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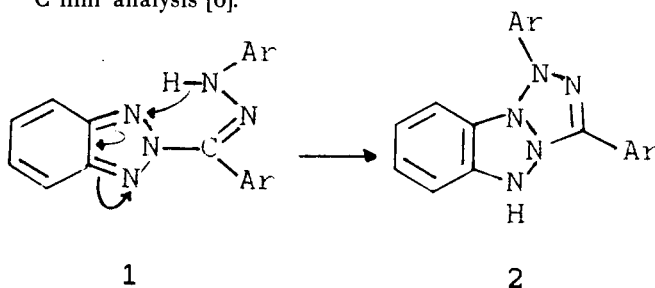
The synthesis of some 1- and 2-hydrazoneoyl-1,2,3-triazoles by reaction of the corresponding 1,2,3-triazoles and nitrilimines is described and their characterization by  $^{13}\text{C}$  nmr and mass spectroscopy is provided. The structure of a 2-hydrazoneoyl derivative **6b** was determined by X-ray analysis.

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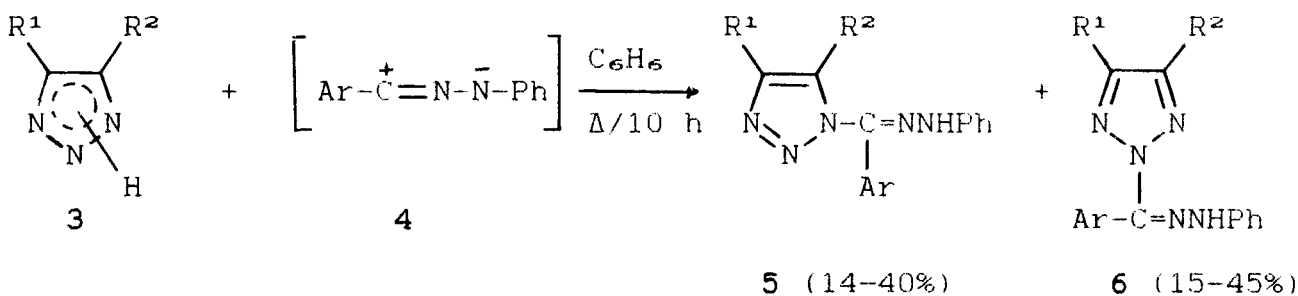
It has been shown previously [1] that the 1,3-dipolar cycloaddition of 1-(*N*-arylidene)amino-1,2,3-triazoles with diphenylnitrilimine leads to the formation of 1,2,3- and 1,2,4-triazoles as well as 1- and 2-hydrazoneoyl-1,2,3-triazoles. The formation of the latter products was explained considering a further reaction of nitrilimine with the corresponding triazoles formed upon cleavage of the initial cycloadducts.

The synthesis of several *N*-hydrazoneoyl-heterocycles [2-4] has been achieved by the addition of nitrilimine to N-H bond of the corresponding heterocyclic system and in a previous study [5], concerning the reaction of benzotriazole with nitrilimines, the formation of 1-hydrazoneoyl-benzotriazoles and 1*H*,9*H*-tetrazolo[1,2-*a*]benzotriazoles **2** was proposed. Compounds **2** could be obtained either by cycloaddition of the nitrilimine to benzotriazole N=N bond [5] or by a hydrogen shift occurred in 2-hydrazoneoyl-benzotriazole **1**. Although the mass fragmentation pattern is in favour of the structure **2**, the products of the reaction of benzotriazole with diphenylnitrilimine are actually 1- and 2-hydrazoneoylbenzotriazoles and the structure **2** was

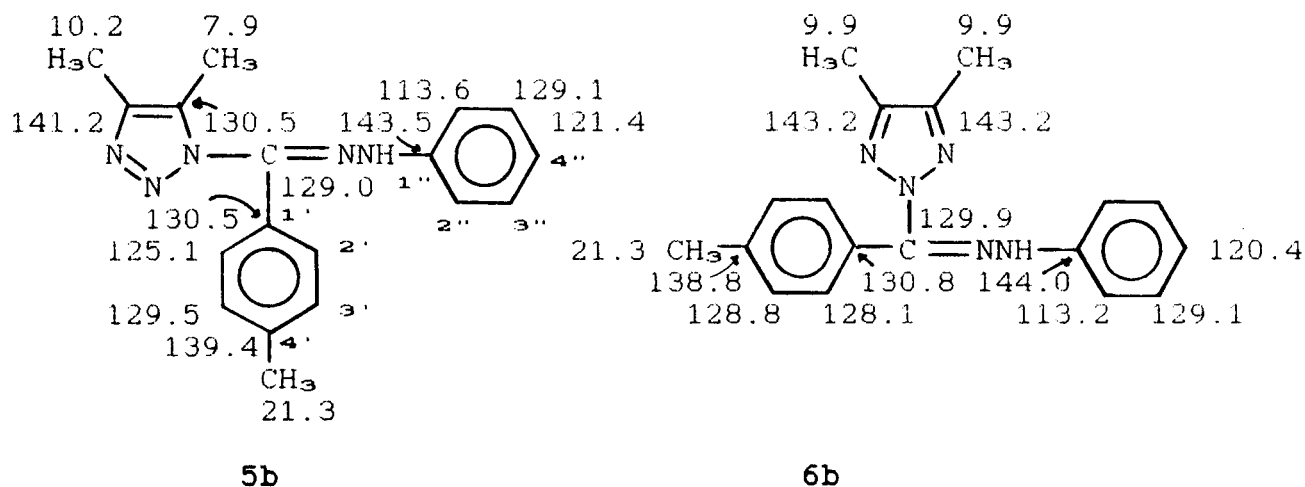
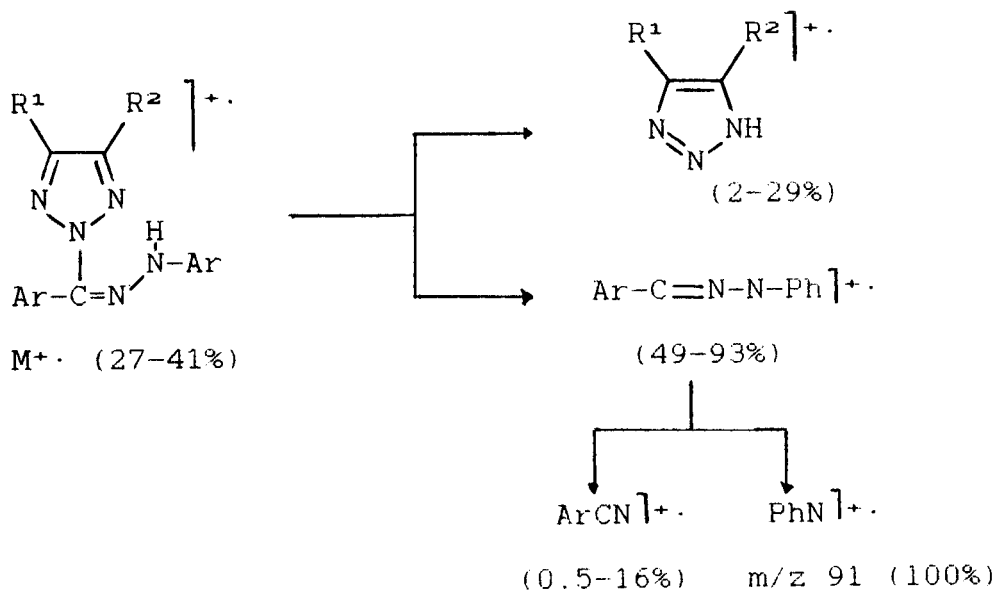
reassigned on the basis of a careful and complete  $^1\text{H}$  and  $^{13}\text{C}$  nmr analysis [6].



The aim of this work is the structure elucidation of 1- and 2-hydrazoneoyl-1,2,3-triazoles and their characterization and differentiation by spectroscopic means. The hydrazoneoyltriazoles **5** and **6** were synthesized in moderate yields by the reaction of the corresponding 1,2,3-triazoles **3** with nitrilimines **4** in refluxing benzene and they were separated by column chromatography. It has been found that the yields in **5** and **6** are remarkably increased in refluxing benzene instead of tetrahydrofuran, which was previously used [1] as reaction solvent.



	R <sup>1</sup>	R <sup>2</sup>		Ar	R <sup>1</sup>	R <sup>2</sup>	Ar			
<b>3</b>	a	CH <sub>3</sub>	<b>4</b>	a	C <sub>6</sub> H <sub>5</sub>	<b>5,6</b>	a	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
	b	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>		b	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		b	CH <sub>3</sub>	CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
		H		c	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>		c	CH <sub>3</sub>	CH <sub>3</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>
							d	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>

Scheme 1.  $^{13}\text{C}$  Shifts of **5b** and **6b** in  $\text{CDCl}_3$ Scheme 2. Fragmentation pattern in the mass spectra of compounds **6**.

The compounds **5(a-c)** exhibit in  $^{13}\text{C}$  nmr spectra two resonance signals for triazole C-4 and C-5 at 141 and 130 ppm respectively and two also signals for  $\text{CH}_3$ -4 and  $\text{CH}_3$ -5 carbon atoms at about 10 and 7.7 ppm respectively. These signals are very typical for 1-substituted-4,5-dimethyl-1,2,3-triazoles [7,8]. In contrast, the isomeric compounds **6(a-c)** exhibit for the same triazole carbon atoms only one signal at 143 ppm (see Scheme 1) and one signal for the methyl carbons at 9.9 ppm. This finding is an evidence against the structure analogous to **2**.

Very characteristic are also the mass spectra of the compounds **5** and **6** and they can be used for their differentiation. Thus, the compounds **6** give, besides the molecular ion  $\text{M}^{+\bullet}$ , very strong ion peaks corresponding to the ions  $\text{PhN}^{+\bullet}$  and  $\text{ArCNNPh}^{+\bullet}$  (Scheme 2). The nitrilimine ion fragment is readily explained considering a retro-cycloaddition from a structure analogous to **2**. Although the products **6** unambiguously have the structure of 2-hydrazono-1,2,3-triazole, as evidenced by X-ray analysis, the possibility of a ring transformation similar to

Table 1

Positional Parameters (x 10<sup>4</sup>) for the Non-hydrogen Atoms

ATOM	X	Y	Z
N(1)	994(2)	5352.9(9)	1785(2)
N(2)	601(2)	5984.8(9)	2167(2)
N(3)	1849(2)	5440.4(9)	1115(2)
N(4)	1211(2)	4044.0(9)	2001(2)
N(5)	2269(2)	3979(1)	1485(2)
C(1)	629(3)	4660(1)	2133(2)
C(3)	1211(3)	6498(1)	1705(2)
C(4)	1980(3)	6164(1)	1058(2)
C(5)	1015(3)	7296(1)	1884(3)
C(6)	2826(3)	6511(1)	367(3)
C(11)	-539(3)	4641(1)	2694(2)
C(12)	-2121(3)	5002(1)	2135(2)
C(13)	-3203(3)	4923(1)	2657(2)
C(14)	-2743(3)	4497(1)	3741(2)
C(15)	-1160(3)	4143(1)	4303(2)
C(16)	-79(3)	4209(1)	3782(2)
C(17)	-3906(4)	4431(2)	4333(3)
C(21)	2794(3)	3277(1)	1364(2)
C(22)	3733(3)	3192(1)	726(3)
C(23)	4251(3)	2503(2)	586(3)
C(24)	3851(3)	1898(1)	1063(3)
C(25)	2928(3)	1982(1)	1703(3)
C(26)	2401(3)	2668(1)	1860(2)

Table 2

Bond [a] Lengths (Å) and Angles (°) of **6b**

Length	(Å)	Angle [b]	(°)
N2-N1	1.346 (2)	N3N1N2	114.2
N3-N1	1.352 (2)	C1N1N2	122.2
C1-N1	1.417 (2)	C1N1N3	123.5
C3-N2	1.328 (3)	C3N2N1	103.9
C4-N3	1.330 (3)	C5C3N2	121.9
C5-C3	1.496 (3)	C4C3N2	109.2
C4-C3	1.393 (3)	C4C3C5	128.9
C6-C4	1.497 (3)	N3C4C3	109.2
C11-C1	1.483 (3)	N3C4C6	121.9
N4-C1	1.279 (3)	C4N3N1	103.6
N5-N4	1.356 (2)	C11C1N1	117.5
C21-N5	1.397 (3)	N4C1N1	125.8
N5-H	0.909 (21)	N4C1C11	116.7
C5-H	0.960 (0)	C12C11C1	123.2
C17-H	0.960 (0)	C16C11C1	118.6
		N5N4C1	123.0
		C21N5N4	117.9
		C22C21N5	118.8
		C26C21N5	121.9
		C17C14C13	121.3
		C17C14C15	120.6

[a] Average values for *C*-phenyl C-C 1.381(3), C-H 0.963(2), internal angle 120.0(2) and for *N*-phenyl C-C 1.377(3), C-H 0.970(2), internal angle 120.0(2).

[b] Standard deviation for angle bonds 0.2°.

**1** → **2** during the ionization process can not be rigorously excluded.

On the other hand compounds **5** give a more complicated fragmentation pattern with main characteristics the prominent ion peaks  $M^+$ ,  $[M-28]^+$ ,  $\text{PhNH}^+$  and the hydrazone fragment  $\text{ArC}=\text{NNHPh}$ . The nitrogen elimination  $[M-28]^+$  ion is a very typical fragmentation [9] for 1-substituted 1,2,3-triazoles and it can be used for their differentiation from the isomeric 2-substituted derivatives.

The structure of the products **6** was fully determined from the X-ray crystallographic analysis carried out on 2-(*p*-methylbenzoyl)-4,5-dimethyl-2*H*-1,2,3-triazole phenylhydrazone **6b**. It is evident from the study that the compounds in question adopt the 2-hydrazoneyl-1,2,3-triazole structure **6** and the hydrazone function is in *Z*-form, in agreement with other similar observations [2,10]. In this form the distance between hydrazone hydrogen (N5-H) and N-3 of the triazole ring (Figure 1) is equal to 1.99 Å and it is almost located in the plane of the triazole ring, its deviation from this plane being equal to 0.006 Å.

The proximity of these two atoms might be the reason for the appearance of the nitrilimine ion fragment  $\text{ArCN-NPh}^+$  and subsequently of the ions  $\text{PhN}^+$  and  $\text{ArCN}^+$  as well as the triazole ion in the mass spectra of compounds **6**, as it is shown in Scheme 2.

X-Ray study of 2-(*p*-Methylbenzoyl)-4,5-dimethyl-2*H*-1,2,3-triazole Phenylhydrazone (**6b**).

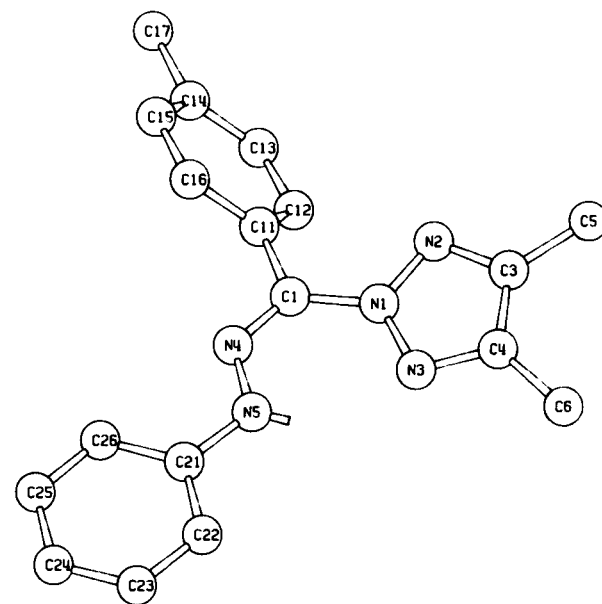


Figure 1.

these data is clearly evident the stereochemistry of **6b** and the *Z*-form of the hydrazone function. In this structure the planar triazole ring and the hydrazone function are found in an almost coplanar position, the dihedral angles between the planes N1C1N4 and N3N1C1 and between C1N4N5 and N1C1N4 (Figure 1) being  $-0.58^\circ$  and  $8.38^\circ$  respectively. The *N*-phenyl group and the hydrazone group are also found almost at the same plane forming a dihedral angle of  $173.82^\circ$  between the planes N4N5C21 and N5C21C22. On the other hand, the *C*-phenyl group is out of the hydrazone plane, forming a dihedral angle between the planes C16C11C1 and C11C1N4 equal to  $45.13^\circ$ .

## EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 297 spectrometer as Nujol mulls. The  $^1\text{H}$  nmr spectra were obtained on a Bruker AW 80 spectrometer (80 MHz) and  $^{13}\text{C}$  nmr were obtained on a Varian CFT-20 spectrometer (20 MHz), in deuteriochloroform with tetramethylsilane (TMS) as internal standard. The mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6L spectrometer and elemental microanalyses were performed with a Perkin-Elmer 240B CNH analyser. Column chromatography was performed over Merk Kieselgel 60, particle size 0.063-0.200 mm.

### Compounds 3.

These were prepared from the corresponding 1-amino-1,2,3-triazoles by deamination reaction [11] with nitrous acid and their analytical and spectral data are in agreement with their structure and those given in the literature [11].

### Compounds 4.

These were prepared *in situ* by the action of triethylamine on the corresponding *N*-phenylbenzhydrazonoyl chloride [1].

### Reaction of 1,2,3-Triazoles **3** with Nitrilimines **4**.

#### General Procedure.

To a mixture of equivalent amounts of triazole **3** and *N*-phenylbenzhydrazonoyl chloride (1-3 mmoles) in benzene (5 ml) a solution of triethylamine in slight excess (1.5-3.5 mmoles) were added at once and after the mixture had been refluxed for 8-10 hours the triethylammonium chloride was filtered off and the residue was chromatographed on a silica gel column using a mixture of *n*-hexane:dichloromethane (from 9:1 to 1:1) as eluant to give compounds **6** and **5**.

### Reaction of 4,5-Dimethyl-1,2,3-triazole (**3a**) with Diphenylnitrilimine (**4a**).

A mixture of **3a** (0.3 g, 3.1 mmoles), *N*-phenylbenzhydrazonoyl chloride (0.71 g, 3.1 mmoles) and triethylamine (0.56 ml, 4 mmoles) in benzene (10 ml) was refluxed for 10 hours and treated as above and after column chromatography gave:

a: 2-Benzoyl(4,5-dimethyl-2*H*-1,2,3-triazole) Phenylhydrazone (**6a**).

Compound **6a** was obtained in 33% yield (0.3 g) mp 113-114°

(from *n*-hexane) (lit [1] 109-110°); ir: 3280 (NH), 1600, 1580 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  2.42 (6H, s, CH<sub>3</sub>-4, CH<sub>3</sub>-5), 7.12-7.46 (7H, m), 7.66 (2H, m), 10.5 (1H, s, N-H);  $^{13}\text{C}$  nmr: (for numbering see Scheme 1, **5b**) 9.95 (CH<sub>3</sub>-4, CH<sub>3</sub>-5, q,  $^1\text{J} = 128.6$  Hz), 113.31 (C-2'', C-6''), 120.56 (C-4''), 128.11 (C-2', C-6', C-3', C-5'), 128.79 (C-4'), 129.19 (C-3'', C-5''), 129.79 (C=N), 133.64 (C-1'), 143.11 (C-4tr, C-5tr), 144.28 (C-1''); ms: *m/z* (%), 291 (M<sup>+</sup>, 41), 194 (82), 103 (15), 97 (2), 91 (100).

b: 1-Benzoyl(4,5-dimethyl-1*H*-1,2,3-triazole) Phenylhydrazone (**5a**).

This compound was obtained in 41% yield (0.37 g) mp 199-201° (from *n*-hexane-ether) (lit [1] 194-195°); ir: 3180 (NH), 1600, 1580 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  2.04 (3H, s, CH<sub>3</sub>-4), 2.20 (3H, s, CH<sub>3</sub>-5), 6.84-7.40 (10H, m), 8.10 (1H, bs, NH);  $^{13}\text{C}$  nmr: 7.67 (CH<sub>3</sub>-5, q,  $^1\text{J} = 129.9$  Hz), 10.5 (CH<sub>3</sub>-4, q,  $^1\text{J} = 128.2$  Hz), 113.75 (C-2'', C-6''), 121.41 (C-4''), 125.00 (C-2', C-6'), 128.58 (C=N), 128.71 (C-3', C-5'), 129.01 (C-4'), 129.18 (C-3'', C-5''), 130.62 (C-5tr), 133.34 (C-1'), 141.21 (C-4tr), 143.54 (C-1''); ms: *m/z* (%), 291 (M<sup>+</sup>, 18), 263 (13), 195 (28), 104 (36), 92 (100).

Reaction of 4,5-Dimethyl-1,2,3-triazole (**3a**) with *p*-Methylphenyl-*N*-phenylnitrilimine (**4b**).

A mixture of **3a** (0.25 g, 2.6 mmoles), *N*-phenyl-*p*-methylbenzhydrazonoyl chloride (0.635 g, 2.6 mmoles) and triethylamine (0.42 ml, 3 mmoles) in benzene (5 ml) was refluxed for 8 hours and treated as above and after column chromatography gave:

a: 2-(*p*-Methylbenzoyl)(4,5-dimethyl-2*H*-1,2,3-triazole) Phenylhydrazone (**6b**).

This compound was obtained in 32% yield (0.25 g) mp 130-132°; ir: 3260 (NH), 1598, 1585 (C=N),  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  2.33 (9H, s, CH<sub>3</sub>-4, CH<sub>3</sub>-5, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>), 7.12-7.32 (6H, m), 7.54 (2H, d,  $^3\text{J} = 8$  Hz, H-2', H-6'), 10.45 (1H, bs, NH);  $^{13}\text{C}$  nmr: 9.94 (CH<sub>3</sub>-4, CH<sub>3</sub>-5, q,  $^1\text{J} = 128.5$  Hz), 21.31 (CH<sub>3</sub>-4',  $^1\text{J} = 126.6$  Hz), 113.23 (C-2'', C-6''), 120.36 (C-4''), 128.11 (C-2', C-6'), 128.76 (C-3', C-5'), 129.14 (C-3'', C-5''), 129.93 (C=N), 130.85 (C-1'), 138.81 (C-4'), 143.25 (C-4tr, C-5tr), 144.03 (C-1''); ms: *m/z* (%), 305 (M<sup>+</sup>, 37), 208 (80), 117 (8), 97 (7), 91 (100).

*Anal.* Calcd. for C<sub>18</sub>H<sub>19</sub>N<sub>5</sub>: C, 70.80; H, 6.27; N, 22.93. Found: C, 70.83; H, 6.16; N, 23.05.

b: 1-(*p*-Methylbenzoyl)(4,5-dimethyl-1*H*-1,2,3-triazole) Phenylhydrazone (**5b**).

This compound was obtained in 32% yield (0.25 g) mp 225-226°; ir: 3220 (NH), 1605, 1580 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  2.01 (3H, s, CH<sub>3</sub>-4), 2.35 (6H, s, CH<sub>3</sub>-5 and CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>), 6.80-7.04 (1H, m), 7.04-7.5 (8H, m), 8.05 (1H, s, NH);  $^{13}\text{C}$  nmr: 7.86 (CH<sub>3</sub>-5, q,  $^1\text{J} = 130.3$  Hz), 10.20 (CH<sub>3</sub>-4, q,  $^1\text{J} = 128.5$  Hz), 21.33 (CH<sub>3</sub>-4', q,  $^1\text{J} = 126$  Hz), 113.64 (C-2'', C-6''), 121.37 (C-4''), 125.14 (C-2', C-6'), 129.14 (C-3'', C-5''), 129.51 (C-3', C-5'), 130.56 (C-1' and C-5tr), 139.38 (C-4'), 141.25 (C-4tr), 143.50 (C-1''); ms: *m/z* (%), 305 (M<sup>+</sup>, 12), 277 (8), 195 (28), 118 (33), 92 (100).

*Anal.* Calcd. for C<sub>18</sub>H<sub>19</sub>N<sub>5</sub>: C, 70.80; H, 6.27; N, 22.93. Found: C, 70.94; H, 6.29; N, 22.72.

Reaction of 4,5-Dimethyl-1,2,3-triazole (**3a**) with *p*-Chlorophenyl-*N*-Phenylnitrilimine (**4c**).

A mixture of **3a** (0.3 g, 3.1 mmoles), *N*-phenyl-*p*-chlorobenzhydrazonoyl chloride (0.82 g, 3.1 mmoles) and triethylamine (0.56 ml, 4 mmoles) in benzene (5 ml) was refluxed for 10 hours and treated as above and after column chromatography gave:

a: 2-(*p*-Chlorobenzoyl)(4,5-dimethyl-2*H*-1,2,3-triazole) Phenylhydrazone (**6c**).

This compound was obtained in 45% yield (0.45 g) mp 137-138°; ir: 3240 (NH), 1600, 1598, 1580 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  2.34 (6H, s, CH<sub>3</sub>-4, CH<sub>3</sub>-5), 6.8-7.40 (1H, m), 7.12-7.40 (6H, m), 7.60 (2H, d,  $^3J = 9$  Hz, H-2', H-6''), 10.55 (1H, s, NH);  $^{13}\text{C}$  nmr: 9.97 (CH<sub>3</sub>-4, CH<sub>3</sub>-5, q,  $^1J = 128.6$ ), 113.32 (C-2'', C-6''), 120.77 (C-4''), 128.26 (C-3', C-5'), 128.59 (C=N), 129.25 (C-3'', C-5''), 129.44 (C-2', C-6'), 132.11 (C-1'), 134.65 (C-4'), 143.25 (C-4tr, C-5tr), 144.03 (C-1''); ms:  $m/z$  (%), 327/325 (M<sup>+</sup>, 27), 230/228 (49), 139/137 (0.5), 97 (4), 91 (100).

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>ClN<sub>5</sub>: C, 62.67; H, 4.95; N, 21.50. Found: C, 62.71; H, 4.78; N, 21.56.

b: 1-(*p*-Chlorobenzoyl)(4,5-dimethyl-1*H*-1,2,3-triazole) Phenylhydrazone (**5c**).

This compound was obtained in 35% yield (0.35 g) mp 212-213°; ir: 3200 (NH), 1602, 1595, 1575 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  2.07 (3H, s, CH<sub>3</sub>-4), 2.41 (3H, s, CH<sub>3</sub>-5), 6.88-7.03 (1H, m), 7.14-7.40 (8H, m), 8.45 (1H, s, NH);  $^{13}\text{C}$  nmr: 7.69 (CH<sub>3</sub>-5tr, q,  $^1J = 130.0$  Hz), 10.05 (CH<sub>3</sub>-4tr, q,  $^1J = 128.3$  Hz), 113.86 (C-2'', C-6''), 121.73 (C-4''), 126.15 (C-2', C-6'), 127.34 (C=N), 129.01 (C-3', C-5'), 129.25 (C-3'', C-5''), 130.84 (C-5tr), 131.94 (C-1'), 134.96 (C-4'), 141.31 (C-4tr), 143.31 (C-1''); ms:  $m/z$  (%), 327/325 (M<sup>+</sup>, 11), 299/297 (6), 231/229 (13), 140/138 (18), 92 (100).

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>ClN<sub>5</sub>: C, 62.67; H, 4.95; N, 21.50. Found: C, 62.65; H, 5.08; N, 21.55.

In another experiment a mixture of **3a** (0.1 g, 1.03 mmoles), *N*-phenyl-*p*-chlorobenzhydrazonoyl chloride (0.272 g, 1.03 mmoles) and triethylamine (0.21 ml, 1.5 mmoles) in THF (5 ml) was refluxed for 10 hours and treated as above and after column chromatography gave: a: **6c**, 0.02 g (6%), mp 136-138°; b: **5c**, 0.02 g (6%), mp 212-214°. Both compounds were identified by their ir and ms spectra.

Reaction of 4-(*p*-Chlorophenyl)-1,2,3-triazole (**3b**) with Diphenylnitrilimine (**4a**).

A mixture of **3b** (0.18 g, 1 mmole), *n*-phenylbenzhydrazonoyl chloride (0.23 g, 1 mmole) and triethylamine (0.21 ml, 1.5 mmoles) in benzene (5 ml) was refluxed for 10 hours and treated as above and after column chromatography gave:

a: 2-Benzoyl[4-[*p*-chlorophenyl]-2*H*-1,2,3-triazole] Phenylhydrazone (**6d**).

This compound was obtained in 15% yield (0.055 g), yellow needles, mp 136-137°; ir: 3260 (NH), 1600, 1585 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  6.84-7.20 (1H, m), 7.16-7.52 (9H, m), 7.63-7.68 (2H, m), 7.80 (2H, d,  $^3J = 8$  Hz, H-2'', H-6''), 10.5 (1H, s, NH);  $^{13}\text{C}$  nmr: 113.53 (C-2'', C-6''), 121.14 (C-4''), 127.61 (C-2''', C-6'''), 128.07 (C-2', C-6', C-3', C-5'), 128.55 (C=N), 129.01 (C-4'), 129.34 (C-3'', C-5'', C-3''', C-5'''), 131.60 (C-5tr,  $^1J = 193.3$  Hz), 133.94 (C-1'), 135.44 (C-4''), 143.88 (C-1''), 147.71 (C-4tr); ms:  $m/z$  (%), 375/373 (M<sup>+</sup>, 27), 194 (93), 181/179 (29), 103 (16), 91 (100).

*Anal.* Calcd. for C<sub>21</sub>H<sub>16</sub>ClN<sub>5</sub>: C, 67.47; H, 4.31; N, 18.73. Found: C, 67.61; H, 4.66; N, 18.73.

b: 1-Benzoyl[4-[*p*-chlorophenyl]-1*H*-1,2,3-triazole] Phenylhydrazone (**5d**).

This compound was obtained in 14% yield (0.05 g), mp 149-151°; ir: 3325 (NH), 3150, 1600, 1585, 1575 (C=N),  $\text{cm}^{-1}$ ;  $^1\text{H}$

nmr:  $\delta$  6.80-7.02 (1H, m), 7.18-7.30 (3H, m), 7.34-7.62 (8H, m), 7.82 (2H, d,  $^3J = 8$  Hz, H-2''', H-6'''), 7.88 (1H, s, H-5tr), 9.80 (1H, s, NH);  $^{13}\text{C}$  nmr: 113.66 (C-2'', C-6''), 120.08 (C-4tr,  $^1J = 196$  Hz), 121.53 (C-4''), 126.75 (C-2', C-6'), 127.18 (C-2''', C-6'''), 127.58 (C-1'''), 127.97 (C=N), 128.89 (C-3', C-5'), 129.29 (C-3'', C-5'', C-3''', C-5'''), 129.5 (C-4'), 133.09 (C-1'), 134.71 (C-4''), 143.50 (C-1''), 145.93 (C-5tr); ms:  $m/z$  (%), 375/373 (M<sup>+</sup>, 7), 347/345 (15), 195 (10), 138/136 (37), 104 (26), 103 (100), 92 (56), 91 (48).

*Anal.* Calcd. for C<sub>21</sub>H<sub>16</sub>ClN<sub>5</sub>: C, 67.47; H, 4.31; N, 18.73. Found: C, 67.66; H, 4.57; N, 18.61.

In another experiment a mixture of **3b** (0.15 g, 0.83 mmole), *N*-phenylbenzhydrazonoyl chloride (0.19 g, 0.83 mmole) and triethylamine (0.21 ml, 1.5 mmoles) in THF (5 ml) was refluxed for 10 hours and treated as above and after column chromatography gave: a: **6d**, 0.01 g (3%), mp 133-135°; b: **5d**, 0.04 g (13%), mp 145-147°. Both compounds were identified by their ir and ms spectra.

X-Ray Analysis of Compound **6b**.

The compound **6b**, C<sub>18</sub>H<sub>19</sub>N<sub>5</sub>, *M* = 305.38 crystallizes (from hexane) as light yellow monoclinic crystals; space group P<sub>21/C</sub>, *z* = 4, *a* = 8.890(1), *b* = 18.263(3), *c* = 11.785(2) Å,  $\beta = 119.94(2)^\circ$ , *V* = 1657.9(5) Å<sup>3</sup>, *D<sub>m</sub>* = 1.15 g. cm<sup>-3</sup>, Mo-K $\alpha$  Zr-filtered radiation,  $\lambda = 0.71069$  Å,  $\mu = 0.4$  cm<sup>-1</sup>.

Data were collected using a crystal of *ca* 0.29 x 0.33 x 0.42 mm dimensions mounted on a Nicolet Pz<sub>1</sub> diffractometer, *w*/ $2\theta$  mode, with scan width 1.8° ( $2\theta$ ) and scan speed 2.18°  $2\theta$ /min ( $2\theta_{max} = 48^\circ$ ). Out of 3202 independent reflexions collected 2309 with  $I \geq 2.06(I)$  were considered observed. The data were corrected for the Lorentz and polarization factors (*Lp*) but not for absorption.

The structure was solved by the direct methods using SHELX program [12] and full-matrix least squares refinements of the same program, with all non-H atoms anisotropic and hydrogen isotropic. Final *R*/*R<sub>w</sub>* 0.045/0.041 and unit weights gave satisfactory agreement analysis. Methyl groups refined as rigid groups with hydrogen riding on C-atoms at 0.96 Å. All other H-atoms were located from Fourier maps and then were refined.

## REFERENCES AND NOTES

- [1] A. Bojilova, N. A. Rodios and N. E. Alexandrou, *J. Chem. Soc., Perkin Trans. I*, 3233 (1988).
- [2] R. N. Bulter, K. J. Fitzgerald and M. T. Fleming, *Tetrahedron Letters*, **27**, 4921 (1986); R. N. Butler and K. J. Fitzgerald, *J. Chem. Soc., Perkin Trans. I*, 1587 (1988).
- [3] M. Ruccia, N. Vivona, G. Cusmano and G. Macaluso, *J. Heterocyclic Chem.*, **15**, 1485 (1978).
- [4] E. Sayanna, R. V. Venkataratnam and G. Thyagarajan, *Heterocycles*, **23**, 2183 (1985).
- [5] E. Sayanna, R. V. Venkataratnam and G. Thyagarajan, *Heterocycles*, **22**, 1561 (1984).
- [6] R. V. Venkataratnam and J. Elguero, *Heterocycles*, **23**, 2779 (1985).
- [7] N. A. Rodios, C. A. Tsoleridis and N. E. Alexandrou, *J. Heterocyclic Chem.*, **25**, 1161 (1988).
- [8] N. A. Rodios, *J. Heterocyclic Chem.*, **21**, 1169 (1984).
- [9] N. A. Rodios and S. G. Adamopoulos, *J. Heterocyclic Chem.*, **24**, 1461 (1987); N. E. Alexandrou and E. Mikromastoras, *Tetrahedron Letters*, 237 (1968).
- [10] For a general review see A. F. Hegarty, *Acc. Chem. Res.*, **13**, 448

(1980); P. Caramella and P. Grunanger in "1,3-Dipolar Cycloaddition Chemistry", Vol 1, A. Padwa, ed, John Wiley, New York, 1984, p 337; I. D. Cunningham and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 537 (1986).

[11] H. v. Pechmann and W. Bauer, *Ber.*, **42**, 659 (1909); S. Hauptmann, H. Wilde and K. Moser, *Tetrahedron Letters.*, 3295 (1967).

[12] G. M. Sheldrick, SHELX 76 Program for crystal structure determination, University of Cambridge, England, 1976.