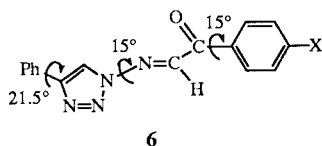


The reactivity and the regioselectivity of the cycloaddition of **1** with diphenylnitrilimine were examined on the basis of CNDO/2 calculations [5] carried out on the compounds **1** and on existing data for the frontier molecular orbitals of diphenylnitrilimine [6]. For the computations the conformation **6** was considered on the basis of existing experimental data, whereas for some bond lengths and angles standard values were used [7]. The FMO energy values and the orbital coefficients of the atoms of C=N bond are given in the Table.



6

Thus, for the reaction of **1a** with diphenylnitrilimine, for which the values $E_{HOMO} = -7.5$ eV and $E_{LUMO} = -0.5$ eV were proposed [6], it is found that the cycloaddition is $HOMO_{(dipole)}$ controlled, the corresponding energy difference ΔE being equal to $\Delta E = E_{LUMO(1a)} - E_{HOMO(dipole)} = 1.42 - (-7.5) = 8.92$ eV. For the $LUMO_{(dipole)}$ process the energy difference $\Delta E'$ is equal to $\Delta E' = E_{LUMO(dipole)} - E_{HOMO(1a)} = -0.5 - (-10.92) = 10.42$ eV and this value is higher than the previous one by 1.50 eV.

Table

HOMO-LUMO Energies and Orbital Coefficients of C=N Atoms for the Compounds **1** (Conformation **6**) from CNDO/2 Calculations

Compound	E_{HOMO}	E_{LUMO}	HOMO		LUMO	
			C_C	C_N	C_C	C_N
1c	-10.90	1.51	0.18	0.10	0.30	-0.39
1a	-10.92	1.42	0.18	0.10	0.29	-0.38
1b	-11.00	1.00	0.17	0.10	0.23	-0.33
1d	-10.92	0.02	0.16	0.08	0.10	-0.19
Diphenylnitrilimine (linear)						
	-7.5	-0.5	-0.53	0.85	0.77	0.46

In respect to the regioselectivity of the cycloaddition the predominant orbital interaction should be similar to that given in the Figure favoring the production of *2H*-1,2,3-triazoles **3**, since the $HOMO$ orbital coefficient on terminous nitrogen atom of diphenylnitrilimine in its linear structure [6] is higher than the coefficient on the carbon atom. Thus, the terminous nitrogen is preferentially combined with the nitrogen atom of the C=N bond having higher orbital coefficient in $LUMO$ (Table). Comparing the reactivity in

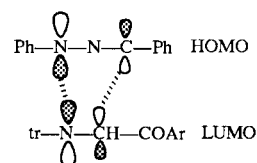


Figure. HOMO-LUMO interaction between diphenylnitrilimine and compounds **1**.

the cycloaddition of diphenylnitrilimine to arylideneamino- [2] and phenacylideneamino-1,2,3-triazoles **1a** it is found that the corresponding energy difference for $HOMO_{(dipole)}$ process of these two cycloadditions is 9.7 and 8.9 eV respectively, suggesting a higher reactivity of **1a** with the diphenylnitrilimine in agreement with the experimental results.

The compounds **2** and **3** exhibit in ir carbonyl absorptions at 1645-1660 cm^{-1} , whereas in the mass spectra give ion peaks corresponding to $M1^+$, $M-291^+$, $M-Ar1^+$, $PhCN-NPh1^+$, $PhCNI^+$, $ArCO1^+$ and $PhNI^+$. In the 1H nmr spectra compounds **2** and **3** give multiplets in the aromatic region ($\delta = 7.0-8.5$ ppm), as expected. Particularly, the *o*-protons of the Ar-CO and Ph-C groups of both compounds appear at $\delta = 8.1-8.4$ ppm, whereas the *o*-protons of the Ph-N group in compounds **2** appear at $\delta 7.4-7.6$ ppm and in compounds **3** at $\delta = 7.8-8.0$, and this can be used for the differentiation between the two isomers.

Their characterization, however, was mainly based on the ^{13}C nmr spectra, where, except of the peaks of the aromatic carbon atoms, compounds **2** give two signals for the C-3 and C-5 carbons of the 1,2,4-triazole ring at $\delta 161.5$ and 150.5 ppm respectively, whereas in compound **3c** the two carbons of the *2H*-1,2,3-triazole ring ArCO-C and Ar-C appear at $\delta = 143.3$ and 150.0 ppm, respectively. Similar resonance signals were previously reported for the carbons of the 1,2,4- and *2H*-1,2,3-triazole rings [2,8].

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The ir spectra were recorded as nujol mulls on Perkin-Elmer 297 spectrometer. The 1H nmr spectra were obtained with a Bruker AW 80 spectrometer (80 MHz) and the ^{13}C nmr spectra were obtained with 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 high resolution mass measurements were obtained with an AEI MS 30 mass spectrometer. Elemental microanalyses were performed with a Perkin-Elmer 240B CHN analyser. Column chromatography separations were performed over Merk Kieselgel 60, particle size 0.063-0.200mm.

Preparation of Compounds **1**.

These were prepared by condensation of the 1-amino-4-phenyl-

1,2,3-triazole (1 mmole) with an excess (2 mmoles) of the appropriate arylglyoxals as described previously [2,9] and they were recrystallized from ethanol.

1-(*N*-Phenacylidene)amino-4-phenyl-1,2,3-triazole (**1a**).

This compound was obtained in 72% yield, mp 120-121°; ir: ν C=O 1650 cm^{-1} ; ^1H nmr: δ 9.32 (1H, s, CH=N), 8.12 (1H, s, H-5tr), 8.10-8.25 (2H, m), 7.80-7.95 (2H, m), 7.36-7.70 (6H, m); ^{13}C nmr: 187.78 (C=O), 150.17 (CH=N, $^1J_{\text{CH}} = 175.6$ Hz), 148.41 (C-4tr), 120.57 (C-5tr, $^1J_{\text{CH}} = 198.3$ Hz); aroyl-carbons: 134.94 (C-*ipso*), 130.10 (C-*o*), 129.01 (C-*m*), 134.45 (C-*p*); phenyl-carbons: 129.57 (C-*ipso*), 125.77 (C-*o*), 128.87 (C-*m*, C-*p*); ms: m/z (%) 276 (M^+ , 1.2), 248 (M^+ -28, 1.5), 220 (18), 145 (18), 105 (73), 102 (100).

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}$: C, 69.55; H, 4.38; N, 20.28. Found: C, 69.53; H, 4.08; N, 20.10.

1-(*N*-*p*-Chlorophenacylidene)amino-4-phenyl-1,2,3-triazole (**1b**).

This compound was obtained in 80% yield, mp 149-151°; ir: ν C=O 1675 cm^{-1} ; ^1H nmr: δ 9.25 (1H, s, CH=N), 8.11 (1H, s, H-5tr), 8.14 (2H, d, $J = 8.5$ Hz), 7.80-7.95 (2H, m), 7.52 (2H, d, $J = 8.5$ Hz), 7.38-7.55 (3H, m); ^{13}C nmr: 186.71 (C=O), 149.93 (CH=N, $^1J_{\text{CH}} = 175.8$ Hz), 148.51 (C-4tr), 120.09 (C-5tr, $^1J = 199.0$ Hz); aroyl-carbons: 133.17 (C-*ipso*), 131.51 (C-*o*), 129.18 (C-*m*), 141.14 (C-*p*); phenyl-carbons: 129.41 (C-*ipso*), 125.76 (C-*o*), 129.0 (C-*m*, C-*p*); ms: m/z (%) 312/310 (M^+ , 0.2), 284/282 (M^+ -28, 0.3), 256/254 (6), 145 (6), 141/139 (35), 102 (100).

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{ClN}_4\text{O}$: C, 61.84; H, 3.57; N, 18.03. Found: C, 61.97; H, 3.52; N, 17.89.

1-(*N*-*p*-Methoxyphenacylidene)amino-4-phenyl-1,2,3-triazole (**1c**).

This compound was obtained in 80% yield, mp 112-113°; ir: ν C=O 1625 cm^{-1} ; ^1H nmr: δ 9.30 (1H, s, CH=N), 8.12 (1H, s, H-5tr), 8.20 (2H, d, $J = 9.0$ Hz), 7.76-7.95 (2H, m), 7.38-7.54 (3H, m), 7.02 (2H, d, $J = 9.0$ Hz), 3.9 (3H, s, CH_3O); ^{13}C nmr: 185.63 (C=O), 150.57 (CH=N, $^1J_{\text{CH}} = 174.1$ Hz), 148.28 (C-4tr), 120.02 (C-5tr, $^1J_{\text{CH}} = 198.3$ Hz), 55.65 (CH_3O , $^1J_{\text{CH}} = 144.9$ Hz); aroyl-carbons: 127.97 (C-*ipso*), 132.58 (C-*o*), 114.23 (C-*m*), 164.83 (C-*p*); phenyl-carbons: 129.63 (C-*ipso*), 125.93 (C-*o*), 128.98 (C-*m*), 128.86 (C-*p*); ms: m/z (%) 306 (M^+ , 0.3), 278 (M^+ -28, 0.3), 250 (2.3), 145 (16), 135 (100), 102 (61).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_2$: C, 66.66; H, 4.61; N, 18.29. Found: C, 66.48; H, 4.66; N, 18.17.

1-(*N*-*p*-Nitrophenacylidene)amino-4-phenyl-1,2,3-triazole (**1d**).

This compound was obtained in 95% yield, mp 181-183°; ir: ν C=O 1675 cm^{-1} ; ^1H nmr: δ 9.23 (1H, s, CH=N), 8.35 (4H, s), 8.11 (1H, s, H-5tr), 7.80-7.93 (2H, m), 7.38-7.53 (3H, m); ^{13}C nmr (DMSO- d_6): 187.64 (C=O), 150.77 (CH=N, $^1J_{\text{CH}} = 178.8$ Hz), 147.16 (C-4tr), 118.66 (C-5tr, $^1J_{\text{CH}} = 201.5$ Hz); aroyl-carbons: 139.70 (C-*ipso*), 131.35 (C-*o*), 123.54 (C-*m*), 150.21 (C-*p*); phenyl-carbons: 129.59 (C-*ipso*), 125.34 (C-*o*), 128.94 (C-*m*), 128.78 (C-*p*); ms: m/z (%) 321 (M^+ , 0.1), 293 (M^+ -28, 0.5), 266 (1.7), 150 (2.7), 145 (2.3), 102 (100).

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{N}_5\text{O}_3$: C, 59.81; H, 3.45; N, 21.80. Found: C, 60.03; H, 3.51; N, 21.70.

Reaction of Compounds **1** with Diphenylnitrilimine.

General Procedure.

To a stirred solution of compound **1** (0.5 mmole) and *N*-phenylbenzohydrazonoyl chloride [2] (1 mmole) in THF (3 ml) triethylamine (1 mmole) was added at once. The reaction mixture was

refluxed for 3-20 hours and the precipitated triethylammonium chloride was filtered off. The filtrate was evaporated and the residue was chromatographed on a silica gel column with a mixture of *n*-hexane:ethyl acetate (from 9:1 to 1:1) as eluant to give compounds **3**, **2**, **4** and **5**, in order as they eluted from the column.

Reaction of 1-(*N*-Phenacylidene)amino-4-phenyl-1,2,3-triazole (**1a**) with Diphenylnitrilimine.

From this reaction, after refluxing for 8 hours, the following compounds were isolated:

a: 2,4-Diphenyl-5-benzoyl-2*H*-1,2,3-triazole (**3a**).

This compound was obtained in 3% yield, mp 110-112°; ir: ν C=O 1655; ^1H nmr: δ 8.09-8.24 (4H, m), 7.85-7.98 (2H, m, H-*o* of Ph-N), 7.37-7.63 (9H, m); ms: m/z (%) 325 (M^+ , 99), 296 (M^+ -29, 2), 248 (10), 220 (3), 194 (5), 105 (100), 103 (15), 91 (21).

Exact mass. Calcd. for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}$: m/z 325.1215. Found: m/z 325.1243.

b: 1,3-Diphenyl-5-benzoyl-1,2,4-triazole (**2a**).

This compound was obtained in 71% yield, mp 134-136°; ir: ν C=O 1650 cm^{-1} ; ^1H nmr: δ 8.17-8.37 (4H, m), 7.39-7.67 (11H, m); ^{13}C nmr: 183.44 (C=O), 161.51 (C-3tr), 150.38 (C-5tr); aroyl-carbons: 135.45 (C-*ipso*), 130.96 (C-*o*), 128.66 (C-*m*), 134.35 (C-*p*); C-phenyl-carbons: 130.10 (C-*ipso*), 126.76 (C-*o*), 129.18 (C-*m*), 129.82 (C-*p*); *N*-phenyl-carbons: 137.99 (C-*ipso*), 124.94 (C-*o*), 128.66 (C-*m*), 129.18 (C-*p*); ms: m/z (%) 325 (M^+ , 100), 296 (M^+ -29, 46), 248 (3), 220 (2), 194 (19), 105 (18), 103 (2), 91 (59).

Anal. Calcd. for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}$: C, 77.52; H, 4.65; N, 12.91. Found: C, 77.33; H, 4.79; N, 13.08.

c: 4(5)-Phenyl-1,2,3-triazole (**4**).

This compound was isolated in 75% yield, mp 145-147°, with spectroscopic data identical to that of an authentic sample [2].

d: *N*¹-Phenyl-*N*²-benzoylbenzoic Acid Hydrazide (**5a**).

This compound was obtained in 19% yield, mp 177-178°, (lit [10] 176-177°); ir: ν NH 3190, ν C=O 1690, 1680 cm^{-1} ; ms: m/z (%) 316 (M^+ , 11), 194 (5), 149 (9), 105 (100).

In a test experiment a mixture of compound **1a** (0.5 mmole) and triethylamine (0.1 mmole) in THF (4 ml) was refluxed for 2 hours. From the reaction mixture, after treating as above, compound **4** was isolated in 85% yield as well as other unidentified products.

Reaction of 1-(*N*-*p*-Chlorophenacylidene)amino-1,2,3-triazole (**1b**) with Diphenylnitrilimine.

From this reaction after refluxing for 20 hours the following compounds were isolated:

a: 2,4-Diphenyl-5-(*p*-chlorobenzoyl)-2*H*-1,2,3-triazole (**3b**).

This compound was obtained in 6% yield, mp 167-168°; ir: ν C=O 1665 cm^{-1} ; ^1H nmr: δ 8.12 (2H, d, $J = 8.5$ Hz), 8.07-8.24 (2H, m), 7.85-7.98 (2H, m, H-*o* of Ph-N), 7.38-7.56 (8H, m); ms: m/z (%) 361/359 (M^+ , 73), 332/330 (M^+ -29, 2.5), 248 (9), 194 (9), 141/139 (100), 113/111 (55), 103 (7), 91 (50).

Exact mass. Calcd. for $\text{C}_{21}\text{H}_{14}\text{ClN}_3\text{O}$: m/z 359.0825. Found: m/z 359.0847.

b: 1,3-Diphenyl-5-(*p*-chlorobenzoyl)-1,2,4-triazole (**2b**).

This compound was obtained in 56% yield, mp 154-156°; ir: ν C=O 1660 cm^{-1} ; ^1H nmr: δ 8.30 (2H, d, $J = 8.5$ Hz), 8.16-8.24

(2H, m), 7.40-7.56 (10H, m); ^{13}C nmr: 181.84 (C=O), 161.58 (C-3tr), 150.00 (C-5tr); aroyl-carbons: 133.85 (C-*ipso*), 132.42 (C-*o*), 129.01 (C-*m*), 141.17 (C-*p*); C-phenyl-carbons: 130.19 (C-*ipso*), 126.73 (C-*o*), 129.21 (C-*m*), 129.40 (C-*p*); N-phenyl-carbons: 138.04 (C-*ipso*), 125.10 (C-*o*), 128.72 (C-*m*), 129.94 (C-*p*); ms: m/z (%) 361/359 (M^+ , 75), 332/330 (M^+ -29, 27), 248 (0.7), 220 (1.5), 194 (20), 141/139 (25), 103 (8), 91 (100).

Anal. Calcd. for $\text{C}_{22}\text{H}_{14}\text{ClN}_3\text{O}$: C, 70.10; H, 3.92; N, 11.68. Found: C, 69.83; H, 3.95; N, 11.74.

c: Compound **4** was obtained in 62% yield.

Reaction of 1-(*N-p*-Methoxyphenacylidene)amino-1,2,3-triazole (**1e**) with Diphenylnitrilimine.

From this reaction after refluxing for 20 hours the following compounds were isolated:

a: 2,4-Diphenyl-5-(*p*-methoxybenzoyl)-2H-1,2,3-triazole (**3c**).

This compound was obtained in 28% yield, mp 147-148°; ir: ν C=O 1645 cm^{-1} ; ^1H nmr: δ 8.10-8.25 (4H, m), 7.82-7.98 (2H, m, H-*o* of Ph-N), 7.35-7.62 (6H, m), 6.97 (2H, d, J = 9.0 Hz), 3.85 (3H, s, CH_3O); ^{13}C nmr: 186.35 (C=O), 150.03 (C-4tr), 143.34 (C-5tr), 55.33 (CH_3O); aroyl-carbons: 129.59 (C-*ipso*), 133.02 (C-*o*), 113.74 (C-*m*), 164.08 (C-*p*); C-phenyl-carbons: 130.08 (C-*ipso*), 128.44 (C-*o*), 128.72 (C-*m*), 128.25 (C-*p*); N-phenyl-carbons: 139.39 (C-*ipso*), 119.29 (C-*o*), 129.40 (C-*m*), 129.24 (C-*p*); ms: m/z (%) 355 (M^+ , 51), 326 (M^+ -29, 5), 324 (21), 248 (3), 194 (2), 135 (100), 107 (18), 91 (27).

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.70; H, 4.90; N, 11.78.

b: 1,3-Diphenyl-5-(*p*-methoxybenzoyl)-1,2,4-triazole (**2c**).

This compound was obtained in 40% yield, mp 122-124°; ir: ν C=O 1645 cm^{-1} ; ^1H nmr: δ 8.29 (2H, d, J = 9.0 Hz), 8.17-8.32 (2H, m), 7.40-7.55 (8H, m), 6.98 (2H, d, J = 9.0 Hz), 3.85 (3H, s, CH_3O); ^{13}C nmr: 182.02 (C=O), 161.37 (C-3tr), 150.77 (C-5tr), 55.59 (CH_3O); aroyl-carbons: 128.51 (C-*ipso*), 133.50 (C-*o*), 114.05 (C-*m*), 164.83 (C-*p*); C-phenyl-carbons: 130.21 (C-*ipso*), 126.75 (C-*o*), 129.16 (C-*m*, C-*p*); N-phenyl-carbons: 138.02 (C-*ipso*), 124.81 (C-*o*), 128.67 (C-*m*), 129.76 (C-*p*); ms: m/z (%) 355 (M^+ , 43), 326 (M^+ -29, 73), 278 (5), 220 (2), 194 (10), 135 (67), 107 (20), 103 (10), 90 (90), 77 (100).

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.42; H, 4.97; N, 11.62.

c: Compound **4** was obtained in 55% yield.

d: *N*¹-Phenyl-*N*²-benzoyl-*p*-methoxybenzoic Acid Hydrazide (**5c**).

This compound was obtained in 9% yield, mp 195-196° [11]; ir: ν NH 3300, ν C=O 1680, 1650 cm^{-1} ; ms: m/z (%) 346 (M^+ , 5), 194 (8), 152 (8), 149 (12), 135 (100), 105 (21).

In a test experiment a mixture of compound **1c** (0.5 mmole) and triethylamine (0.1 mmole) in THF (4 ml) was refluxed for 2 hours. From the reaction mixture, after treating as above, the starting compound **1c** was recovered in 80% yield.

Reaction of 1-(*N-p*-Nitrophenacylidene)amino-1,2,3-triazole (**1d**) with Diphenylnitrilimine.

From this reaction, after refluxing for 3 hours, the following compounds were isolated:

a: 1,3-Diphenyl-5-(*p*-nitrobenzoyl)-1,2,4-triazole (**2d**).

This compound was obtained in 32% yield, mp 184-186°; ir: ν C=O 1655 cm^{-1} ; ^1H nmr: δ 8.60 (2H, d, J = 8.5 Hz), 8.35 (2H, d, J = 8.5 Hz), 8.15-8.32 (2H, m), 7.42-7.57 (8H, m); ms: m/z (%) 370 (M^+ , 20), 341 (M^+ -29, 3), 220 (5), 194 (11), 150 (26), 105 (100), 103 (15), 91 (50).

Anal. Calcd. for $\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_3$: C, 68.10; H, 3.81; N, 15.13. Found: C, 68.34; H, 3.72; N, 15.34.

b: *N*¹-Phenyl-*N*²-benzoyl-*p*-nitrobenzoic Acid Hydrazide (**5d**).

This compound was obtained in 11% yield, mp 160-162° (lit [10] 161-162°); ir: ν NH 3230, ν C=O 1685, 1650 cm^{-1} ; ms: m/z (%) 361 (M^+ , 12), 194 (28), 150 (15), 105 (100).

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