of bis(azolyl)alkanes are given in Table I.

1-(3-Methylindazol-1-yl)methanol (2). To a solution of 3-methylindazole (1.12 g, 8.45 mmol) in 20% hydrochloric acid (1.2 mL) was added with stirring 40% formalin (1.2 mL). After 1 h, the mixture was diluted with water (6 mL) and put aside for 1 h. The precipitate was collected and washed with cold water. Recrystallization from water yielded 0.85 g of pure **2** (62%): mp 105–106 °C; ^1H NMR ($CDCl_3$) δ 2.52 (s, 3 H, CH_3), 5.81 (s, 2 H, CH_2), 7.18 (ddd, 1 H, J = 8.1, 6.7, 1.1 Hz, H-5), 7.41 (ddd, 1 H,

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Table I. Isolated Yields and Physical Constants of Bis(azolyl)alkanes

reactions	method	compds (yields, %)	mp, °C	lit. mp, °C	formula	elemental analyses: calcd C	calcd H	calcd N	found C	found H	found N	M+ m/z
1 + 3	A[a]	**5** (38)	144–145	143–144[b]	$C_{15}H_{12}N_4$	72.54	4.88	22.58	72.76	4.82	22.42	248
		7 (37)	105–107	107[c]	$C_{15}H_{12}N_4$	72.54	4.88	22.58	72.49	4.82	22.69	248
1 + 3 ($ZnCl_2$)	B[a]	**5** (20)										
		7 (23)										
1 + 3 ($NiCl_2$)	B[a]	**5** (23)										
		7 (18)										
2 + 4 ($NiCl_2$)	B[a]	**6** (49)	171–173		$C_{17}H_{16}N_4$	73.89	5.85	20.27	73.65	6.27	20.40	276
		8 (7)	120–122		$C_{17}H_{16}N_4$	73.89	5.85	20.27	73.96	6.11	19.93	276
3 + 10	A[e]	**13** (0)										
		16 (29)	78–80		$C_{16}H_{14}N_4$	73.26	5.38	21.36	72.89	5.37	21.18	262
3 + 10	C[e]	**13** (0)										
		16 (12.5)										
3 + 11	A[f]	**14** (~1)[g]										
		17 (21.5)	99–101		$C_{17}H_{16}N_4$	73.89	5.84	20.27	73.82	6.01	20.59	276
3 + 11	C[f]	**14** (~1)										
		17 (38)										
3 + 12	A[f]	**15** (1)[g]										
		18 (35.5)	153–155		$C_{18}H_{18}N_4$	74.45	6.25	19.29	74.20	6.39	19.47	290
3 + 12	C[f]	**15** (~1)										
		18 (35.5)										
3 + 20	A[d]	**21** (43)[h]	79–81									198
		5 (39)										
		7 (22)										
3 + 20 ($NiCl_2$)	B[d]	**21** (37)										
		5 (8)										
		7 (28)										
1 + 4	A[a]	**5** (4)										
		7 (7)										
		6 (22)										
		22 (36)[h]	113–114									262
		23 (10)	108–109		$C_{16}H_{14}N_4$	73.26	5.38	21.36	73.34	5.60	21.10	262
1 + 4 ($NiCl_2$)	B[a]	**5** (3)										
		7 (2)										
		6 (19)										
		22 (22)										
		23 (9)										

[a] Chromatographic eluent: CH_2Cl_2/ethyl acetate (9/1). [b] Reference 1. [c] Reference 9b. [d] Chromatographic eluent: hexane/ethyl acetate (7/3). [e] Chromatographic eluent: CH_2Cl_2/ethyl acetate (95/5). [f] Chromatographic eluent: hexane/ethyl acetate (95/5). [g] Characterized by ^1H NMR. [h] The purity has been determined by ^1H and ^{13}C NMR.

J = 8.4, 6.7, 1.1 Hz, H-6), 7.54 (ddd, 1 H, J = 8.4, 1.1, 1.1 Hz, H-7), 7.65 (ddd, 1 H, J = 8.1, 1.1, 1.1 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 11.5 (q, J = 128.0 Hz, CH_3), 70.5 (t, J = 157.1 Hz, CH_2), 109.3 (d, J = 163.7 Hz, C-7), 120.5 (d, J = 159.9 Hz, C-5), 120.7 (d, J = 160.1 Hz, C-4), 123.9 (s, C-3a), 127.3 (d, J = 160.7 Hz, C-6), 140.3 (s, C-7a), 143.4 (s, C-3); MS m/z 162 (36, M^+). Anal. Calcd for $C_9H_{10}N_2O$: C, 66.65, H, 6.21, N, 17.27. Found: C, 66.26; H, 6.11; N, 17.24.

1-(Indazol-1-yl)ethanol (10). Indazole (0.59 g, 5 mmol) and acetaldehyde (1.12 mL, 20 mmol) were dissolved in boiling diethyl ether. The solution was filtered and kept for 12 h at 25 °C to give the alcohol as needles which were washed with pentane an dried in vacuo at 25 °C. Recrystallization from water yielded 0.32 g of pure **10** (40%): mp 109–111 °C; ^1H NMR ($CDCl_3$) δ 8.05 (s, 1 H, H-3), 6.30 (q, 1 H, J = 5.1 Hz, C*H*OH), 2.17 (d, 3 H, CH_3).

1-(Indazol-1-yl)propanol (11). Indazole (0.59 g, 5 mmol) was dissolved in propionaldehyde (0.29 g, 5 mmol) by gentle warming and then kept at 25 °C. The liquid was cooled and dissolved in diethyl ether containing 10% of the aldehyde. The solution was cooled slowly from 30 to −5 °C to give crystalline **11** unstable at room temperature: ^1H NMR ($CDCl_3$) δ 8.08 (s, 1 H, H-3), 6.00 (t, 1 H, J = 7.4 Hz, C*H*OH), 2.33 (m, 2 H, CH_2), 0.9 (t, 3 H, J = 7.4 Hz, CH_3).

1-(Indazol-1-yl)butanol (12). Obtained from indazole (0.59 g, 5 mmol) and butyraldehyde (0.36 g, 5 mmol) by the same procedure used for **11**. Compound **12** was a crystalline product at −5 °C but unstable at room temperature: ^1H NMR ($CDCl_3$) δ 8.05 (s, 1 H, H-3), 6.07 (t, 1 H, J = 6.7 Hz, C*H*OH), 2.26 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 0.9 (q, 3 H, J = 7.1 Hz, CH_3).

Reaction of 1-(Hydroxyalkyl)azole and Azole. General Method A. A one-necked round-bottomed flask was fitted with a reflux condenser attached to a drying tube ($CaCl_2$) and with a magnetic stirrer. The flask was charged with azole and 1-(hydroxymethyl)azole (1:1 molar ratio). The mixture was heated with stirring in an oil bath at 120–125 °C for 16–20 h. After being cooled to room temperature the reaction mixture was purified by column chromatography using the eluents indicated in Table I.

Reaction of 1-(Hydroxymethyl)azole and Azole in the Presence of Lewis Acids. General Method B. A flask, with the same characteristics of method A, was charged with azole, 1-(hydroxymethyl)azole, and Lewis acid ($ZnCl_2$ or $NiCl_2$) (1:1:1/20 molar ratio). The mixture was heated and worked up as in method A.

Reaction of 1, 10–12, and 3 in the Presence of TsOH. General Method C. A one-necked round-bottomed flask was equipped with a Dean-Stark water separator. The flask was charged with **1**, **10–12** (2.03 mmol), **3** (0.24 g, 2.03 mmol), TsOH (0.38 g, 0.20 mmol), and 15 mL of dried toluene. The mixture was heated under reflux and monitored by TLC and ^1H NMR.

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Registry No. **1**, 1006-29-7; **2**, 142801-04-5; **3**, 271-44-3; **4**, 3176-62-3; **5**, 1029-34-1; **6**, 142801-05-6; **7**, 84661-57-4; **8**, 142810-16-0; **10**, 142801-06-7; **11**, 142801-07-8; **12**, 142801-08-9; **13**, 142801-09-0; **14**, 142801-10-3; **15**, 142801-11-4; **16**, 142801-12-5; **17**, 142801-13-6; **18**, 142801-14-7; **19**, 288-13-1; **20**, 1120-82-7; **21**, 142801-15-8; **22**, 142810-17-1; **23**, 142801-16-9; CH_3CH_2CHO, 123-38-6; $CH_3CH_2CH_2CHO$, 123-72-8.

Supplementary Material Available: Time course of changes observed in the reactions of compounds 10–12 with 3 by methods A and C (Figures 1–3) (the zero value is considered when compounds 13–15 are not detected by ^{1}H NMR), ^{1}H chemical shifts (δ) and coupling constants (Hz) of 5–8, 14–18, and 21–23 (Table II), and ^{13}C chemical shifts of compounds 5–8, 16–18, and 21–23 (Table III) (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Notes

Medium-Sized Cyclophanes. 19.[1] Preparation and Conformational Studies of [*m.n*]Metacyclophanes

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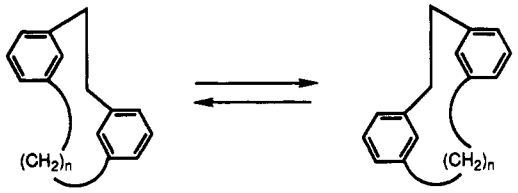
Introduction

The synthesis and stereochemical aspects of conformationally mobile [*m.n*]metacyclophanes (MCP = metacyclophane) have been of interest for the past decade,[2] with particular attention[3] paid to [2.2]MCPs, which possess an anti-stepped conformation. The pioneering work of the conformational investigation of 2,11-dithia[3.3]MCPs was reported by Vögtle et al.[4] Sato and his co-workers have also reported the conformational behavior in the 2-thia-[3.2]MCPs and their analogues.[5] While in [3.3]MCP the aromatic rings preferentially appear to adopt the syn arrangement, its lower and higher homologues, i.e., [3.2]-, [4.2]-, and [4.3]-MCPs, appear to have the mobile anti conformation.[6]

The ring inversion barriers for the higher [*m.n*]MCPs have been determined and increase with decreasing length of the bridges (eq 1).[6] Most of the reported [*m.n*]MCPs,

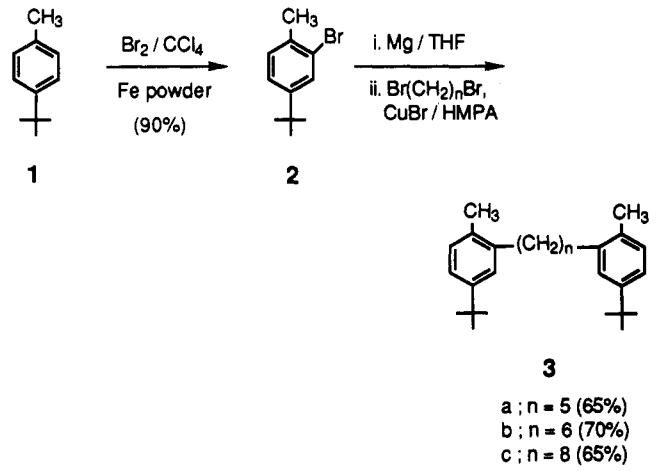


(eq. 1)

n	T_c (°C)	$\Delta G_c^{\ddagger}$ (kcal/mol)
2	>190	>27
3	90	17.5
4	35	14.3

however, are internally unsubstituted ones. Introduction of intraannular substituents such as $-CH_3$ increases the barrier to conformational flipping;[7] for example, both *syn*- and *anti*-9,18-dimethyl-2,11-dithia[3.3]MCP exist as discrete compounds, whereas 2,11-dithia[3.3]MCP itself is conformationally mobile.[8,9] Surprisingly, none of the higher MCPs containing internal methyl substituents appears to have been studied despite the fact that the chemical shift of the $-CH_3$ group provides a convenient probe by ^{1}H NMR of any possible conformation changes. Hence, introduction of substituents into internal positions of higher [*m.n*]MCPs may influence not only the ring inversion but also may give rise to a change of the equilibrium position of syn and anti conformers.

Scheme I



Recently, we have reported[10] the preparation of *anti*-8,16-dimethyl[2.2]MCP, *anti*-9,17-dimethyl[3.2]MCP, and *anti*-10,18-dimethyl[4.2]MCP from toluene by using the *tert*-butyl function as a positional protective group.

We report here the preparation of the [*m.n*]MCPs higher than [4.2]MCP and their conformational behaviors.

Results and Discussion

Preparation of 1,*n*-Bis(5-*tert*-butyl-2-methyl-

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