

## SYNTHESIS OF SUBSTITUTED TRIAZOLES BY REACTION OF DIAZOMETHANE WITH CARBODIIMIDES AND KETENIMINES

A. MARTVOŇ, Š. STANKOVSKÝ and J. SVĚTLÍK

*Department of Organic Chemistry,  
Slovak Institute of Technology, 880 37 Bratislava*

Received February 25th, 1974

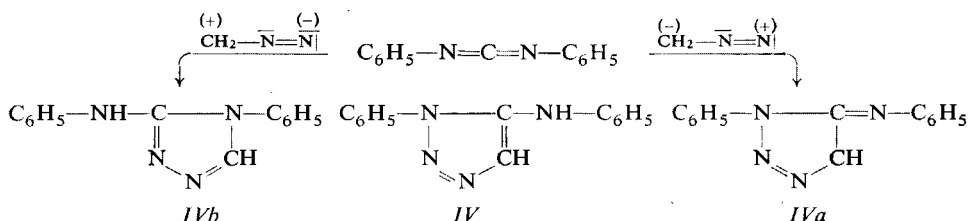
The reaction of diazomethane with carbodiimides of the general formula  $X-C_6H_4-N=C=N-C_6H_4-Y$  and ketenimines  $(C_6H_5)_2-C=C=N-C_6H_4-X$  has been investigated. The products have been shown by IR, UV and  $^1H-NMR$  spectroscopy to be 1-(4-X-phenyl)-5-(4-Y-anilino)-1,2,3-triazoles and 1-(4-X-phenyl)-5-diphenylmethyl-1,2,3-triazoles.

It is known that diazomethane can undergo a 1,3-addition reaction with various systems<sup>1</sup>. By a cyclisation of symmetrical diphenylcarbodiimide, Rotter<sup>2</sup> obtained a product which he described as 1-phenyl-5-anilino-1,2,3-triazole. This compound was identical with the compound, synthesized by Dimroth<sup>3</sup> by reaction of 5-chloro-1-phenyl-1,2,3-triazole with aniline. Cyclisation reactions of ketenimines with diazomethane, leading to 1,2,3-triazoles<sup>4-6</sup>, are also known. In the present study we try to reinvestigate the reaction of diazomethane with a series of substituted aromatic carbodiimides and ketenimines.

Carbodiimides, used in this study, were prepared by desulphuration of the substituted diphenylthioureas with yellow mercuric oxide<sup>7</sup>, and ketenimines by dehydration of the corresponding diphenylacetic acid anilides<sup>8</sup>. Because of their instability, these compounds were prepared directly before the reaction. The products of the cycloaddition reaction of diazomethane with ketenimines and carbodiimides were identified as substituted triazoles. The yields of these products are relatively low and neither variation in the components ratios, nor prolonged reaction time improved substantially the yields. These low yields of the cycloaddition products are caused by the decomposition of the reaction components during the long reaction time.

When comparing the reaction of diazomethane with systems containing  $C=N$  bond, e.g. with azomethines, one can suppose that the first step of the reaction is the formation of *IVa* (Scheme 1). However, the results of spectral measurements indicate that the final products are 1,2,3-triazole derivatives since the IR spectrum exhibits no absorption bands at  $1680-1640\text{ cm}^{-1}$  due to  $C=N$  vibrations but it contains the absorption bands at  $3400\text{ cm}^{-1}$  which can be ascribed to vibrations of a secondary amino group. Also the  $^1H-NMR$  spectrum of the compound *IV*

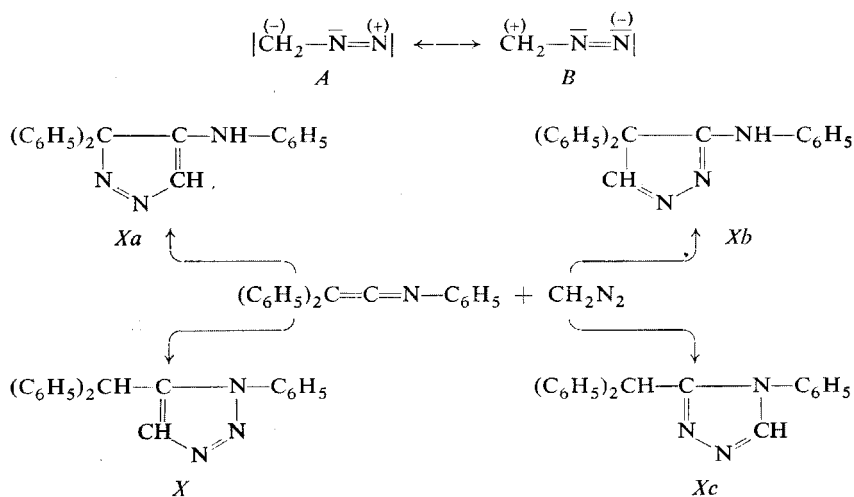
exhibits only a signal at  $\sigma$  6.2, corresponding to an amino proton, and a complex multiplet  $\sigma$  6.75–7.7 due to eleven aromatic protons. This leads to the assumption that in the further step of the cycloaddition reaction the proton of the methylene group migrates to the nitrogen of the C=N bond under formation of *IV* (Scheme 1) (ref.<sup>9</sup>).



SCHEME 1

Symmetrically substituted carbodiimide with two equivalent C=N bonds should afford two products (Scheme 1). The mesomeric structure *A* of diazomethane indicates the possibility of formation of 1,5-disubstituted 1,2,3-triazoles, the mesomeric structure *B* should lead to 1-phenyl-5-anilino-1,3,4-triazoles. Ketenimines have two non-equivalent multiple bonds C=C and N=C, and therefore four heterocyclic systems could be formed (Scheme 2).

Simple addition of diazomethane to a multiple bond leads to five-membered ring with the exocyclic C=X bond (X = C, N). As evident from the absence of characteristic bands at 1680–1640  $\text{cm}^{-1}$  in the IR spectra of the products (Table II), the



SCHEME 2

TABLE I  
Properties and Analyses of the Synthesized Derivatives

Compound	X Y	Formula (m. w.)	Calculated/Found			M.p., °C yield, %
			% C	% H	% N	
1-(4-X-Phenyl)-5-(Y-anilino)-1,2,3-triazoles						
<i>I</i>	N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>22</sub> N <sub>6</sub>	67.05	6.87	26.06	180—183
	N(CH <sub>3</sub> ) <sub>2</sub>	(322.4)	66.81	6.59	26.18	43.5
<i>II</i>	OCH <sub>3</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub>	64.85	5.44	18.90	176—176.5
	OCH <sub>3</sub>	(296.3)	64.75	5.24	18.88	36.0
<i>III</i>	CH <sub>3</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub>	72.70	6.10	21.19	166—166.5
	CH <sub>3</sub>	(264.3)	73.00	6.00	21.38	52.8
<i>IV</i>	H	C <sub>14</sub> H <sub>12</sub> N <sub>4</sub>	71.17	5.11	23.71	144.5—146
	H	(236.3)	71.34	5.04	23.66	41.1
<i>V</i>	Cl	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>4</sub>	55.10	3.30	18.36	162.5—165.5
	Cl	(305.2)	55.35	3.35	18.38	17.1
<i>VI</i>	Br	C <sub>14</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>4</sub>	42.67	2.55	14.21	220—221
	Br	(394.1)	42.98	2.86	13.98	39.3
<i>VII</i>	COCH <sub>3</sub>	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub>	67.49	5.03	17.49	176—178.5
	COCH <sub>3</sub>	(320.3)	67.16	5.21	17.27	16.1
<i>VIII</i>	OCH <sub>3</sub>	C <sub>15</sub> H <sub>14</sub> N <sub>4</sub> O	67.64	5.29	21.03	145—155
	H	(266.3)	67.89	5.21	21.10	17.4
1-(4-X-Phenyl)-5-diphenylmethyl-1,2,3-triazoles						
<i>IX</i>	CH <sub>3</sub>	C <sub>22</sub> H <sub>19</sub> N <sub>3</sub>	81.20	5.88	12.91	148—149
			(325.4)	81.41	6.02	12.86
<i>X</i>	H	C <sub>21</sub> H <sub>17</sub> N <sub>3</sub>	81.00	5.50	13.49	153—154
			(311.4)	80.77	5.42	13.22
<i>XI</i>	Cl	C <sub>21</sub> H <sub>16</sub> ClN <sub>3</sub>	72.93	4.66	12.15	175—177
			(345.8)	72.85	4.69	11.83
<i>XII</i>	Br	C <sub>21</sub> H <sub>16</sub> BrN <sub>3</sub>	64.62	4.13	10.76	176—177
			(390.3)	64.57	4.11	10.41

C=N exocyclic bond is not formed. Similarly, the <sup>1</sup>H-NMR spectra of the compound *X* indicate the presence of a benzhydryl proton at  $\delta$  5.35, and of 15 aromatic protons at  $\delta$  7.4–6.88. Also for ketenimines we can anticipate that in the further reaction step the methylene hydrogen is shifted to the exocyclic C=X bond, under formation of a more stable heterocyclic system. The IR spectroscopic data exclude the structures *Xa* and *Xb* (Scheme 2) because no NH bands in the region 3400 cm<sup>-1</sup>

TABLE II  
Infrared Absorption Bands ( $\text{cm}^{-1}$ )

Compound	Triazole deformation vibrations			Triazole valence vibrations			$\nu(\text{C}=\text{C})$ arom.	$\nu(\text{NH})$
1-(4-X-Phenyl)-5-(4-Y-anilino)-1,2,3-triazoles								
<i>I</i>	959	1 070	1 129	—	1 480		1 621 3 370	3 420
<i>II</i>	983	1 048	1 092	1 398	1 475	1 582	1 606	3 420
<i>III</i>	983	1 044	1 096	1 395	1 462	1 578	1 607	3 419
<i>IV</i>	983	1 059	1 102	1 409	1 467	1 579	1 610	3 421
<i>V</i>	981	1 040	1 102	1 393	1 439	1 576	1 604	3 419
<i>VI</i>	980	1 023	1 085	1 418	1 433	1 580	1 608	3 425
<i>VII</i>	969	1 022	1 093	1 400	1 422	1 574	1 602	3 420
							1 616	
<i>VIII</i>	982	1 048	1 098	1 410	1 475	1 580	1 610	3 420
1-(4-X-Phenyl)-5-diphenylmethyl-1,2,3-triazoles								
<i>IX</i>	987	1 023	1 088	—	1 463		1 611	
<i>X</i>	987	1 026	1 099	—	1 463		1 608	
<i>XI</i>	987	1 022	1 103	1 412	1 464		1 609	
<i>XII</i>	987	1 019	1 078	1 410	1 464		1 610	

TABLE III  
Ultraviolet Absorption Bands of the Substituted 1,2,3-Triazoles

Compound	$\lambda_{\text{max}}$ , nm (log $\epsilon$ )		
<i>I</i>	—	247 (4.23)	272 (4.43)
<i>II</i>	—	242 (4.29)	278 (4.12)
<i>III</i>	—	241 (4.27)	286 (4.03)
<i>IV</i>	205 (4.52)	328 (4.21)	283 (3.98)
<i>V</i>	205 (4.57)	245 (4.37)	290 (4.05)
<i>VI</i>	—	245 (4.39)	290 (4.05)
<i>VII</i>	205 (4.47)	261 (4.26)	215 (4.30)
<i>VIII</i>	205 (4.61)	240 (4.35)	276 (4.19)
<i>IX</i>	205 (4.59)	—	—
<i>X</i>	205 (4.58)	—	—
<i>XI</i>	205 (4.67)	—	—
<i>XII</i>	205 (4.56)	—	—

are present. On the other hand, the IR spectra exhibit strong bands at 1070, 1020 and 980  $\text{cm}^{-1}$  which are characteristic for a 1,2,3-triazole ring. On the basis of this evidence, we assume that the form *A* of diazomethane affords in the cycloaddition reaction with ketenimines 1-phenyl-5-benzhydryl-1,2,3-triazoles (Scheme 2).

## EXPERIMENTAL

### Preparation of 1,5-Disubstituted 1,2,3-Triazoles

A freshly prepared ethereal solution of diazomethane (12 mmol) was added to a solution of freshly prepared carbodiimide or ketenimine (10 mmol) in a sufficient quantity of ether and the mixture was allowed to stand for 4 days at room temperature. The separated crystals were filtered, washed with ether and crystallized from methanol or aqueous acetone. The properties and analytical data of the synthesized triazoles are given in Table I.

### Spectral Measurements

The IR spectra in the region 700–3600  $\text{cm}^{-1}$  were taken on a double beam UR-20 Zeiss spectrophotometer; concentration  $2 \cdot 10^{-2}$  mol/l in chloroform, 1 mm NaCl cells. Characteristic frequencies of the studied compounds are listed in Table II. The UV spectra were measured in ethanol on a Specord UV-VIS spectrophotometer, concentration  $2-5 \cdot 10^{-5}$  mol/l. The UV data are given in Table III. The  $^1\text{H}$ -NMR spectra were measured in  $\text{CDCl}_3$  on a Tesla BS 847 (80 MHz) instrument, using tetramethylsilane as internal standard.

## REFERENCES

1. Huisgen R.: *J. Org. Chem.* 33, 2291 (1968).
2. Rotter R.: *Monatsh. Chem.* 47, 353 (1926).
3. Dimroth O.: *Ann.* 364, 225 (1909).
4. Barker M. W., Coker M. E.: *J. Heterocycl. Chem.* 4, 155 (1967).
5. Weidler-Kubanek H. M., Litt M. H.: *J. Org. Chem.* 33, 1844 (1968).
6. Barker M. W., Gardner J. H.: *J. Heterocycl. Chem.* 5, 881 (1968).
7. Huig S., Lehmann H., Grinner G.: *Ann.* 579, 235 (1953).
8. Bestmann J., Lienert J., Mott L.: *Ann.* 718, 24 (1968).
9. Buckley G. D.: *J. Chem. Soc.* 1954, 1850.

Translated by M. Tichý.