REACTIVITY OF 1-ARYL-4-DIMETHYLAMINO-2-PHENYL-1,3-DIAZA-1,3-BUTADIENES TOWARDS DIENOPHILES, 1,3-DIPOLES AND CARBANIONS

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Abstract - The reactivity of 1-aryl-4-dimethylamino-2-phenyl-1,3-diaza-1,3-butadienes (**1**) towards dienophiles, 1,3-dipoles and C-nucleophiles was investigated. *N*-Phenylmethylene-benzenesulfonamide (**2**), phenylisocyanate (**6**), *C,N*-diphenylnitrone (**9**) and acylacetates (**10**) reacted with **1** giving quinazoline or pyrimidine derivatives. The possible mechanisms involved in products formation are discussed.

The usefulness of heterodienes in the synthesis of heterocyclic compounds (in particular natural products) through pericyclic reactions has been widely demonstrated.[1] Hetero Diels-Alder reactions with azadienes represent a good method to obtain six-membered heterocycles.[2]

As part of our interest concerning the synthesis of heterocyclic compounds through cycloaddition reactions of heterodienes,[3-5] we examined the reactivity of 1-aryl-4-dimethylamino-2-phenyl-1,3-diaza-1,3-butadienes (**1**) towards some different classes of compounds, with the intention of studying the effect of the dimethylamino group on the diazadiene reactivity.

In some previously papers, products (**1**) reacted with ketenes,[6-9] sulfene,[10] 2-oxazolin-5-ones[11] and α–nitrososty renes[12] affording pyrimidinones / azetidinones, dihydro-1,2,4-thiadiazines, pyrimidinones and cyclic nitrones respectively. With dienophiles as phenylketene,[6] haloketenes[7] or vinylketenes[8] and sulfene[10] **1** reacted according to a [4+2] cycloaddition giving dihydropyrimidinones and dihydro-1,2,4-thiadiazine-1,1-dioxides respectively. With diphenylketene,[6,9] for steric hindrance, the reaction follows a [2+2] cycloaddition between the ketene C=C double bond and the diazadiene N_1=C_2 double bond leading to an azetidinone derivative.

Finally a nucleophilic attack of the carbanionic form of 2-oxazolin-5-ones[11] on the zwitterionic form of 1,3-diaza-1,3-butadiene could be responsible of the tetrahydropyrimidinones formation, whereas an unusual [3+2] cycloaddition between α–nitrosostyrenes[12] and the N_1=C_2 double bond of the diazadiene was assumed to explain the nitrones formation.

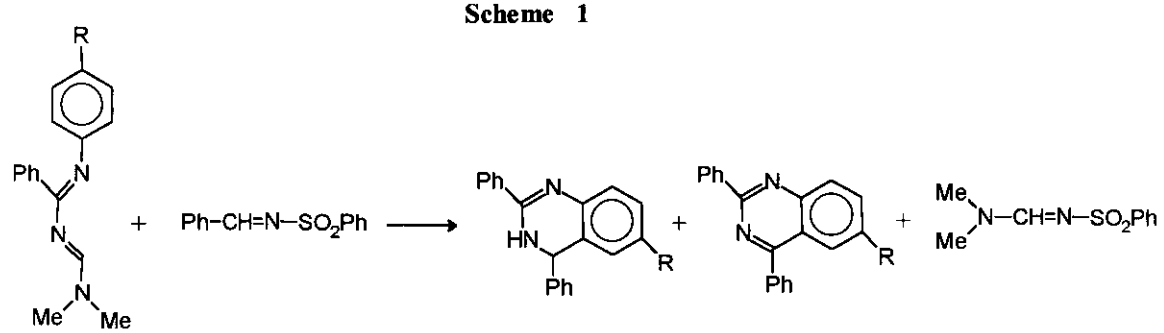
From these results it could be concluded that **1** follow an hetero Diels-Alder reaction with reactive dienophiles as ketenes and sulfenes when sterically possible, otherwise the N_1=C_2 double bond reacts preferentially following a [2+2] or a [3+2] cycloaddition .

To verify these conclusions and with the aim to synthetize new heterocyclic compounds, we studied the reactivity of 1,3-diaza-1,3-butadienes (**1a-c**)[13] towards others dienophiles, some 1,3-dipoles and *C*-nucleophiles. All reactions were performed in toluene solution, at reflux temperature and nitrogen atmosphere. 1,3-Diaza-1,3-butadienes (**1**) failed to react with electron-rich dienophiles as *N*-(1-cyclohexenyl)morpholine and ethyl vinyl ether confirming its character of electron rich diene due to the presence of the dimethylamino group. On the contrary **1a** reacted with dimethyl acetylenedicarboxylate and *N*-phenylmaleimide but unfortunately gave very complex mixtures from which none pure compound was isolated.

A positive result was obtained with an electron poor C=N dienophile, namely the *N*-phenylmethylene-benzenesulfonamide (**2**). As shown in Scheme 1, **1a-c** reacted with **2** giving a mixture of three products (**3**, **4** and **5**) which were separated by column chromatography and further purified by crystallization.

Analytical and spectroscopic data allowed to assign the structure of 2,4-diphenyl-3,4-dihydroquinazoline and 2,4-diphenyl-quinazoline respectively to **3** and **4**[14] and *N*-dimethylaminomethylenebenzenesulfonamide to **5**. Their identities were confirmed with literature data.

Scheme 1

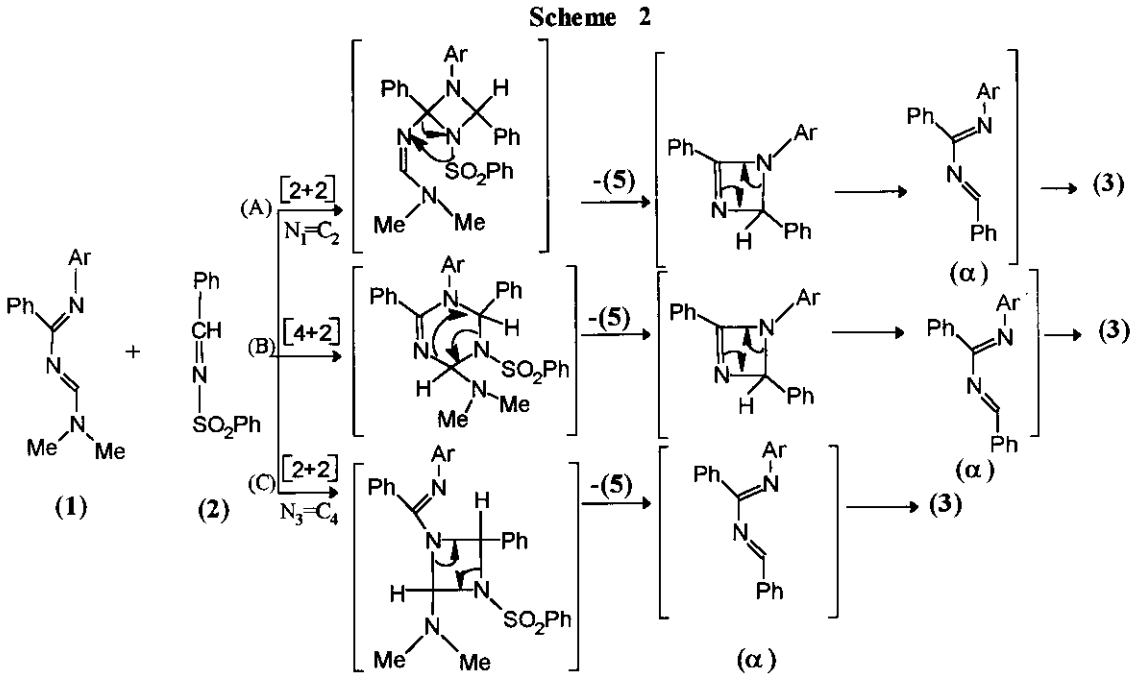


(1) **(2)** **(3)** **(4)** **(5)**

(1,3,4a) R = H
(1,3,4b) R = Me
(1,3,4c) R = NO_2

In Scheme 2 are depicted all the possible pathways to explain the formation of the products: a [4+2] (path B) or [2+2] cycloaddition between the N_1=C_2 (path A) or N_3=C_4 (path C) respectively and the dipolarophilic C=N double bond.

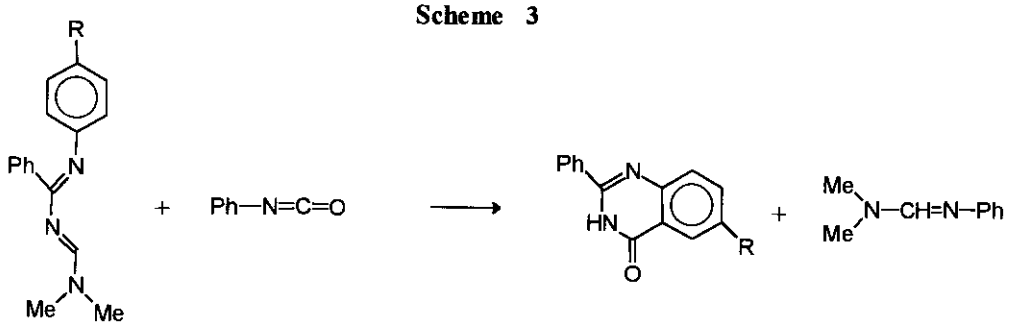
Scheme 2



In all cases the elimination of *N*-dimethylaminomethylenebenzenesulfonamide (**5**) from the primary cycloadduct lead to the intermediate 1-aryl-2,4-diphenyl-1,3-diaza-1,3-butadiene (α) which is known[15] to undergoes a 6π-electrocyclic ring closure followed by a [1,5] hydrogen shift with the formation of 3,4-dihydroquinazolines. In the attempt to isolate the primary cycloaddition adduct and to confirm the real mechanism, we repeated the reaction between **1a** and **2** at room temperature. In this case the reaction time was very long (50 days) but it was not possible to isolate the reaction intermediate: product (**5**) was obtained with 91% yield and products (**3**) and (**4**) with a total yield of only 10%. This result and the isolation of the 1,2,4,6-tetraphenyl-1,2-dihydro-1,3,5-triazine can be explained with the formation of intermediate (α) which, analogously to other 1,3-diaza-1,3-butadienes,[16] reacts at room temperature with *N*-phenylbenzamidine giving an azatriene which cyclizes to 1,3,5-triazine. In conclusion it was not possible to determine the true mechanism leading to the observed products. We consider the path C is the most probable because it allows to obtain the intermediate (α) directly from the primary adduct, even if it is not possible to exclude completely path B.[17]

Another reactive dienophile tested was phenylisocyanate (**6**) (Scheme 3): **1a-c** reacted with **6** giving a mixture of products (**7**) and (**8**) ; the last was isolated by distillation of the reaction mixture whereas products (**7a-c**) were purified by column chromatography of the distillation residue.

Scheme 3

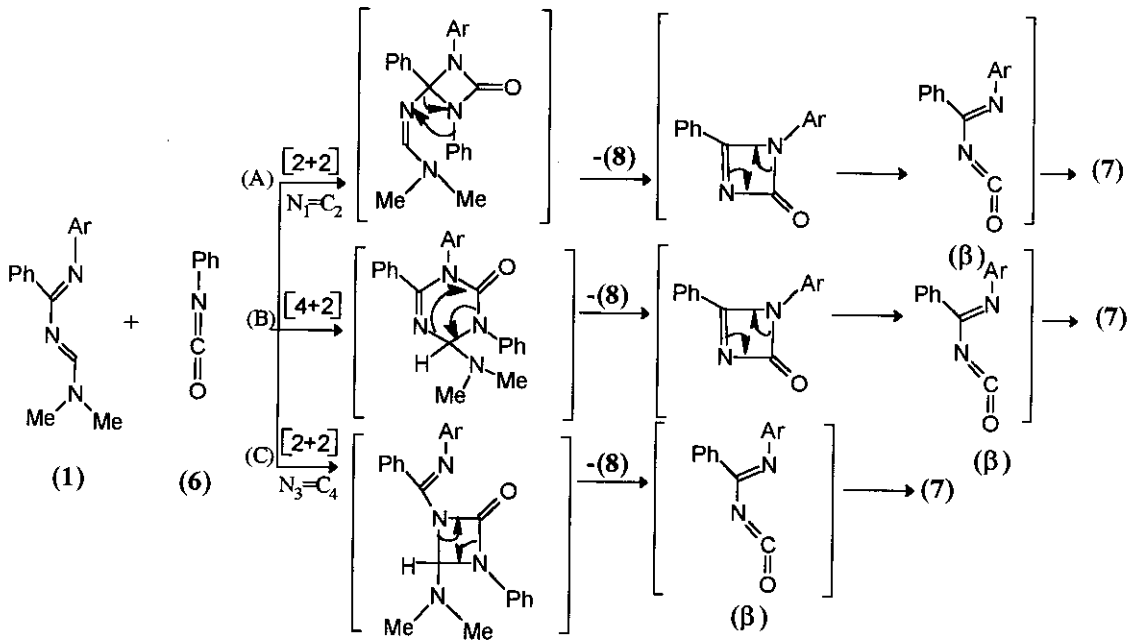


(1) (6) (7) (8)

(1,7a) R = H
(1,7b) R = Me
(1,7c) R = NO_2

The structures of 2-phenyl-3,4-dihydro-quinazolin-4-ones and *N,N*-dimethyl-*N'*-phenylformamidine were assigned to products **(7)** and **(8)** respectively on the basis of their analytical and spectroscopic data and further confirmed with literature data. The formation of products **(7)** and **(8)** can be explained according to Scheme 4.

Scheme 4



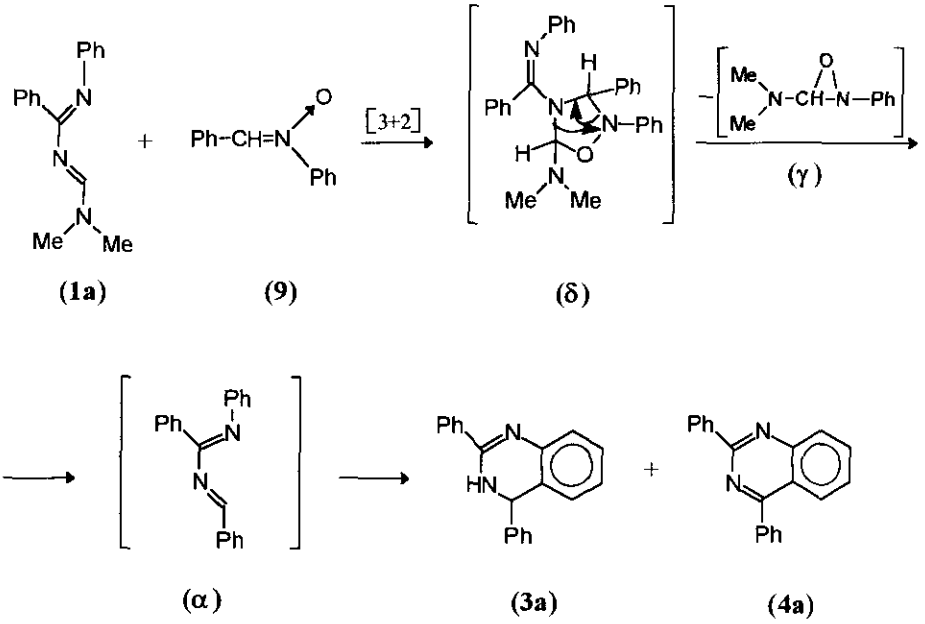
(1) (6) (β) (β)

Also in this case the elimination of *N,N*-dimethyl-*N'*-phenylformamidine **(8)** from the various primary cycloadducts leads to the same intermediate imidoylisocyanate (β) whose thermal cyclization to quinazolidinone is well documented.[18]

Also in this case it was not possible to isolate any primary adduct so to determine the reaction mechanism; reported examples of cycloaddition reactions between arylisocyanates and some other 1,3-diaza-1,3-butadienes show the formation of 1,3,5-triazinones through a [4+2] cycloaddition,[19] but in our case it is not possible to exclude completely path C.

Successively we examined the reactivity of 1,3-diaza-1,3-butadienes (**1**) towards some 1,3-dipoles . Compound (**1a**) reacted with *C,N*-diphenylnitrone (**9**) (Scheme 5) giving a mixture of the same products (**3a**) and (**4a**) obtained in the reaction with the *N*-phenylmethylenebenzenesulfonamide (**2**). Beside these products we assumed the formation of 3-dimethylamino-2-phenyloxaziridine (γ) (or the corresponding nitrone derived from the thermal isomerization of (γ)). In fact only a [3+2] cycloaddition of the 1,3-dipole with the N_3=C_4 double bond of diazadiene (**1a**) accounts for the obtained products.

Scheme 5



The intermediate 1,2,4-oxadiazolidine (δ) rearranges to (γ) and the diazadiene (α) which cyclizes affording **3a**.[20] As it was not possible to isolate product (γ), to demonstrate its formation we repeated the reaction in the presence of an equimolar quantity of triphenylphosphine: this is able to deoxygenate oxaziridines affording the corresponding imines and triphenylphosphinoxide.[21]

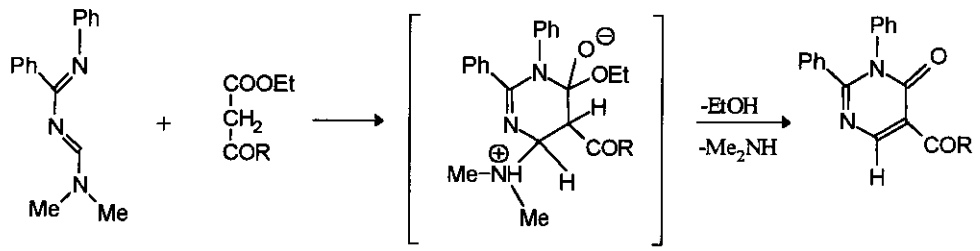
So the 3-dimethylamino-2-phenyloxaziridine (γ) could be transformed into the same *N,N*-dimethyl-*N'*-phenylformamidine (**8**) obtained in the reaction of **1** with phenylisocyanate (**6**). In fact the reaction of **1a** with **9** in the presence of triphenylphosphine led to a mixture of **3a**, **4a** and **8** beside an equimolar quantity of triphenylphosphinoxide.

This result is in contrast with the reported reactivity of 1,3-diaza-1,3-butadienes (**1**) with diphenylketene[6,9] and α-nitrosostyrenes[12] that react with the N_1=C_2 double bond. The increased polarization of the N_3=C_4 double bond due to the presence of the dimethylamino group, (important in cycloaddition reaction with dipoles as nitrones), together with the smaller steric hindrance offered from this double bond respect to the N_1=C_2 one, could be responsible of the observed regioselectivity.

Successively some other dipoles were tested towards **1**: 2,4-diphenyl-3-methylmunchnone, 3,4-diphenylsydnone and benzonitrile oxide did not react probably because they are, in the reaction conditions, less stable than nitrones.

Another class of compounds tested was that of *C*-nucleophiles. 1,3-Diaza-1,3-butadienes (**1**) did not react with sulfur ylides as dimethyl-phenacylsulfonium ylide or dimethylsulfoxonium methylide. On the contrary the reaction of **1a** with acylacetates (**10a,b**) afforded the 5-acyl-2,3-diphenyl-4(3*H*)-pyrimidinones (**11**) (Scheme 6).

Scheme 6



(1a) **(10)** **(ε)** **(11)**

(10,11a): R = Me
(10,11b): R = Ph

The structure of new products (**11**) was assigned on the basis of their analytical and spectroscopic data: in particular ^{1}H-NMR spectra show a singlet at 8.4-8.75 δ for H_6 proton in agreement with similar 4(3*H*)-pyrimidinones.[6a,8]

The carbanion generated from deprotonation of **10** by the dimethylamino group attacks the C_4 of **1a** leading to the zwitterionic adduct (ε) that loses a molecule of alcohol and of dimethylamine affording **11**. In this case the diazadiene (**1a**) reacts with a [4+2] cycloaddition likewise with the carbanionic form of 2-oxazolin-5-ones.[11]

In conclusion 1-aryl-4-dimethylamino-2-phenyl-1,3-diaza-1,3-butadienes (**1**) can react with electron poor dienophiles through a [4+2] or [2+2] cycloaddition giving not isolable intermediates that evolve to final quinazoline (**3**)/(**4**) or quinazolone (**7**) derivatives. The same quinazolines (**3**)/(**4**) are obtained with *C,N*-diphenylnitrone through a [3+2] cycloaddition reaction with the more reactive N_3=C_4 double bond.

Finally the new 5-acyl-2,3-diphenyl-4(3*H*)-pyrimidinones (**11**) can be obtained by reaction of **1** with acyl-acetates (**10**).

The presented study allowed to confirm the good reactivity of 1,3-diaza-1,3-butadienes (**1**) towards some classes of compounds both like 2π or 4π system. The presence of the electron-rich dimethylamino group affects the electronic distribution of this heterodiene and so its reactivity ; moreover it makes the primary cycloaddition adducts less stable owing to the easy elimination of dimethylamino group to give stable compounds such as **5** and **8**.

Table 1. Physical, Analytical and Spectroscopic Data of Compounds (**3**)-(**11**).

Compound	Yield (%)	mp (°C) (solvent)	^{1}H - NMR	Elemental Analysis (%) Found (Calcd) C	H	N
3a	55	159[24] (A)	1.6(s,1H,NH);5.9(s,1H,H_4); 6.8-7.8(m,14H,aromatics)	84.07 (84.51)	5.30 (5.63)	9.72 (9.86)
4a	21	118[25] (B)	7.5-8.7(m,aromatics)	84.95 (85.11)	4.66 (4.96)	9.71 (9.93)
3b	79	169[15] (A)	1.6(s,1H,NH);2.2(s,3H,Me); 5.8(s,1H,H_4);6.6(s,1H,H_5); 6.9-7.8(m,12H,aromatics)	84.01 (84.56)	5.90 (6.04)	9.15 (9.39)
4b	18	179[26] (B)	2.5(s,3H,Me);7.5-8.7(m,13H aromatics)	84.97 (85.13)	5.12 (5.40)	9.03 (9.45)
3c	25	195 (A)	1.5(s,1H,NH);6.0(s,1H,H_4); 7.4-8.2(m,13H,aromatics)	72.36 (72.95)	4.12 (4.55)	12.33 (12.76)
4c	25	240[27] (A)	7.5-9.1(m,aromatics)	73.19 (73.39)	3.66 (3.97)	12.51 (12.84)
5	89	130[28] (C)	3.0(s,3H,N-Me);3.1(s,3H, N-Me);7.4-7.5(m,3H,$H_{m,p}$); 7.9(d, J=7.5 Hz,2H,H_o);8.1 (s,1H,CH)	50.78 (50.94)	5.33 (5.66)	12.82 (13.20)
7a	84	240[18c] (C)	7.4-8.4(m,9H,aromatics); 11.3(s,1H,NH)	75.26 (75.66)	4.22 (4.50)	12.30 (12.60)
7b	88	235[29] (C)	2.5(s,3H,Me);7.5-8.4(m,8H, aromatics);11.4(s,1H,NH)	75.86 (76.27)	4.83 (5.08)	11.53 (11.86)
7c	70	300[30] (D)	7.5-8.3(m,8H,aromatics); 10.4(s,1H,NH)	62.66 (62.92)	3.05 (3.37)	15.21 (15.73)
8	73	liq[31]	3.0(s,6H,NMe_2);6.9-7.2(m, 5H,aromatics);7.5(s,1H,CH)	72.49 (72.97)	7.93 (8.10)	18.60 (18.91)
11a	47	142 (B)	2.7(s,3H,Me);7.1-7.4(m,10H aromatics);8.7(s,1H,H_6)	74.18 (74.48)	4.79 (4.82	9.43 (9.65)
11b	32	187 (C)	7.1-7.6(m,13H,aromatics); 7.9(d, J=7 Hz,2H,H_o); 8.4 (s,1H,H_6)	78.12 (78.40)	4.32 (4.54)	7.89 (7.95)

(A): toluene; (B): isopropanol; (C): ethanol; (D): 1,2-dichlorobenzene

EXPERIMENTAL

Melting points were measured with a Büchi apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer using $CDCl_3$ as solvent. Chemical shifts are expressed as δ values (ppm) from tetramethylsilane. J values are expressed in Hz. IR spectra were recorded on a Perkin Elmer 298 spectrophotometer and MS with a VG 7070 EQ-HF mass spectrometer. Compounds (**1a**),[13] (**1b**),[6a,13] (**2**),[22] and (**9**)[23] were prepared following the reported methods, and **6** and **10a,b** were commercial products.

4-Dimethylamino-1-(4-nitrophenyl)-2-phenyl-1,3-diaza-1,3-butadiene (**1c**) was prepared as reported for **1a,b**.[13] Yield : 75%; mp 123-124° C (cyclohexane). ^{1}H NMR : 2.95, 3.0 (2s, 6H, $N(CH_3)_2$); 6.95 (d, J=9.4 Hz, 2H, H_{meta} to the NO_2 group); 7.3-7.8 (m, 6H, aromatics + N=CH); 8.1 (d, J=9.4 Hz, 2H, H_{orto} to the NO_2 group).

Cycloaddition reactions of **1a-c** with *N*-phenylmethylenebenzenesulfonamide (**2**). General procedure.

A solution of **1a-c** (2 mmol) and **2** (0.49 g, 2 mmol) in 25 mL of dry toluene was heated at 110° C under nitrogen for 4 days. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with toluene/ethyl acetate=50/50 gave products (**3a-c**), (**4a-c**) and (**5**) (Table 1).

Cycloaddition reaction of **1a** with *N*-phenylmethylenebenzenesulfonamide (**2**) at room temperature.

A solution of **1a** (0.5 g, 2 mmol) and **2** (0.49 g, 2 mmol) in 25 mL of dry toluene was maintained at rt under nitrogen for 50 days. After evaporation of the solvent the residue was chromatographed on silica gel (toluene/ethyl acetate = 95/5) affording products **3a** (0.04 g, 7%), **4a** (0.02 g, 3%), **5** (0.39 g, 91%), 1,2,4,6-tetraphenyl-1,2-dihydro-1,3,5-triazine (0.07 g, 9%); mp 154-155° C; ^{1}H NMR : 6.4 (s, 1H, H_6); 7.0-8.4 (m, 20H, aromatics) and *N*-phenylbenzamidine (0.31 g, 79%).

Cycloaddition reactions of **1a-c** with phenylisocyanate (**6**). General procedure.

A solution of **1a-c** (2 mmol) and **6** (0.24 g, 2 mmol) in 25 mL of dry toluene was heated at 110° C under nitrogen for 4 days. The solvent was evaporated off and the residue distilled under reduced pressure (0.4 mm Hg, T=125-130° C) to obtain product (**8**) (Table 1). The distillation residue was chromatographed on silica gel. Elution with toluene/ethyl acetate = 75/25 gave products (**7a-c**) (Table 1).

Cycloaddition reaction of **1a** with *C,N*-diphenylnitrone (**9**).

A solution of **1a** (0.5 g, 2 mmol) and **9** (0.39 g, 2 mmol) in 25 mL of dry toluene was heated at 110° C under nitrogen for 4 days. The solvent was evaporated off and the residue chromatographed on silica gel .

Elution with toluene/ethyl acetate = 90/10 gave products (**3a**) (0.2 g, 36%) and (**4a**) (0.25g, 44%).

Cycloaddition reaction of **1a** with *C,N*-diphenylnitrone (**9**) in the presence of Ph_3P.

A solution of **1a** (0.5 g, 2 mmol), **9** (0.39 g, 2 mmol) and Ph_3P (0.52 g, 2 mmol) in 25 mL of dry toluene was heated at 110° C under nitrogen for 4 days. The solvent was evaporated off and the residue distilled under reduced pressure (0.4 mm Hg, T=125-130° C) to obtain product (**8**) (0.16 g, 54%). The distillation residue was chromatographed on silica gel (toluene/ethyl acetate = 90/10) affording products (**3a**) (0.17 g, 30%), (**4a**) (0.23 g, 40%) and Ph_3PO (0.53 g, 95%).

Cycloaddition reaction of **1a** with acylacetates (**10a,b**). General procedure.

A solution of **1a** (0.5 g, 2 mmol) and ethyl acetoacetate (**10a**) or ethyl benzoylacetate (**10b**) (2 mmol) in 25 mL of dry toluene was heated at 110° C under nitrogen for 3 days. The solvent was evaporated off and the residue chromatographed on silica gel. Elution with toluene/ethyl acetate = 90/10 gave products (**11**) (Table 1).

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REFERENCES AND NOTES

1. J. Barluenga and M. Tomas,'Advances in Heterocyclic Chemistry', Vol. 57, ed. by Alan R. Katritzky, FRS, Academic Press, S. Diego, 1993, p. 1.
2. D.L. Boger and S.N. Weinreb,'Hetero Diels-Alder Methodology in Organic Synthesis', ed. by Harry H. Wasserman, Academic Press, S. Diego,1987.
3. P. Dalla Croce, R. Ferraccioli, C. La Rosa, and T. Pilati,*J. Chem. Soc., Perkin Trans. 2*, 1993,1511.
4. P. Dalla Croce, R. Ferraccioli, and C. La Rosa,*J. Chem. Soc., Perkin Trans. 1*, 1994, 2499.
5. R.Consonni, P.Dalla Croce,R.Ferraccioli,and C. La Rosa,*J. Chem. Soc., Perkin Trans. 1*, 1996, 1809.
6. a) S.N. Mazumdar, I. Ibnusaud, and M.P. Mahajan, *Tetrahedron Lett.*, 1986, **27**, 5875. b) S.P. Singh, A.R. Mahajan, D. Prajapati, and J.S. Sandhu, *Synthesis*, 1991, 1026.
7. S.N. Mazumdar, S. Mukherjee, A.K. Sharma, D. Sengupta, and M.P. Mahajan, *Tetrahedron*, 1994, **50**, 7579.
8. A.K. Sharma and M.P. Mahajan, *Heterocycles*, 1995, **40**, 787.
9. P. Luthardt and E.-U. Würthwein, *Tetrahedron Lett.*, 1988, **29**, 921.
10. a) S.N. Mazumdar, M. Sharma, and M.P. Mahajan, *Tetrahedron Lett.*, 1987, **28**, 2641. b) D. Prajapati, S.P. Singh, A.R. Mahajan, and J.S. Sandhu, *Synthesis*, 1993, 468.

11. a) B. Sain, S.P. Singh, and J.S. Sandhu, *Tetrahedron Lett.*, 1991, **32**, 5151. b) B. Sain, S.P. Singh, and J.S. Sandhu, *Tetrahedron*, 1992, **48**, 4567.
12. A.K. Sharma, S.N. Mazumdar, and M.P. Mahajan, *Tetrahedron Lett.*, 1993, **34**, 7961.
13. M. Nishi, S. Tanimoto, M. Okano, and R. Oda, *Yuki Gosei Kagaku Kyokai Shi*, 1969, **27**, 754 (Chem.Abstr., 1969, **71**, 101438v).
14. Products (**4**) derived from oxidation of the corresponding dihydro derivatives (**3**) by means of the oxygen dissolved in the solvent (not degassed).
15. E. Rossi, D. Calabrese, and F. Farma, *Tetrahedron*, 1991, **47**, 5819.
16. D.H. Hunter and S.K. Sim, *Can. J. Chem.*, 1972, **50**, 669.
17. Reactivity of 1,3-diaza-1,3-butadienes (**1**) was successively tested with other dienophiles containing a C=N double bond as the *N,N'*-dicyclohexylcarbodiimide, the *N*-phenylmethylenebenzamine and electron poor C=N as the *N*-phenylmethylene-4-nitrobenzamine and the ethyl *N*-phenylmethylenecarbamate: in all cases the reagents were recovered unchanged. Obviously the presence of the phenylsulfonyl group in **2** enhances the reactivity of the C=N double bond and destabilizes the primary cycloadducts.
18. a) L.I. Samaraj, V.A. Bondar, and G.I. Derkatsch, *Angew. Chem., Int. Ed.*, 1967, **6**, 864. b) J. Goerdeler and R. Richter, *Synthesis*, 1978, 760. c) W.D. Dean and E.P. Papadopoulos, *J. Heterocycl. Chem.*, 1982, **19**, 171.
19. a) I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1678. b) J. Barluenga, M. Tomas, A. Ballesteros, and L.A. Lopez, *Synthesis*, 1989, 228.
20. The other possible attack of the 1,3-dipole on the N_1=C_2 double bond of **1a** was ruled out because the corresponding 1,2,4-oxadiazolidinic intermediate does not lead to the obtained products.
21. a) L. Horner and E. Jurgens, *Chem. Ber.*, 1957, **90**, 2184. b) Y. Hata and M. Watanabe, *J. Am. Chem. Soc.*, 1979, **101**, 6671.
22. R. Albrecht, G. Kresza, and B. Mlakar, *Chem. Ber.*, 1964, **97**, 483.
23. I. Bruning, R. Grashey, H. Hauck, R. Huisgen, and H. Seidl, *Org. Synth.*, 1966, **46**, 127.
24. J.G. Smith and J.M. Sheepy, *J. Heterocycl. Chem* ., 1975, **12**, 231.
25. J. Bergman, A. Brynolf, B. Elman, and E. Vuorinen, *Tetrahedron*, 1986, **42**, 3697.
26. D. Hunter, D.G. Neilson, and T.J.R. Weakley, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2709.
27. A.L. Nelson, *Chem. Ind.*, 1965, 653.
28. H. Groβ and B. Costisella, *Liebigs Ann. Chem.*, 1971, **750**, 44.
29. F.C. Cooper and W. Partridge, *J. Chem. Soc.*, 1955, 991.
30. J. Goerdeler and R. Sappelt, *Chem. Ber.*, 1967, **100**, 2064.
31. E. Cereda, E. Bellora, and A. Donetti, *Synthesis*, 1986, 288.

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