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Robert Pajewski[a]; Ryszard Ostaszewski[a]; Janusz Jurczak[ab]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw [b] Department of Chemistry, Warsaw Uniwersity, Warsaw, Poland

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The Reaction of 2,5-Bis(Dimethyfurfuryl)Furan Dialdehyde with Primary α,ω-Diamines

ROBERT PAJEWSKI[a], RYSZARD OSTASZEWSKI[a] and JANUSZ JURCZAK[ab]*

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, 01–224, Warsaw and* [b]*Department of Chemistry, Warsaw Uniwersity, 02–093 Warsaw, Poland*

The influence of the H-bond acceptors strength of heteroatoms present in α,ω-diamines on the reaction course leading to the formation of macrocyclic Schiff bases was studied. For strong acceptors like oxygen and nitrogen atoms the highest yield was obtained. Similar effect was observed for diamines possessing two oxygen atoms, while the presence of three oxygen resulted only in polymerisation reactions.

Keywords: Macrocycle, furan derivatives, Schiff base, hydrogen bond

In the synthesis of macrocyclic compounds of crown ethers and cryptands type the selectivity of macrocyclization reaction strongly depends on the structure of substrates [1] and reaction conditions [2]. In many cases, formation of polymers predominates [3,4]. Thus, the knowledge of the factors controlling macrocyclization reaction selectivity is still of great interest for synthetic chemists.

In the synthesis of macrocyclic azacoronands derived from bis(dimethyfurfuryl)furan dialdehyde (**1**) we decided to concentrate on only one factor which influences the reaction course, namely on a reagent. Since it is already known that heteroatoms like oxygen and nitrogen are good H-bond acceptors, we expected that their presence in the molecule should influence the reaction selectivity towards single product. Incorporation of the benzene ring into diamines can also give similar effect. Increasing the number of heteroatoms in substrate can substantially change the selectivity of the macrocyclization reaction since the number of H-bond acceptors increases.

As a model reaction, we have chosen the formation of Schiff bases from α,ω-diamines and dialdehyde **1**. This reaction is widely used for the synthesis of azacoronadsands and proceeds under mild, easy reproducible conditions [5–12]. Initially formed macrocylic Schiff bases can be reduced to respective diamines and separated into single compounds after protection of the amino groups. As a protecting group we have chosen the BOC group which gave stable amino derivatives and could be easily removed under mild reaction conditions.

The structures of several α,ω-diamines used for the model reaction are presented in Chart 1.

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* Author for correspondence.

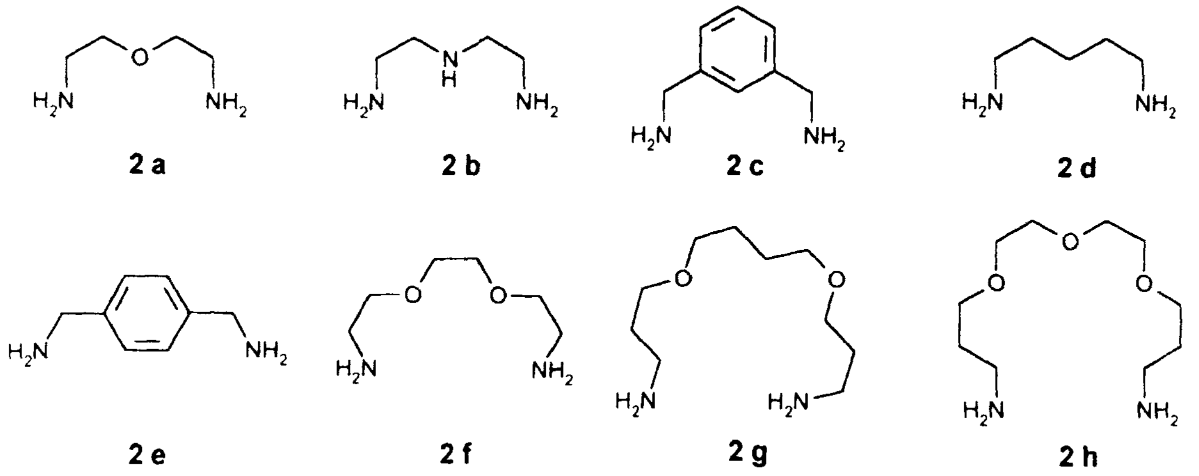


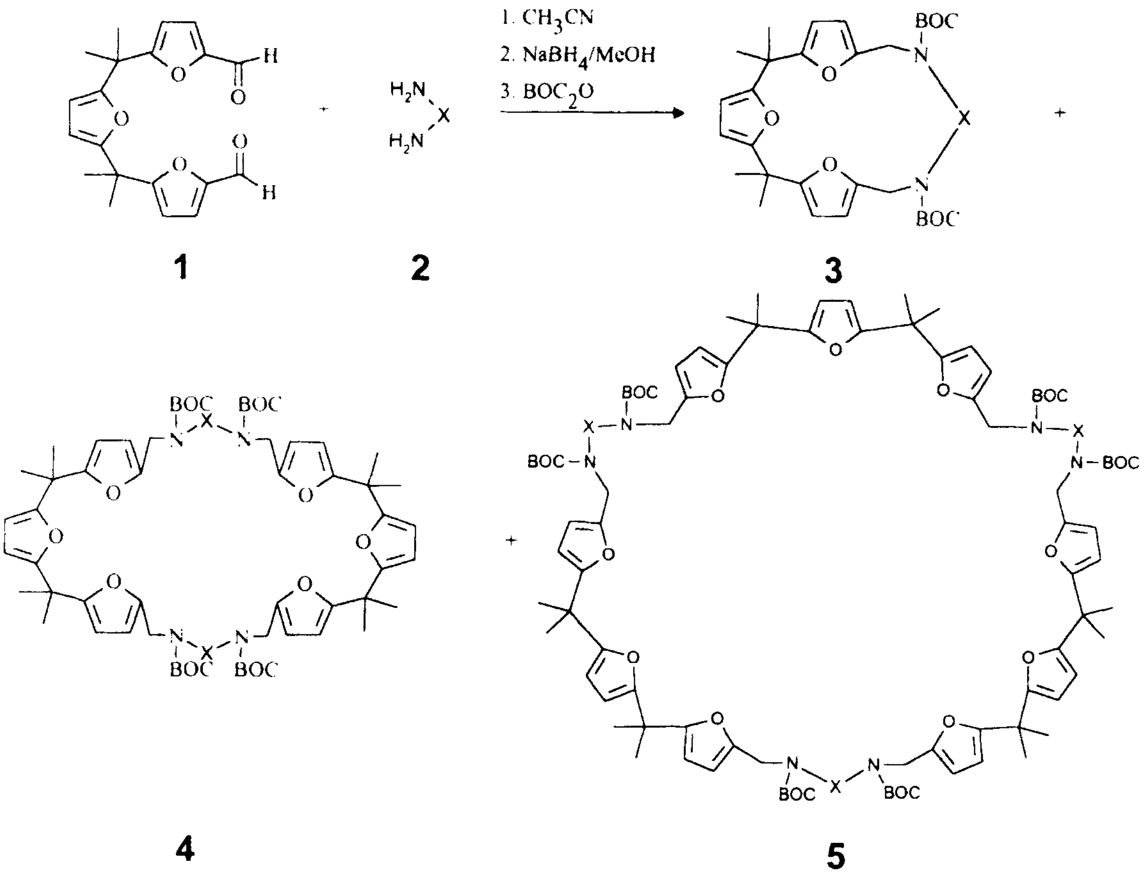
CHART 1

TABLE I The Influence of Conformation Mobility of α,ω-Diamines on The Selectivity of Macrocyclization Reaction with 2,5-bis(Dimethylfurfuryl)furan Dialdehyde

Entry	*Substrate*	*Products [%]*			*Polymers [%]*
		3	*4*	*5*	
1	**2a**	51	–	–	49
2	**2b**	30	–	–	70
3	**2c**	12	1	–	87
4	**2d**	4	5	2	89
5	**2e**	–	–	–	100
6	**2f**	16	–	–	84
7	**2g**	7	20	–	72
8	**2h**	–	–	–	100

Macrocyclization reactions were carried out in acetonitrile and crude products were reduced ($NaBH_4$, MeOH). Subsequent protection of the amino group was followed by separation of products by flash chromatography. In all cases, macrocyclic products of general structure **3**, **4** and **5**, shown in Scheme 1, were analyzed using NMR, mass spectrometry, and combustion analysis; additionally IR spectra were taken for all compounds [13]. Yields of the reactions investigeted are collected in Table I.

For amine **2a**, only one product of structure **3** was obtained in 51% yield (Entry 1). This high selectivity towards formation of a single macrocycle was also observed for the next reaction studied using amine **2b**, although in this case the yield decreased to 30% (Entry 2). This phenomenon can be easily associated with H-bond acceptor capabilities of central heteroatom present in both diamines **2a** and **2b**. The presence of the benzene ring in diamine **2c** (Entry 3) caused decrease in selectivity towards compound **3**. Parallel formation of compound **4** in 1% yield was observed. Application of aliphatic diamine **2d** for reaction decreased the overall selectivity (entry 4). The selectivity was lost for isomeric p-xylilene diamine **2e** (Entry 5), where only polymeric materials were obtained. Increased number of heretoatoms in amine **2f** did not improve the yield of the reaction while the selectivity remained very high (Entry 6). To our surprise, we found that the presence of two carbon atoms in the structure of amine **2g** increased the yield of the reaction and its selectivity towards product **4** which was obtained in 20% yield (Entry 7). The presence of three oxygen atoms in amine **2h** resulted in formation of polymers only (Entry 8). The method used for the synthesis of diazacoronand is thus limited to amines possessing one or two oxygen atoms.



SCHEME 1

Incorporation of heteroatoms into α,ω-diamines resulted in an increase of reaction yield and selectivity. The presence of H-bond acceptors can be correlated with the reaction efficiency. For strong acceptors like oxygen and nitrogen atoms, the highest yield was obtained. Similar effect was observed for amines **2f** and **2g**, possessing two oxygen atoms, while the presence of three oxygen atoms resulted only in the polymerization reaction.

Acknowledgements

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[13] Selected analytical data for **3a:** **^{1}H NMR** (200 MHz, $CDCl_3$, δ), 1.45 (18H, s, $C(CH_3)_3$), 1.58 (12H, s, $C(CH_3)_2$), 3.28–3.40 (8H, m, OCH_2, NCH_2), 4.27–4.34 (4H, m, $C_{AR}CH_2N$), 5.84–5.91 (4H, m, C_{AR}**H**), 5.95–6.12 (2H, m, C_{AR}**H**); **^{13}C NMR** (50 MHz, $CDCl_3$, δ), 26.50, 28.58, 37.27, 46.21. 47.08, 47.14, 47.17, 47.51, 68.80, 80.83, 104.02, 104.37, 107.35, 150.72, 155.22, 158.32, 158.43, 159.85; **IR** 3374.1, 2977.0, 2935.0, 1771.3, 1697.2, 1549.7, 1458.7, 1410.3, 1366.8, 1249.7, 1168.2, 1020.4, 784.1, 756.8 cm^{-1}; **L-SIMS** m/z 635 ($[M+Na]^+$, 100%), 612 ($[M]^+$, 8%); **HRMS** m/z 635.3297 (635.3308 calcd. for $C_{34}H_{48}N_2O_8Na$, $[M+Na]^+$); **Anal. calcd.** for $C_{34}H_{48}N_2O_8+0.4CHCl_3$: C, 62.65; H, 7.40; N, 4.25. Found: C, 62.65; H, 7.62; N, 3.91.