

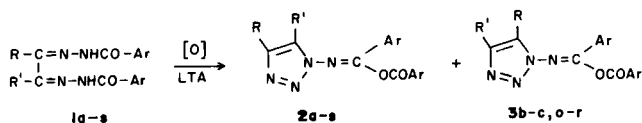
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The <sup>13</sup>C nmr spectra of the title compounds are reported. Chemical shifts of C-4 and C-5 carbons of the triazole ring are used for structural assignment of the 4,5-unsymmetrically substituted 1-( $\alpha$ -aroyloxyarylideneamino)-*v*-triazoles (triazolyloisimides). A complete assignment of the shifts of the  $\alpha$ -aroyloxyarylideneamino group is given. Some  $J_{C-H}$  values are also reported.

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Oxidation of bis-aroylhydrazones of symmetrically substituted  $\alpha$ -dicarbonyl compounds, R = R', (**1a**, **d-h**), yields one triazolyloisimide such as **2a**, **d-h**, whereas oxidation of bis-aroylhydrazones of unsymmetrically substituted  $\alpha$ -dicarbonyl compounds where R and R' are different, such as **1b-c**, **i-s**, can give two isomers **2** and **3** [1-2].



<b>a</b>	R = R' = H,	Ar = C <sub>6</sub> H <sub>5</sub>	
<b>b</b>	R = H, R' = CH <sub>3</sub>	Ar = C <sub>6</sub> H <sub>5</sub>	
<b>c</b>	R = H, R' = CH <sub>3</sub> ,	Ar = <i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	
<b>d</b>	R = R' = CH <sub>3</sub>	Ar = C <sub>6</sub> H <sub>5</sub>	
<b>e</b>	R = R' = CH <sub>3</sub>	Ar = <i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	
<b>f</b>	R = R' = CH <sub>3</sub>	Ar = <i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	
<b>g</b>	R = R' = CH <sub>3</sub>	Ar = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	
<b>h</b>	R = R' = CH <sub>3</sub>	Ar = <i>p</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	
<b>i</b>	R = C <sub>6</sub> H <sub>5</sub> , R' = H,	Ar = C <sub>6</sub> H <sub>5</sub>	
<b>k</b>	R = C <sub>6</sub> H <sub>5</sub> ,	R' = H,	Ar = <i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>
<b>l</b>	R = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> ,	R' = H,	Ar = C <sub>6</sub> H <sub>5</sub>
<b>m</b>	R = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> ,	R' = H,	Ar = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>
<b>n</b>	R = <i>p</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> ,	R' = H,	Ar = C <sub>6</sub> H <sub>5</sub>
<b>o</b>	R = C <sub>6</sub> H <sub>5</sub> ,	R' = CH <sub>3</sub> ,	Ar = C <sub>6</sub> H <sub>5</sub>
<b>p</b>	R = C <sub>6</sub> H <sub>5</sub> ,	R' = CH <sub>3</sub> ,	Ar = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>
<b>q</b>	R = <i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> ,	R' = CH <sub>3</sub> ,	Ar = C <sub>6</sub> H <sub>5</sub>
<b>r</b>	R = <i>p</i> -Br-C <sub>6</sub> H <sub>4</sub> ,	R' = CH <sub>3</sub> ,	Ar = C <sub>6</sub> H <sub>5</sub>
<b>s</b>	R = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> ,	R' = CH <sub>3</sub> ,	Ar = C <sub>6</sub> H <sub>5</sub>

Identification of the isomer derived from the above oxidations has been made by means of the benzene induced shifts in <sup>1</sup>H nmr spectra [3] and by dipole moment measurements [4-5]. The first method can be applied only to isomers bearing at least one methyl group at the 4- or 5-position of the triazole ring, whereas the second, except for being laborious and time consuming, can give reliable results only for isomers with polar substituents [4]. Recently <sup>13</sup>C nmr data were successfully used for the structural assignment in analogously substituted 1-amino- and 1-(*N*-arylacetyl amino)-1,2,3-triazoles [6].

Since <sup>13</sup>C nmr is a more convenient and easy to use method for structural problems like this, we have undertaken this study for an unequivocal identification of the

4,5-unsymmetrically substituted triazolyloisimides. We have also tried to assign all the carbons of the triazole and the other aromatic rings.

The chemical shifts extracted for the carbons of the compounds under investigation are given in Table 1.

### Results and Discussion.

In the 4,5-unsubstituted compound **2a** the two carbons of the triazole ring appeared at 132.1 and 123.5 ppm for C-4 and C-5 respectively. They were easily differentiated from the other aromatic carbon peaks, since in the coupled spectrum the two peaks were resolved into two doublets of doublets. Assignment of these peaks to C-4 and C-5 have been made by comparison of the data given by Alexandrou *et al.* [6] for analogous *v*-triazole derivatives, according to which the C-5 of the triazole ring, that is adjacent to a nitrogen of sp<sup>3</sup>-hybridization shows a diamagnetic shift, whereas the C-4, adjacent to a nitrogen of sp<sup>2</sup>-hybridization shows a paramagnetic shift. In agreement with the above findings Elguero *et al.* [7-8] have found that the shifts of C-4 and C-5 in 1-methyl-*v*-triazole are 133.6 and 124.1 ppm respectively, whereas the shifts in 1-acetyl-*v*-triazole are 134.2 ppm for C-4 and 121.1 ppm for C-5.

In the mono-substituted derivatives **2b-c**, **i-n**, **3b-c**, the peak due to the unsubstituted carbon of the triazole ring was easily recognised by its splitting to a doublet in the off-resonance or the coupled spectrum, whereas in the 4-substituted derivatives **2i-n**, **3b-c**, the C-4 appeared always between 146 and 141 ppm, *i.e.* out of the overcrowded aromatic region, thus making the assignment relatively easy. More difficult were the assignments of the methyl- or aryl-substituted carbons at the 5-position which appeared in the aromatic region of the spectrum, *i.e.* between 127 and 133 ppm. The assignment for these carbons has been made after determination of all the other aromatic carbon signals or by analogy to well resolved spectra of other unambiguously assigned C-5 carbons. However for some of these carbons the assignment is not certain (see Table 1).

It is worth mentioning here the substituent effects caused by the methyl and phenyl groups on the C-4 and C-5 of the triazole ring. Thus a methyl group at the 4-position

Table 1

<sup>13</sup>C-Chemical Shifts (ppm from TMS) of 1-( $\alpha$ -Aroyloxyarylideneamino)-1,2,3-triazoles **2**, **3** and **4**  
(Spectra taken in deuteriochloroform at 20 MHz. For numbering see **4** and **5**)

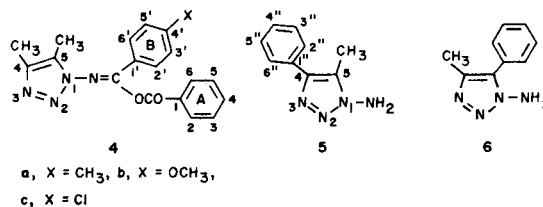
	C-4tr	C-5tr	CH <sub>3</sub> -4	CH <sub>3</sub> -5	C-1	C-2	C-3	C-4	C-1'	C-2'	C-3'	C-4'	C-1''	C-2''	C-3''	C-4''	C=O	C=N	X,Y
<b>2a</b>	132.1	123.5	—	—	127.5	130.7	128.9	134.5	129.8	128.1	128.9	132.9					162.3	153.4	
<b>2b</b>	130.8	133.0	—	8.35	127.9	130.8	128.8 [a]	134.3	130.5 [b]	128.1	129.9 [a]	132.7					162.4	152.6	
<b>3b</b>	141.5	121.1	10.8	—	127.5	130.7	128.8	134.3	130.3	128.0	128.8	132.7					162.3	152.3	
<b>2c</b>	130.7	132.4	—	8.25	120.0	132.9	114.1 [a]	164.5	122.5	130.1	114.3 [a]	163.4					162.0	153.9	55.5
<b>3c</b>	141.5	120.5	10.9	—	119.8	132.9	114.1 [a]	164.6	122.5	130.1	114.3 [a]	163.4					—	153.4	55.5
<b>2d</b>	138.5	129.6 [c]	10.3	7.75	—	130.7	128.7 [a]	134.2	129.6 [c]	127.9	128.8 [a]	132.5					162.5	151.5	
<b>2e</b>	138.4	129.2 [d]	10.3	7.8	125.3	130.8	129.4 [a]	145.1	127.8 [d]	128.8	129.5 [a]	143.3					162.5	152.4	21.6
<b>2f</b>	138.4	129.0	10.4	7.8	120.3	133.0	114.1 [a]	164.7	122.9	130.0	114.3 [a]	163.2					162.1	152.8	55.5
<b>2g</b>	138.7	129.9 [a]	10.3	7.8	126.4	132.1	129.2	141.0	129.1 [a]	129.2	129.3	139.0					161.8	149.8	
<b>2h</b>	139.0	130.8	10.3	7.9	133.2	132.1	124.0 [a]	151.3	136.2	128.9	124.1 [a]	150.2					161.1	147.3	
<b>4a</b>	138.5	129.4	10.35	7.8	128.2	130.8	128.7	134.1	127.8	128.0	129.6	143.4					162.6	152.1	21.6
<b>4b</b>	138.5	129.2	10.4	7.8	128.2	130.8	128.7	134.1	122.8	130.0	114.3	163.3					162.6	152.2	55.5
<b>4c</b>	138.6	129.7 [f]	10.3	7.85	128.0	130.8	128.8	134.3	129.7 [f]	129.3	129.3	139.0					162.5	150.5	
<b>2i</b>	145.7	119.8	—	—	127.7	130.9	128.9	134.5	130.0 [a]	128.2	128.9	132.9	130.1 [a]	125.7	128.9	128.4	162.4	153.1	
<b>2k</b>	145.6	119.1	—	—	119.7	133.0	114.2 [a]	164.6	122.1	130.2	114.3 [a]	163.5	130.3 [d]	125.6	128.8	128.2	162.0	154.1	55.5
<b>2l</b>	144.6	119.9	—	—	127.6	130.8	129.0	134.5	129.9	128.2	129.0	133.0	128.6	126.9	129.0	134.2	162.3	153.3	
<b>2m</b>	144.6	120.2	—	—	—	132.2	129.4	141.4	—	129.4	129.4	139.4	128.6	126.9	129.1	134.4	161.6	151.7	
<b>2n</b>	143.5	121.2	—	—	127.5	130.9	129.0	134.7	129.8	128.3	129.0	133.3	136.3	126.2	124.3	147.5	162.3	154.2	
<b>2o</b>	142.3	130.6	—	9.4	—	131.0	128.9 [a]	134.4	129.7	128.2	129.0 [a]	132.8	131.5	127.0	128.8	127.8	162.6	152.3	
<b>2p</b>	142.3	129.8 [a]	—	9.3	126.3	132.2	129.3	141.2	129.1 [a]	129.3	129.3	139.3	131.2	126.9	128.7	127.9	161.8	150.5	
<b>2q</b>	142.3	129.7 [a]	—	9.2	127.8 [d]	130.8	128.8	134.2	130.6 [a]	128.1	128.8	132.6	123.9	128.0	114.1	159.3	162.5	151.8	55.3
<b>2r</b>	141.2	129.8 [k]	—	9.4	—	130.9	128.9 [a]	134.4	130.4	128.2	129.0 [a]	132.8	129.8 [k]	128.4	131.9	121.9	162.5	152.5	
<b>2s</b>	141.2	130.0	—	9.3	—	130.9	128.9	134.4	130.5	128.1	128.9	132.8	129.7	128.1	128.9	133.7	162.5	152.5	
<b>3o</b>	139.5	131.8	11.3	—	127.8 [g]	130.9	128.9	134.3	130.5	128.2	128.9	132.7	126.9	129.8	128.5	128.8 [h]	162.4	153.0	
<b>3p</b>	139.5	131.1 [i]	11.3	—	126.3	132.2	129.3	141.2	129.1 [a]	129.3	129.3	139.2	126.7	129.8	128.5	128.9 [a]	161.6	151.2	
<b>3q</b>	138.9	—	11.3	—	127.9	130.8	128.8	134.3	130.5	128.1	128.8	132.6	119.1	131.1	114.0	160.1	162.4	152.7	55.3
<b>3r</b>	139.6	—	11.3	—	127.8	130.8	128.9	134.4	130.3	128.2	128.9	132.8	125.9	131.3	131.8	123.4	162.3	153.3	
<b>5</b>	142.9	129.7	—	8.94	—								131.5	126.7	128.7	127.7			
<b>6</b>	140.5	132.6	11.53	—	—								126.7	129.4	128.7	129.0			

[a] Shift assignments may be interchanged. [b] Shift of C-1' may be at 129.9 ppm (from fully coupled spectrum). [c] Shift at 129.6 ppm may be assigned either to C-1' or C-5tr. [d] Peaks assigned from the off-resonance spectrum. [e] Shift of C-1 may be at 127.6 ppm. [f] Shift at 129.7 ppm may be assigned either to C-1' or C-5tr. [g] Shift of C-1 may be at 128.0 ppm. [h] Shift of C-4'' assigned from the off-resonance spectrum by analogy to **3p**. [i] Shift of C-5tr assigned by analogy to **3p**. [k] Peak at 129.8 ppm may be assigned either to C-1'' or C-5tr.

causes a downfield shift on C-4 of about 9.5 ppm and an upfield shift on C-5 of about 3 ppm in comparison with the 4,5-unsubstituted derivative **2a**. A methyl group at the 5-position results in an upfield shift on C-4 and a downfield shift on C-5 of about 1.5 and 9.0 ppm respectively. On the other hand a phenyl group at the 4-position of the triazole ring results in a downfield shift on C-4 and an upfield shift on C-5 of about 14 and 2.5-4.0 ppm respectively. In the 4,5-dimethyl derivatives, where the two effects act additively, there is a downfield shift for both C-4 and C-5 of 6.5-7.0 and 5.5-7.0 ppm respectively.

Methyl carbons attached to the triazole ring resonate between 7.7 and 11.4 ppm (Table 1). The 5-methyl derivative **2b**, which is the main product of the oxidation with lead tetraacetate of **1b** [3,9], showed in the <sup>13</sup>C nmr spectrum a peak due to CH<sub>3</sub>-5 at 8.3 ppm. Another sample from the same reaction, consisting of a mixture of both 4- and 5-methyl derivatives **2b**, **3b**, gave two peaks for the methyl carbons at 8.3 and 10.8 ppm. On the other hand the 5-methyl-4-aryl derivatives **2o-s**, which are the main oxidation products [2,4] of the bis-aryloxyhydrazones **1o-s**, gave a peak due to CH<sub>3</sub>-5 at 9.3 ppm, whereas the corres-

ponding 4-methyl-5-aryl derivatives **3o-r** gave peaks for the CH<sub>3</sub>-4 at 11.3 ppm. In the 4,5-dimethyl derivatives **2d-h**, **4a-c**, the two methyl carbons appeared at 7.8 and 10.4 ppm, which according to the above findings should be assigned to CH<sub>3</sub>-5 and CH<sub>3</sub>-4 respectively. It should be noticed that hydrolysis of **2o** and **3o** with concentrated hydrochloric acid [6] led to the known 1-amino-4-phenyl-5-methyl-*v*-triazole (**5**) and 1-amino-4-methyl-5-phenyl-*v*-triazole (**6**) respectively, which gave peaks for the methyl carbon at 8.9 (CH<sub>3</sub>-4) and 11.4 (CH<sub>3</sub>-5) ppm respectively, in agreement with the above assignments.



From the above data it is seen that the <sup>13</sup>C chemical shifts of the carbon atoms of the triazole ring C-4 and C-5, as well as the shifts of CH<sub>3</sub>-4 and CH<sub>3</sub>-5 can be used for the structural assignment of the 4,5-unsymmetrically substitu-

ted *v*-triazolyloisoimides. Thus, appearance of a peak at 119-122 ppm, which is split to a doublet in the off-resonance spectrum indicates a 4-monosubstituted derivative, which in addition shows a peak for C-4 at 141-146 ppm. On the other hand, absence of a peak in the region of 141-146 ppm indicates the lack of a substituent in the 4-position of the ring. Furthermore, a peak at about 11 ppm indicates a 4-methyl derivative, whereas a peak at 7.5 to 9.5 ppm indicates a 5-methyl derivative. Moreover, the 4-aryl-5-methyl derivatives can be distinguished from their 4-methyl-5-aryl isomers, besides the difference in the shifts of the methyl carbons, from the shifts of C-4, which in the 4-aryl isomer should be found at 141-145 ppm, whereas in the 4-methyl isomer at 138-139 ppm.

The shifts of the aromatic carbons of the aryl group attached at the 4- or 5-position of the triazole ring have been determined after assigning all the carbons of the two aromatic rings A and B adjacent to the isoimido-moiety and by using substituent chemical shift additivities [10] of the substituents on the phenyl ring. The peak of C-1'' (5) in some cases was masked by other peaks, therefore it was assigned by analogy to other derivatives or from the off-resonance spectra.

Table 2

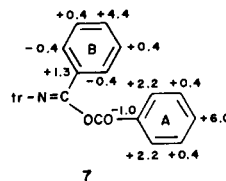
Chemical Shifts Induced by the Triazole Ring on the Carbons of the Phenyl Ring Attached to the 4- or 5-Position, Relative to the Benzene Carbon Shift, Taken at 128.5 ppm [10] Downfield from TMS  
 $\Delta_{C_i} = \delta_{C_i} - 128.5$  ppm

Compound	$\Delta_{C_i}$ ppm			
	C-1''	C-2'' C-6''	C-3'' C-5''	C-4''
<b>2i</b>	1.6	-2.8	0.4	-0.1
<b>2k</b>	1.8	-2.9	0.3	-0.3
<b>2o</b>	3.0	-1.5	0.3	-0.7
<b>2p</b>	2.8	-1.6	0.2	-0.6
<b>5</b>	3.0	-1.8	0.3	-0.8
<b>3o</b>	-1.6	1.3	0.0	0.3
<b>3p</b>	-1.8	1.3	0.0	0.4
<b>6</b>	-1.8	0.9	0.2	0.5

Concerning the shifts induced by the triazole ring on the carbons of the phenyl ring it is interesting to note their dependence on the position of the triazole ring at which the phenyl is attached (Table 2). Thus in the 4-phenyl derivatives **2i-k,o-p** C-1'' is shifted downfield of 1.6-3.0 ppm, whereas C-2'' and C-4'' are shifted upfield of 1.5-3 and 0.4 ppm respectively, in respect to the benzene carbon shift taken at 128.5 ppm [10]. The situation is reversed in the 5-phenyl derivatives **3o-p**, where C-1'' is shifted upfield of about 2 ppm, whereas C-2'' and C-4'' are shifted downfield of about 1.5 and 0.5 ppm respectively. The same behaviour has been found for the phenyl carbons of the compounds **5** and **6**. It should be noticed that the shift difference of C-1'' is similar to that found for the methyl carbons, where the one at the 4-position resonated at lower

field than that at the 5-position of the triazole ring. For C-2'' however the behaviour is analogous to the methyl protons in the <sup>1</sup>H nmr spectrum [3], where CH<sub>3</sub>-4 resonates at higher field ( $\delta = 2.4$ ) than CH<sub>3</sub>-5 ( $\delta = 2.6$ ).

Two sets of peaks belonging to the aromatic carbons of rings A and B were found in the aromatic region of the spectrum, *i.e.* between 127 and 135 ppm in the unsubstituted in the isoimido moiety compounds. Their differentiation has been made by correlation to the corresponding shifts of the monosubstituted isoimido derivatives, *i.e.* compounds **4a-c**, where ring B attached to the imino carbon bears a substituent to the *para* position, but ring A attached to the carbonyl carbon is unsubstituted. Substituent chemical shift additivities [10] as well as peak intensities have been used for the assignment of the individual carbons of each ring. The observed shifts are presented in Table 1. The chemical shifts induced by the isoimido-moiety on the carbons of the phenyl rings A and B relative to the benzene carbon shift,  $\Delta_{C_i} = \delta_{C_i} - 128.5$  ppm, for the compound **2a** are illustrated in 7. It is seen that the ipso-carbon is shielded by 1.0 ppm in ring A but deshielded by 1.3 ppm in ring B. The *ortho* carbons in ring A are deshielded by 2.2 ppm but shielded by 0.4 ppm in ring B. The *meta* and *para* carbons in both rings are deshielded by 0.4 and 4.4-6.0 ppm respectively.



The carbons of the isoimido group, *i.e.* C=O and C=N, showed two peaks of low intensity at about 162 and 152 ppm respectively. The assignment has been tentatively made on the assumption that the carbonyl carbon is likely to be found at lower field than the imino carbon. These values are in agreement with those reported for carbon atoms of other groups analogous to the isoimido function, such as the carbonyl carbon, which resonates at 167.3 ppm in methyl benzoate and at 162.8 and 163.6 ppm in benzoic acid and phthalic acid anhydrides respectively [11] and the imino carbon, which resonates at 157-163 ppm in aromatic imines [11-12], at 148-155 ppm in aromatic oximes [11,13] and at 153-156 ppm in aromatic imino ethers [11,13].

It should be mentioned that in the presence of a methoxy group at the *para* position of the rings A and B the signals of the *ipso* aromatic carbons, *i.e.* C-4 and C-4', could be confused with that of the carbonyl carbon. The same also holds for the imino carbon in the case of the *p*-nitro derivative **2f**. For the methoxy derivatives the assignments given in Table 1 have been made with the aid of the shift correlation diagram (Figure 1) and by comparison to the shifts found in **4b**. For the nitro derivative **2f** the assign-

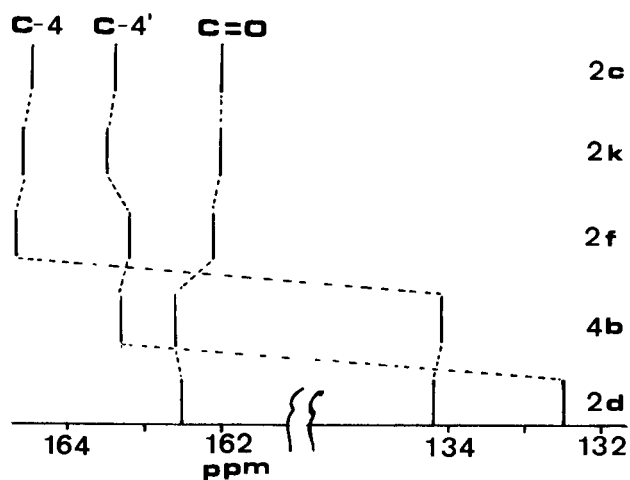


Figure 1. Shift correlation diagram of the C=O group and C-4 and C-4' of the compounds **2c-d, f, k** and **4b**.

ments of C-4, C-4' and C=N have been made by using the substituent chemical shift of the nitro-group found in *p*-nitrobenzylideneanilines, which is downfield of about 18 ppm for the *ipso* carbon and upfield of about 3 ppm for the imino-carbon [12]. According to these data, the shifts that would be expected in **2f** are  $134.2 + 18 = 152.2$  ppm for C-4,  $132.5 + 18 = 150.5$  ppm for C-4' and  $151.5 - 3 = 148.5$  ppm for C=N, which are very close to the shift values given in Table 1 for the corresponding carbons.

The observed carbon-proton coupling values involving C-4 and C-5 as well as CH<sub>3</sub>-4 and CH<sub>3</sub>-5 of some of the compounds under investigation are presented in Table 3. The <sup>1</sup>J, <sup>2</sup>J and <sup>3</sup>J of the carbon at the 5-position of the triazole ring have magnitudes larger than those corresponding to the carbon at the 4-position. The same also holds for the <sup>1</sup>J<sub>C-H</sub> of the methyl carbons attached at the 4- and

5-position of the triazole ring. Thus the one-bond coupling constant of CH<sub>3</sub>-5 was equal to 130.5 Hz whereas that of CH<sub>3</sub>-4 was equal to 128 Hz. The <sup>1</sup>J<sub>C5-H</sub> has also been found equal to 199.2 Hz in **2a** and ~197 Hz in the 4-methyl and 4-aryl substituted derivatives, **3b-c, 2k-l**, whereas the <sup>1</sup>J<sub>C4-H</sub> had a magnitude of 197.2 Hz in **2a** and of ~193.5 Hz in **2b-c**. The geminal coupling constants of C-5 <sup>2</sup>J<sub>C5-H</sub>, with H-4 and CH<sub>3</sub>-5 were found equal to 15.5 and ~7.5 Hz respectively, whereas those of C-4, <sup>2</sup>J<sub>C4-H</sub>, with H-5 and CH<sub>3</sub>-4 were found equal to ~10.5 and 6.8 Hz respectively. The vicinal coupling values of C-5 with CH<sub>3</sub>-4 in **3b-c** and of C-4 with CH<sub>3</sub>-5 in **2b-c**, <sup>3</sup>J<sub>CCCH</sub>, have been found equal to 4.2 and 3.5 Hz respectively. Although the difference between the two values is very small, it is clear that the C-5 couplings are larger than those of C-4.

It should be mentioned here that the same behaviour of C-5 over C-4 has been found for the <sup>1</sup>J<sub>CH</sub> and <sup>2</sup>J<sub>CCH</sub> in 1-methyl- and 1-acetyl-*v*-triazoles [8]. Thus the reported values for <sup>1</sup>J<sub>C5-H</sub> and <sup>1</sup>J<sub>C4-H</sub> are 196.6 and 194.3 Hz respectively in the 1-methyl-*v*-triazole and 198 and 195.4 Hz in the 1-acetyl-*v*-triazole. Moreover the reported [8] values for <sup>2</sup>J<sub>C5-H</sub> and <sup>2</sup>J<sub>C4-H</sub> are 15.4 and 10.3 Hz respectively in the 1-methyl- and 16.8 and 11.7 Hz respectively in the 1-acetyl derivative in good agreement with the findings in the compounds under study.

## EXPERIMENTAL

The <sup>13</sup>C nmr spectra were obtained at 40° with a Varian CFT 20 spectrometer operating in the Fourier transform mode at 20 MHz, using 10 mm diameter sample tubes. Solutions of 0.2-0.8 M in deuteriochloroform containing 0.5% TMS were employed with broad band proton noise decoupling. Accumulations of 2000-7000 transients were obtained depending on the concentration of the solution. A flip angle between 30-40° corresponding to a pulse width of 7.9 μseconds was applied. Decoupler field was centered at about 6 ppm high field from TMS in the off-resonance spectra.

1-( $\alpha$ -Aroyloxyarylideneamino)-*v*-triazoles **2** have been prepared in

Table 3

Carbon-Proton Coupling Constants, J<sub>C-H</sub>, in Hz, Extracted for the Carbons of the Triazole Ring C-4 and C-5 and for CH<sub>3</sub>-4 and CH<sub>3</sub>-5 of Some of the Compounds **2** and **3**

Compound	<sup>1</sup> J <sub>C-H</sub>				<sup>2</sup> J <sub>CCH</sub>		<sup>2</sup> J <sub>C-CH<sub>3</sub></sub>		<sup>3</sup> J <sub>CC-CH<sub>3</sub></sub>	
	C-4	C-5	CH <sub>3</sub> -4	CH <sub>3</sub> -5	C-4	C-5	C-4	C-5	C-4	C-5
<b>2a</b>	197.2	199.2	—	—	10.5	15.7	—	—	—	—
<b>2b</b>	193.6	—	—	130.7	—	15.0	—	7.5	3.6	—
<b>2c</b>	193.5	—	—	130.4	—	14.8	—	7.1	3.4	—
<b>3b</b>	—	197.0	128.5	—	10.0	—	6.8	—	—	4.1
<b>3c</b>	—	197.1	128.2	—	[a]	—	[a]	—	—	4.3
<b>2d</b>	—	—	128.1	130.1	—	—	≤7	[a]	~3.5	[a]
<b>2f</b>	—	—	127.8	130.0	—	—	[a]	[a]	[a]	[a]
<b>2k</b>	—	197.1	—	—	[a]	—	—	—	—	—
<b>2l</b>	—	197.0	—	—	[a]	—	—	—	—	—
<b>2r</b>	—	—	—	130.5	—	—	—	[a]	[a]	—
<b>3r</b>	—	—	128.7	—	—	—	[a]	—	—	[a]

[a] Not extracted couplings.

60-80% yields by oxidation with lead tetraacetate (LTA) of the corresponding bis-aryloxyhydrazones of  $\alpha$ -dicarbonyl compounds **1** as described in the literature [2,4]. The monosubstituted isomides **4a-c** were supplied by Dr. W. Kehrbach and their preparation has been described previously [14]. Compounds **5** and **6** have been obtained by hydrolysis of **2o** and **3o** respectively with concentrated hydrochloric acid [6].

The 4-methyl-5-aryl derivatives **3o-r**, which were formed at a yield of 10-15% on the oxidation of the corresponding bis-aryloxyhydrazones **1o-r**, have been isolated as mixtures with the 5-methyl-4-aryl isomers in a procedure that was as follows: the crude oxidation product obtained as described in the literature [2,4], was diluted in methylene chloride or in a methylene chloride-methanol mixture and allowed for crystallization. The first and the second fractions consisted of almost pure 5-methyl-4-aryl derivative **2o-r**. The third and the following fractions were mixtures of 5- and 4-methyl isomers **2o-r** and **3o-r**. Recrystallization of these fractions from methanol or ethanol yielded the 4-methyl-5-aryl derivative **3o-r** in a mixture with the 5-methyl-4-aryl isomer **2o-r** of about 95:5, (based on  $^1\text{H}$  nmr spectra). Compounds **3b-c** were isolated in the same manner, but in a 50:50 mixture with the compounds **2b-c**. Efforts for further purification failed. These samples were used for recording their  $^{13}\text{C}$  nmr spectra.

The spectral data, *i.e.* ir,  $^1\text{H}$  nmr and ms and the melting points of the samples used were in agreement to their structure and to that described in the literature [1-6].

Melting points and elemental analyses of the new compounds were as follows: **2a**, 92-93 $^\circ$ ; Calcd. for  $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2$ : C, 65.75; H, 4.13; N, 19.17. Found: C, 65.88; H, 3.98; N, 19.46; **3o**, 155-157 $^\circ$ ; Calcd. for  $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2$ : C, 72.24; H, 4.74; N, 14.65. Found: C, 71.99; H, 4.83; N, 14.72; **3p**, 165-166 $^\circ$ ; Calcd. for  $\text{C}_{23}\text{H}_{16}\text{Cl}_2\text{N}_4\text{O}_2$ : C, 61.21; H, 3.57; N, 12.41. Found: C, 61.23; H, 3.51; N, 12.24; **3q**, 138-146 $^\circ$  [15]; Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_3$ : C, 69.89; H, 4.89; N, 13.59. Found: C, 69.36; H, 4.89; N, 13.37; **3r**, 146-149 $^\circ$ ; Calcd. for  $\text{C}_{23}\text{H}_{17}\text{BrN}_4\text{O}_2$ : C, 59.88; H, 3.71; N, 12.14. Found: C, 59.83; H, 3.70; N, 12.18.

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- [15] It was not possible to obtain compound **3q** in pure form, even after using chromatographic methods, but as a 95:5 mixture with its 4-aryl-5-methyl isomer **2q**, therefore the large difference in its melting point.