Study of product composition of the reaction between 1,1,2,2-tetrabromoethane and imidazole or 1,2,4-triazole in a superbasic medium

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Abstract

Influence of reagent ratio on the composition of products of the reaction between 1,1,2,2-tetrabromoethane and imidazole or 1,2,4-triazole in a superbasic medium (potassium hydroxide – dimethyl sulfoxide) was investigated using GC/MS technique. It was found that nucleophilic substitution reaction is always accompanied by elimination reactions (dehydrobromination and debromination). In addition to 1,1,2,2-tetra(azol-1-yl)ethane, 1,1,2-tri(azol-1-yl)ethenes and 1,2-di(azol-1-yl)ethenes, as well as 1,2-di(azol-1-yl)-1-bromoethenes were detected. Reaction pathway that explains the formation of all major products was proposed.

Keywords: imidazole, triazole, terabromoethane, superbasic medium, nucleophilic substitution, elimination

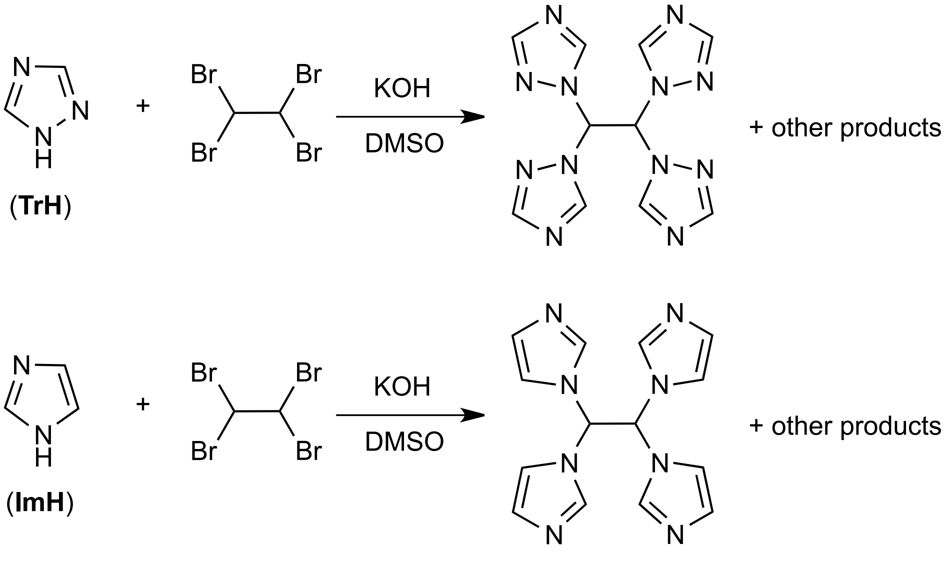
Introduction

Compounds bearing several heterocyclic moieties can act as multidentate ligands for the construction of metal-organic frameworks (MOFs) [1–4]. Constant design of new MOFs is stimulated by their high capacity for gas storage [5–7], photophysical properties [8], sensor capabilities [9] and excellent catalytic performance [10].

Tetra(pyrazolyl)derivatives were successfully used for preparation of coordination polymers and molecular complexes [11–15]. In our preceding studies we have developed a synthetic procedure for the simplest bitopic tetra(pyrazolyl)derivative – 1,1,2,2-tetra(pyrazol-1-yl)ethane [16] and determined the crystal structure of its copper(II) molecular complex [17]. In this communication we report the study of the reaction between 1,2,4-triazole and imidazole and 1,1,2,2-tetrabromoethane with the aim to prepare new tetra(azolyl) polydentate ligands.

Results and discussion

The reactions between 1,2,4-triazole (or imidazole) and 1,1,2,2-tetrabromoethane (TNE) were carried out in a superbasic medium potassium hydroxide – dimethyl sulfoxide (scheme 1). Molar ratio of reagents (TBE to azole) was varied from 1:1 to 1:4, while other parameters (temperature, concentration of the base) were held constant (table 1).



Scheme 1

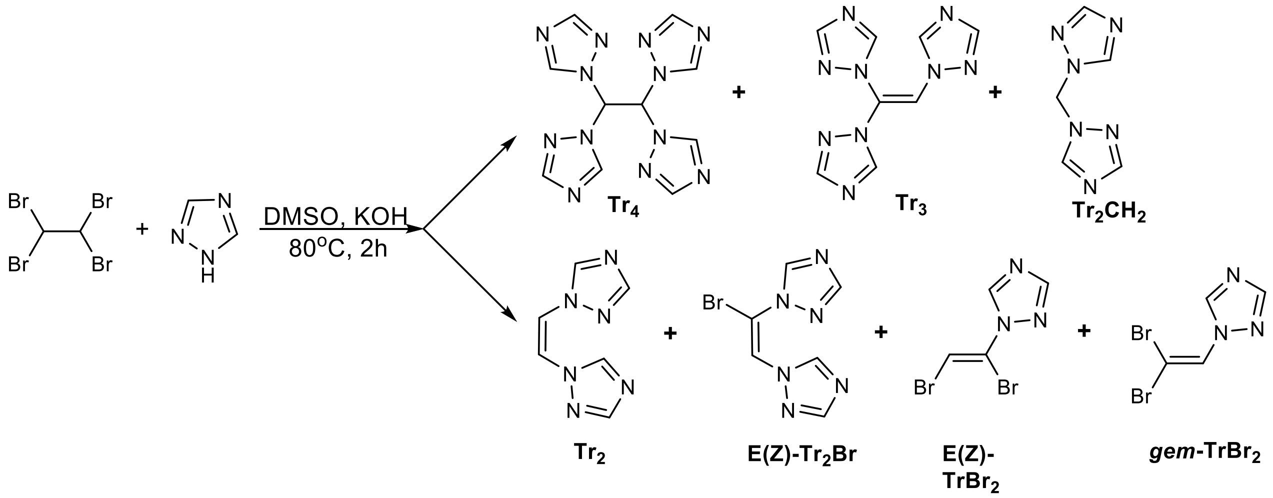
Table 1 – Screening of reaction conditions between azoles and TBE

Run	AzH (mmol)	TBE (mmol)	KOH (mmol)	DMSO (ml)	t (°C)
A	1.0	1.0	2	1	80
B	1.0	0.5	2	1	80
C	1.0	0.25	2	1	80

As it is well known, under basic conditions nucleophilic substitution reactions are accompanied by elimination reactions [18]. In accordance with this, products of both of these processes were detected in the reaction mixtures (table 2, scheme 2).

Table 2 – Composition of product mixtures of the reaction between TrH and TBE

Run	Molar % (GC/MS)							
	Tr_4	Tr_3	Tr_2	Tr_2Br (E & Z)	$TrBr_2$ (E & Z)	gem-$TrBr_2$	Tr_2CH_2	$(Tr_2C)_2$
R.T. (min)	19.5	16.7	12.4	15.1; 15.4	14.6	11.3	10.4	21.5
M (g/mol)	298	229	162	241	252	253	150	296
A	_____	92.0%	_____	30.0%	56.0%	_____	_____	4.9%
B	7.0%	19.7%	_____	19.5%	49.0%	14.8%	_____	3.7%
C	17.6%	33.1%	8.3%	_____	_____	_____	39.5%	_____



Scheme 2

Reaction with imidazole gave similar results and is not discussed in detail in this communication.

Experimental

A suspension of 1mmol of 1,2,4-triazole (or imidazole), 2 mmol of KOH, 0.25-1 mmol of TBE in 1 ml of DMSO were incubated at 80 °C. The reaction progress was monitored by TLC. After two hours, full conversion of the starting azole was achieved. The reaction mixtures were diluted with water (5 ml), DMSO-water mixture was removed on a rotary evaporator, the residue was treated by methylene chloride to extract the organic products, which were then analyzed by GC/MS method.

Gas chromatography-mass spectrometry analysis was performed using Agilent 7890A gas chromatograph equipped with Agilent MSD 5975C mass-selective detector. The relative quantities of the products were determined from peak areas without correction coefficients.

Summary

In all the cases, the reactions yielded complex product mixtures, in which triazolyl- and bromo-substituted ethenes were the dominating components.

When triazole reacted with TBE in 1:1 ratio, bromoethenes containing one or two triazole rings were the major products.

For 2:1 TrH-TBE reaction, 1,1,2-tris(triazol-1-yl)ethane Tr_3 was detected as a second to the dominating product.

In case of 4:1 TrH-TBE ratio, Tr_3 was obtained as a major product, while only little amount of Tr_4 was formed and no $TrBr_2$ was detected at all.

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