1,3-Dipolar Cycloadditions of 1-(*N*-Arylidene)amino-1,2,3-triazoles with Diphenylnitrilimine

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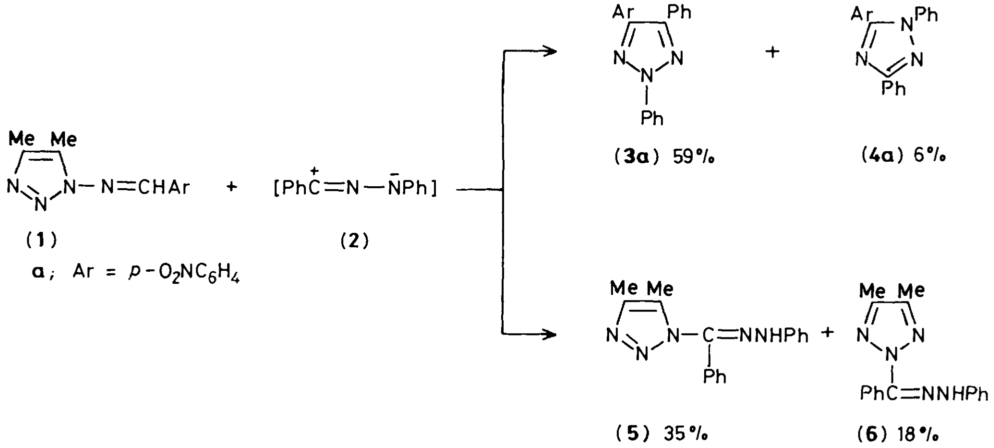
1-(*N*-Arylidene)amino-1,2,3-triazoles (**1**) and (**9**) react with diphenylnitrilimine (**2**) to give the corresponding 1,2,3- and 1,2,4-triazoles (**3**) and (**4**) as well as 1- and 2-benzohydrazonoyl-1,2,3-triazoles (**5**), (**10**) and (**6**) and (**11**) respectively. These products are formed assuming an initial cycloadduct, (**7**), which upon elimination of the triazole ring gives compounds (**3**) and (**4**). Further reaction of the triazole system with (**2**) gives the hydrazone derivatives (**5**), (**6**), (**10**), and (**11**). The reaction is also studied on the basis of frontier molecular orbitals (FMO) of the reacting species.

In an attempt to synthesize *N,N'*-linked 1,2,3-triazoles[1] such as (7), we attempted cycloadditions between the arylideneaminotriazoles (**1**) or (**9**) and diphenylnitrilimine. We found, however, that the C=N bond of these compounds was very unreactive to 1,3-cycloadditions, only the nitro derivatives (**1**) and (**9a**) reacting with diphenylnitrilimine (**2**) to give a variety of products (**3**)—(**6**) and (**10**)—(**11**), in satisfactory yields.

Results and Discussion

The reaction of arylideneaminotriazole (**1**) with diphenylnitrilimine (**2**), generated *in situ* by the action of triethylamine on *N*-phenylbenzohydrazonoyl chloride,[2] in a tetrahydrofuran–benzene (3:1) suspension, was carried out under reflux for *ca.* 50 h. From the reaction mixture, after column chromatography, two regioisomers, 1,2,3- and 1,2,4-triazoles (**3**) and (**4**) respectively, were isolated, as well as the corresponding 1- and 2-benzoyl-1,2,3-triazole phenylhydrazones (**5**) and (**6**) (Scheme 1).



Scheme 1.

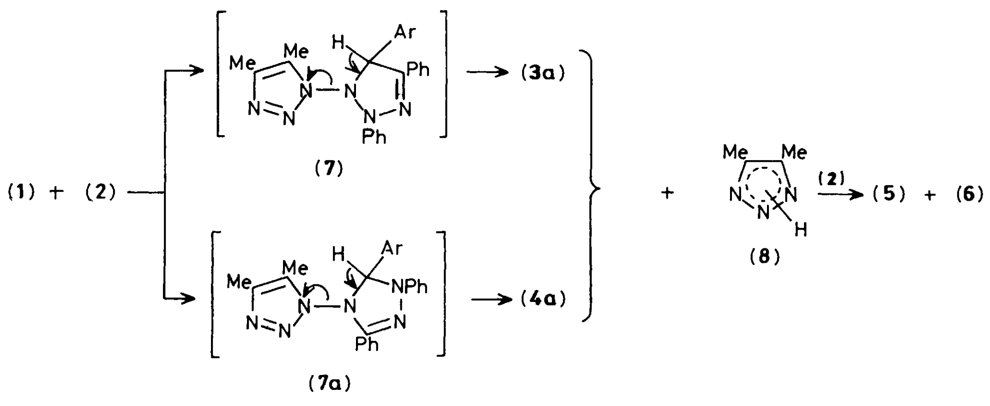
The formation of 2*H*-1,2,3-triazole (**3**) in much higher yield than the corresponding 1,2,4-regio isomer (**4**), which is usually the main product in cycloadditions[3] of (**2**) with nitriles[4] and azomethines,[5] as well as molecular orbital considerations discussed below, provide evidence that the reaction of (**1**) with (**2**) passes *via* an intermediate present in the two regio forms (**7**) and (**7a**). These upon cleavage of the N–N bond give the aromatized reaction products (**3**) and (**4**) respectively, whereas the triazole fragment (**8**) further reacts with (**2**) forming the two isomers (**5**) and (**6**) (Scheme 2). A similar N–N bond fragmentation was previously reported by Huisgen *et al.*[6]

The possibility of a previous elimination of the triazole ring from the Schiff base[7] before the formation of (7) or (**7a**) can be discounted since in test experiments the starting compound (**1**) was almost quantitatively recovered after a long period of heating in the presence of triethylamine.

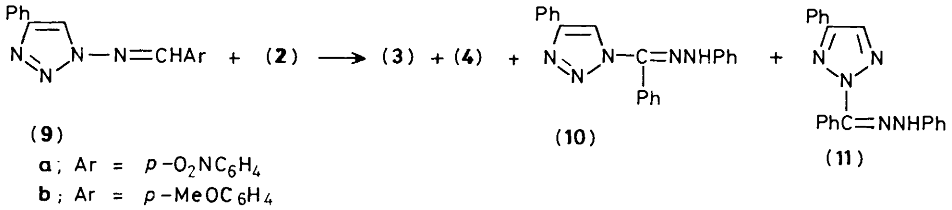
On the other hand, an independent addition of the triazole (**8**) with (**2**) gave the products (**5**) and (**6**) in 26 and 4% yields respectively. Other reactions similar to this have been previously reported.[8,9]

The intermediates (7) and (**7a**) were very unstable and attempts to isolate them were unsuccessful. It was, therefore, assumed that hydrogen replacement of the 5-methyl group in the starting compound (**1**) might increase the reactivity of the system and/or reduce the steric interaction in the initial cycloadducts (7),(**7a**) and hence might increase the possibility of their isolation.

The cycloadditions of (**9a-b**) with (**2**) carried out under the same experimental conditions as those shown in Scheme 1 afforded analogous reaction products (**3**), (**4**) and (**10**), (**11**) (Scheme 3) without isolation of the initial intermediate corresponding to (7). Compounds (**9**) were used rather than the

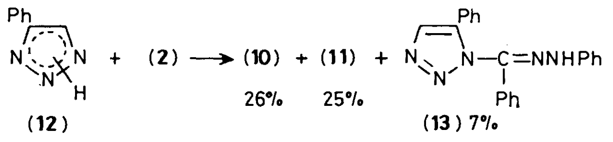


Scheme 2.



Scheme 3.

corresponding 4-methyl derivatives, because of their greater accessibility.[10] It is worth noting that reaction of the phenyltriazole (**12**) with (**2**) gave the three expected hydrazonotriazoles (**10**), (**11**), and (**13**) (Scheme 4).



Scheme 4.

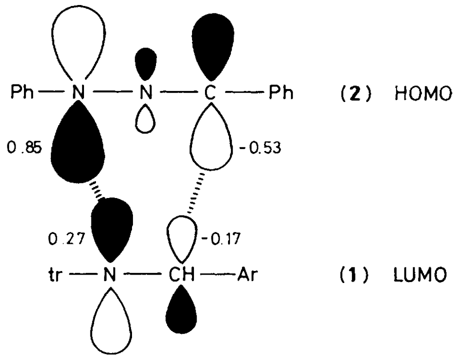


Figure. HOMO-LUMO Interaction between (**2**) and (**1**)

With regard to the regioselectivity of the initial cycloadduct and the reactivity of these Schiff bases with (**2**), it is useful to consider the FMO of the reacting species. On the basis of CNDO/2 calculations[11] carried out on the compounds (**1**) and (**9**) and using existing[3,12] data for the frontier orbitals of diphenylnitrilimine, it is concluded that the present cycloaddition in agreement with other previous findings,[2,3] including the cycloaddition of nitrilimines with electron-deficient dipolarophiles,[12,13] is HOMO$_{(dipole)}$ controlled. In the present system, therefore, the same electronic effect should be operated as in the latter since the electron-withdrawing triazole ring and *p*-nitrophenyl group greatly reduce the energy level of LUMO.

Using the reported[3,12] FMO energy values for diphenylnitrilimine ($E_{HOMO} = -7.5$ eV and $E_{LUMO} = -0.5$ eV) and the corresponding values[11] for (**1**) ($E_{HOMO} = -11.3$ eV and $E_{LUMO} = 0.3$ eV) it is found that the energy difference $\Delta E = E_{LUMO(1)} - E_{HOMO(dipole)}$ is equal to 7.8 eV. This value is smaller by 3 eV assuming that the reaction is LUMO$_{(dipole)}$ controlled [$\Delta E = E_{LUMO(dipole)} - E_{HOMO(1)} = -0.5 - (-11.3) = 10.8$ eV]. Thus, the HOMO$_{(dipole)}$ should be the orbital controlling the cycloaddition. That the energy difference ΔE for the unsubstituted derivative of (**1**; Ar = C_6H_5) for the same interaction [HOMO$_{(dipole)}$] is equal to 9.7 eV, and higher by *ca.* 2 eV than the energy difference for the nitro derivative (**1**), suggests that the last derivative (**1**) should be more reactive. If the reaction of the unsubstituted derivative (**1**; Ar = C_6H_5) with (**2**) were LUMO$_{(dipole)}$ controlled, then the energy difference ΔE should be higher and equal to 10.4 eV giving a higher $\Delta\Delta E$ value (2.6 eV) for the unsubstituted (**1**; Ar = C_6H_5) compound with the nitro derivative (**1**).

In agreement with this prediction, we found that the *p*-methoxy derivative of (**1**) fails to react with (**2**), even after a long period of heating. For this reason, the cycloaddition between (**1**) and (**2**) was the only reaction examined. The regioselectivity of this cycloaddition, which affects the formation of the regio triazoles (**3**) and (**4**), can be explained in terms of the orbital coefficients[11] for the HOMO$_{(dipole)}$ interaction.

In the reaction of (**1**) with (**2**) the major orbital interaction should be similar to that illustrated in the Figure, since the orbital coefficient on nitrogen in LUMO of the C=N bond is higher than the coefficient on the carbon atom ($C_N = 0.27$, $C_C = -0.17$), and this nitrogen is combined with the nitrogen atom of the dipole. The orbital coefficients of (**2**), in its planar structure, were taken to be[3] similar to those of formonitrilimine ($C_N = 0.85$, $C_C = -0.53$), since it is known that the phenyl groups on the dipole termini have little effect on the coefficients compared with those for the parent compound. From this interaction it is expected the 1,2,3-triazole (**3**) would be formed as the main reaction product.

In the cycloaddition of (**9a**) with (**2**), the LUMO orbital coefficients of the C=N bond have the values $C_N = 0.18$ and $C_C = -0.28$ which suggests that the 1,2,4-triazole should be the major isomer. Indeed, although the total yield for compounds (**3**) and (**4**), derived from the cycloadditions of (**1a**) and (**9a**) with (**2**) remains almost the same (*ca.* 60%), the yield ratio for two regio isomers (**3a**/**4a**) is shifted from *ca.* 10:1 to 1:1 respectively for these reactions. The difference in the yield ratio between these two reactions could be attributed to electronic effects as indicated by CNDO/2 calculations and ^{13}C n.m.r. data[11] for compounds (**1**) and (**9**). However, the operation of some steric interactions could not be excluded.

Thus, the reaction of (**2**) with the methoxy derivative (**9b**) proceeds very slowly and even after being heated for 70 h, only (**3b**) in 12% yield was isolated, *ca.* 50% of the starting compound (**3b**) remaining unchanged. The 1,2,3-triazole (**3a**) and the 1,2,4-triazoles (**4a,b**) showed i.r. absorption at *ca.* 1 595 cm^{-1} (C=N of the triazole ring) and in their ^{1}H n.m.r. spectra the expected aromatic signals.

More interesting are the mass spectra, which could also be used to differentiate between the isomeric compounds (**3**) and (**4**). Thus, compounds (**4a**—**b**) showed, besides the abundant molecular ion peak, a fragment ion at *m*/*z* 194 of strong intensity corresponding to a retro-cycloaddition, $\mathrm{PhC{\equiv}N{-}NPh}^{\rceil +\bullet}$, followed by a metastable peak. The base peak of the spectrum corresponds to the ion $\mathrm{PhN}^{+\bullet}$ at *m*/*z* 91 whereas compound (**3a**) gave the molecular ion as the base peak. Further splitting of the molecular ion gives mainly the ion $\mathrm{PhN}^{+\bullet}$ at *m*/*z* 91. The retro-cycloaddition fragments, $\mathrm{PhC{\equiv}N{-}NPh}^{\rceil +\bullet}$ and $\mathrm{ArC{\equiv}N{-}NPh}^{\rceil +\bullet}$, are also found in the mass spectrum but in low intensity. The most interesting fragment, however, is the low abundant ion $\overline{\mathrm{C(Ar){=}C(Ph)N}}^{+}$ which can be formed only from compound (**3a**). The structure of the hydrazonoyl triazoles (**5**), (**6**), (**10**), (**11**), and (**13**) was deduced on the basis of their spectroscopic and analytical data: all showed i.r. absorption at 3 180—3 280 (NH) and at 1 600 and 1 585 cm^{-1} (C=N).

In addition to signals in the aromatic region of its n.m.r. spectrum, compound (**5**) gave two signals for the 4-and 5-methyl groups (δ 2.04 and 2.20); in contrast compound (**6**) gave only one signal for the two methyl groups (δ 2.42). The 5-H triazole ring proton appeared at δ 7.82 (s) for compound (**10**) and at δ 8.16 for compound (**11**), whereas the 4-H triazole proton in (**13**) gave a signal at δ 8.07 (s).

In the ^{13}C n.m.r. spectra of compounds (**10**) and (**11**), C-5 of the triazole ring resonated at δ 120.07 ($^1J_{CH}$ 198 Hz) and δ 131.7 ($^1J_{CH}$ 193 Hz) respectively, in agreement with previous findings,[14] where C-5 carbon in 1-substituted 1,2,3-triazoles appears in the range δ 118—122.

The mass spectra of 1- and 2-substituted derivatives (**5**),(**10**), and (**6**),(**11**) respectively are very distinctive and can be used for their differentiation. Thus, compounds (**5**) and (**10**) eliminate N_2 from the molecular ion, which is diagnostic for the 1-substituted 1,2,3-triazole derivatives[10,15] the main peak being that of the PhNH^+ fragment at *m*/*z* 92, whereas compounds (**6**) and (**11**) gave as the main fragmentation the elimination of the diphenylnitrilimine fragment (*m*/*z* 194) which was the base peak of their spectrum. All the above ion peaks were secured by high resolution mass measurements.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 297 spectrometer. ^{1}H N.m.r. spectra were obtained on a Bruker WH 400 and on a Bruker AW 80 spectrometers and ^{13}C n.m.r. spectra were obtained on a Varian CFT-20 spectrometer, in $CDCl_3$ 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 performed on a Kratos MS 50 operated at 10 000 resolution power at exponential scan mode. Elemental microanalyses were performed with a Perkin-Elmer 240 B CNH analyser. Column chromatography was performed over Merck Kieselgel 60, particle size 0.063—0.200 mm. Ether refers to diethyl ether.

CNDO/2 *Calculations*.—The calculations of HOMO-LUMO state energies and the orbital coefficients of the compounds (**1**) and (**9**) were made by the CNDO/2 method (141 QCPE program), whereas the geometry used was based on existing *X*-ray data[11] for the 1,2,3-triazole ring and the benzylidene function.

Compounds (**1**).—These were prepared from the corresponding 1-amino-1,2,3-triazoles by condensation with the appropriate benzaldehydes as described previously.[10]

Diphenylnitrilimine (**2**).—This was prepared *in situ* by the action of triethylamine on *N*-phenylbenzohydrazonoyl chloride.[2,16]

4,5-*Dimethyl*-1,2,3-*triazole* (**8**) and 4(5)-*phenyl*-1,2,3-*triazole* (**12**).—These were prepared from the corresponding 1-amino-1,2,3-triazoles by deamination reaction[17] with HNO_2.

Reaction of 1-(N-*Arylidene*)*amino*-1,2,3-*triazoles* (**1**) *with Diphenylnitrilimine* (**2**): *General Procedure*.—To a stirred suspension of (**1**) (0.5 mmol) and *N*-phenylbenzohydrazonoyl chloride (1 mmol) in tetrahydrofuran (THF)–benzene (3:1; 2.5 ml) a solution of triethylamine (1 mmol) in the same solvent (1 ml) was added dropwise. The reaction mixture was kept under reflux until all the chloride had been consumed (t.l.c.). The precipitated triethylammonium chloride was filtered off, the filtrate evaporated, and the residue chromatographed on a silica gel column with ethyl acetate–hexane (b.p. 67—69 °C) of slowly increasing polarity as eluant.

Reaction of (**1a**) *with* (**2**).—To a suspension of compound (**1a**) (0.12 g, 0.5 mmol) and *N*-phenylbenzohydrazonoyl chloride (0.23 g, 1 mmol) in THF–benzene (3:1; 3 ml) a solution of Et_3N (0.28 ml) in the same solvent (1 ml) was added. After the mixture had been refluxed for 48 h it was treated as described above and the residue chromatographed on a silica gel column to give the following. (a) 5-(4′-*Nitrophenyl*)-2,4-*diphenyl*-2H-1,2,3-*triazole* (**3a**) (0.1 g, 59%), m.p. 176—178 °C (from ethanol) (Found: C, 70.1; H, 3.9; N, 16.1. $C_{20}H_{14}N_4O_2$ requires C, 70.17; H, 4.12; N, 16.36%); $\nu_{max.}$ 1 595 (C=N), 1 517, and 1 340 cm^{-1} (NO_2); δ_H(400 MHz), 8.22 (2 H, d, *J* 9 Hz), 8.12—8.25 (2 H, m), 7.83 (2 H, d, *J* 9 Hz), 7.57 (2 H, m), 7.50 (2 H, m), 7.43 (3 H, m), and 7.37 (1 H, m as t); δ_C (20 MHz, $CDCl_3$) 147.69, 146.81, 143.54 (C-4tr and C-5tr),* 139.44, 137.24, 130.11, 129.79, 129.37, 128.87, 128.60, 127.96, 123.86, and 118.89; *m*/*z* 342 (M^+, 100%), 312 (M^+ − 30, 3%), 296 (2.5%) 239 (0.5%), 237 (1%), 194 (2.2%), 193 (1%), 192 (1%), 191 (2.2%), 190 (2.5%), 165 (1.5%), 164 (2.5%), 148 (2.5%), 105 (2%), 103 (3%), 91 (52%), and 77 (11%).

(b) 5-(4′-*Nitrophenyl*)-1,3-*diphenyl*-1,2,4-*triazole* (**4a**) (0.01 g, 6%), m.p. 200—201 °C (from ether–hexane) (lit.,[4] 200.5—201 °C); $\nu_{max.}$ 1 597 (C=N), 1 520, and 1 340 cm^{-1} (NO_2); δ_H(400 MHz) 8.23 (2 H, m), 8.22 (2 H, d, *J* 9 Hz), 7.76 (2 H, d, *J* 9 Hz), and 7.40—7.52 (8 H, m); *m*/*z* 342 (M^+, 65%), 312 (M^+ − 30, 1%), 295 (1.5%), 239 (0.5%), 194 (37%), 167 (1.8%), 165 (1.5%),

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* Throughout tr refers to the triazole moiety.

164 (1%), 148 (0.8%), 105 (5%), 103 (5%), 91 (100%), and 77 (11%).

(c) 2-*Benzoyl*-4,5-*dimethyl*-2H-1,2,3-*triazole phenylhydrazone* (**6**) (0.025 g, 18%), yellow crystals, m.p. 109—110 °C (from ether–hexane) (Found: C, 70.0; H, 5.95; N, 24.1. $C_{17}H_{17}N_5$ requires C, 70.08; H, 5.88; N, 24.03%); $\nu_{max.}$ 3 280 (NH), 1 600 (C=N), and 1 580 cm^{-1}; δ_H(80 MHz), 10.5 (1 H, s, NH), 7.66 (2 H, m), 7.12—7.46 (7 H, m), 2.42 (6 H, s, CH_3) (Found: *m/z* 291.1484. $C_{17}H_{17}N_5$ requires *m/z* 291.1484); *m/z* 291 (M^+, 41), 194 (82%), 105 (9%), 104 (8%), 103 (5%), 91 (100%), and 77 (16%).

(d) 1-*Benzoyl*-4,5-*dimethyl*-1H-1,2,3-*triazole phenylhydrazone* (**5**) (0.05 g, 35%), m.p. 194—195 °C (from ethanol) (Found: *m/z* 291.1482. $C_{17}H_{17}N_5$ requires *m/z* 291.1484); $\nu_{max.}$ 3 180 (NH), 1 600 (C=N), and 1 580 cm^{-1}; δ_H(80 MHz), 8.10 (1 H, br s, NH), 6.84—7.40 (10 H, m), 2.20 (3 H, s, 5-Me), and 2.04 (3 H, s, 4-Me); *m/z* 291 (M^+, 18%), 263 ($M^+ - 28$, 12%), 236 (13%), 195 (28%), 171 (22%), 104 (36%), 92 (100%), and 77 (36%).

Reaction of (**9a**) *with* (**2**).—To a suspension of compound (**9a**) (0.15 g, 0.5 mmol) and *N*-phenylbenzohydrazonoyl chloride (0.23 g, 1 mmol) in a mixture of THF–benzene (3:1; 3 ml) a solution of Et_3N (0.28 ml, 2 mmol) in the same solvent was added. After being refluxed for 48 h the mixture was treated as above and the residue chromatographed on a silica gel column to give the following. (a) (**3a**) (0.055 g, 32%), m.p. 173—174 °C and (b) (**4a**) (0.045 g, 26%), m.p. 200—201 °C. Both (**3a**) and (**4**) were identical with that obtained from the previously described reaction of (**1a**) with (**2**).

(c) 2-*Benzoyl*-4-*phenyl*-2H-1,2,3-*triazole phenylhydrazone* (**11**) (0.04 g, 24%), yellow crystals, m.p. 133—134 °C (from ether–hexane) (Found: C, 74.45; H, 5.05; N, 20.65. $C_{21}H_{17}N_5$ requires C, 74.30; H, 5.05; N, 20.63%); $\nu_{max.}$ 3 250 (NH), 3 110, 1 600 (C=N), 1 585, and 1 580 cm^{-1}; δ_H(80 MHz), 10.52 (1 H, s, NH), 8.16 (1 H, s, 5tr-H), 7.65—7.97 (4 H, m), 7.16—7.56 (10 H, m), and 6.80—7.00 (1 H, m); δ_C 148.68 (C-4tr), 148.04 (C=N), 143.99, 133.99, 131.66 (C-5tr, $^1J_{CH}$ 193.4 Hz), 129.32, 129.19, 129.00, 128.16, 126.39, 121.03, and 113.53; *m/z* 339 (M^+, 40%), 194 (100%), 167 (3.5%), 165 (2%), 145 (4%), 104 (8%), 103 (7%), 91 (92%), 77 (18%).

(d) 1-*Benzoyl*-4-*phenyl*-1H-1,2,3-*triazole phenylhydrazone* (**10**) (0.065 g, 38%), m.p. 138—139 °C (from ether–hexane) (Found: C, 74.4; H, 5.25; N, 20.65. $C_{21}H_{17}N_5$ requires C, 74.30; H, 5.05; N, 20.63%); $\nu_{max.}$ 3 270 (NH), 3 100, 1 600 (C=N), and 1 580 cm^{-1}; δ_H(400 MHz) 8.12 (1 H, s, NH), 7.90 (1 H, s, 5tr-H), 7.87 (2 H, m as d), 7.58 (2 H, m), 7.37—7.48 (6 H, m), 7.33 (2 H, m as t), 7.23 (2 H, m as d), and 6.95 (1 H, m as t); δ_C 147 (C-4tr), 143.62, 133.23, 129.47, 129.35, 129.05, 126.82, 125.99, 121.48, and 120.07 (C-5tr, $^1J_{CH}$ 198.3 Hz), and 113.69; *m/z* 339 (M^+, 5%), 311 ($M^+ - 28$, 34%), 248 (5%), 234 (4%), 220 (18%), 219 (23%), 195 (14%), 194 (8%), 145 (5%), 116 (12%), 103 (32%), 92 (100%), and 77 (34%).

Reaction of (**9b**) *with* (**2**).—To a suspension of compound (**9b**) (0.140 g, 0.5 mmol) and *N*-phenylbenzohydrazonoyl chloride (0.23 g, 1 mmol) in THF (4 ml) a solution of Et_3N (0.28 ml, 3 mmol) in THF (3 ml) was added. After the mixture had been refluxed for 70 h and treated as above, the residue was chromatographed on a silica gel column to give the following.

(a) 1,3-*Diphenyl*-5-(4′-*methoxyphenyl*)-1,2,4-*triazole* (**4b**) (0.020 g, 12%), m.p. 105—106 °C (from ethanol) (lit.,[6] 107—108 °C); $\nu_{max.}$(KBr) 1 610, 1 595 (C=N), and 1 578 cm^{-1}; δ_H(80 MHz) 8.22 (2 H, m), 7.35—7.58 (10 H, m), 6.85 (2 H, d, *J* 9.2 Hz), and 3.80 (3 H, s, CH_3O); *m/z* 327 (M^+, 25%), 296 ($M^+ - 31$, 1%), 194 (27%), 167 (4%), 165 (3%), 133 (5%), 105 (10%), 103 (4%), 91 (100%), and 77 (20%).

(b) Compound (**11**) (0.025 g, 14%) as yellow crystals, m.p. 132—134 °C, identical with material obtained from the previous reaction of (**9a**) with (**2**).

(c) Compound (**10**) (0.01 g, 6%), m.p. 137—139 °C, identical with material obtained from the previous reaction of (**9a**) with (**2**).

(d) Compound (**9b**) (0.07 g, 50%), m.p. 155—157 °C, unchanged Schiff base.

Reaction of (**8**) *with* (**2**).—To a solution of compound (**8**) (0.097 g, 1 mmol) and *N*-phenylbenzohydrazonoyl chloride (0.23 g, 1 mmol) in THF (3 ml) a solution of Et_3N (0.28 ml, 0.2 mmol) in THF (3 ml) was added dropwise. After the mixture had been refluxed for 5 h the triethylammonium chloride was filtered off and the residue was chromatographed on a silica gel column to give the following. (a) Compound (**6**) (0.010 g, 3.5%) as yellow crystals, m.p. 108—110 °C (from hexane). (b) Compound (**5**) (0.075 g, 26%), m.p. 194—195 °C (from ethanol).

Both compounds were identical (i.r. ^{1}H n.m.r., and m.s.) with those obtained from the previously described reactions.

Reaction of (**12**) *with* (**2**).—To a solution of compound (**12**) (0.14 g, 1 mmol) and *N*-phenylbenzohydrazonoyl chloride (0.23 g, 1 mmol) in a mixture of THF–benzene (3:1; 3 ml) a solution of Et_3N in the same solvents (3 ml) was added. After the mixture had been refluxed for 24 h and treated as above the residue was chromatographed to give the following. (a) Compound (**11**) (0.085 g, 25%) as yellow crystals, m.p. 133—134 °C (from hexane–ethyl acetate).

(b) Compound (**10**) (0.090 g, 26%), m.p. 138—139 °C (from hexane–ethyl acetate).

Both (**10**) and (**11**) were identical (i.r. ^{1}H n.m.r and m.s.) with those obtained from the previously described reactions.

(c) 1-*Benzoyl*-5-*phenyl*-1H-1,2,3-*triazole phenylhydrazone* (**13**) (0.025 g, 7%), m.p. 166—167 °C (from ether–hexane) (Found: C, 74.55; H, 5.1; N, 20.8. $C_{21}H_{17}N_5$ requires C, 74.30; H, 5.05; N, 20.63%); $\nu_{max.}$ 3 150 (NH), 3 110, and 1 600 cm^{-1} (C=N); δ_H(80 MHz), 8.07 (s, 1 H, 4tr-H), 6.86—7.43 (m, 15 H), and 7.91 (br s, 1 H, NH); m/z 339 (M^+, 19%), 311 ($M^+ - 28$, 18%), 310 (12%), 298 (12%), 234 (5%), 220 (22%), 219 (8%), 195 (10%), 194 (23%), 180 (16%), 145 (21%), 116 (30%), 115 (30%), 105 (70%), 104 (94%), 103 (100%), 102 (45%), 93 (92%), 92 (85%), and 91 (75%).

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