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Substituent Effects on 1,3-Dipolar Cycloadditions to Some 1,1-Diphenyl-2-Aza-1,3-Butadiene Derivatives.

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Abstract *: The reactivity and in particular the siteselectivity of [3+2] electrocyclic additions to 1,1-diphenyl-2-aza -1,3-butadienes, substituted or not on the terminal carbon with methyl and phenyl, and with a 3-carbomethoxyl group, have been investigated with the 1,3-dipolar reagents 4-nitrobenzonitrile oxide and diazomethane. The role of the 3-carbomethoxy substituent in determining the siteselectivity observed in these reactions is discussed in relation to experimental results and to conformational models of some of the tested 2-azadiene dipolarophiles calculated on AM1 bases.*

INTRODUCTION

The reactivity of 1,3-dipolar cycloadditions of nitrile oxides and diazoalkanes involving C=C and C=N bonds have been extensively investigated and have long been rationalized on the basis of FMO theory, together with the factors determining their regio- and stereoselectivity.[1]

In contrast siteselectivity, namely the competition between the additions to C=C and C=N bonds located in the same molecule, has been studied much less. It has been reported that these groups show a comparable dipolarophile reactivity toward nitrile oxides.[2] However, 1-aza-1,3-butadienes,[3-5] and enolizable enamine,[6] react preferentially on the C=N double bond with a variable degree of siteselectivity, while a complete selectivity in favour of C=N has been observed in the reactions of 4-benzalamino-3-methyl-5-styrylisoxazole with nitrile oxides[7] and of azaheptafulvalene with benzonitrile oxide.[8] A selective attack on the C=N bond has also been reported for the reaction of diazomethane with 1,1-bis-trifluoromethyl-2-aza-1,3-butadiene.[9]

Despite these interesting findings on the siteselectivity of 1,3-dipolar cycloadditions to conjugated azapolienes, these reactions still need further investigation.

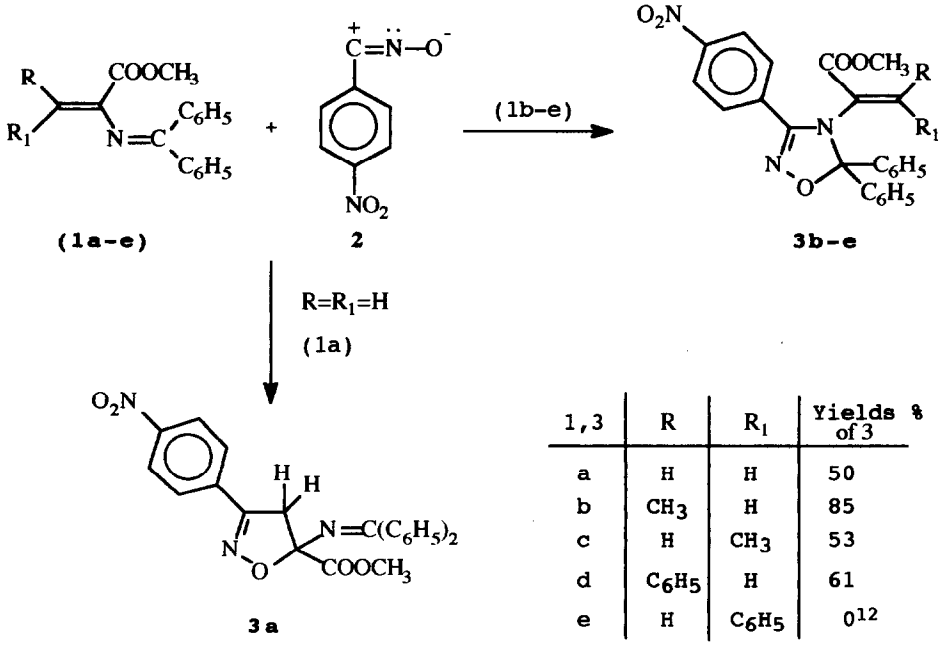
This became rather more evident when we recently described[10] the reactions of benzonitrile, 4-chlorobenzonitrile and *t*-butylnitrile oxides with methyl N-(diphenylmethylene)-α,β-dehydroamino acid derivatives **1a-e**, whose framework is that of a 1,1-diphenyl-2-aza-1,3-butadiene: 2-isoxazolines or 4,5-dihydro-1,2,4-oxadiazoles were obtained as a function of the substituent on the C4 of the 2-azadiene. In particular, in the case of **1a** (R=R'=H), siteselective

cycloadditions of benzonitrile and *t*-butilnitrile oxides to a C=C bond in the presence of a C=N bond were observed for the first time; the C4 substituted terms **1b-e** selectively underwent the cycloadditions to the C=N bond leading to 4,5-dihydro-1,2,4-oxadiazole derivatives.

The present paper reports the results of an investigation addressed to clarify some of the effects of substituents on the reactivity of 2-aza-1,3-butadienes in the cycloadditions of two 1,3-dipoles very different in terms of both their steric hindrance and of electronic properties: 4-nitrobenzonitrile oxide (an *"electrophilic"*, bulky reagent), and diazomethane (a *"nucleophilic"*, small 1,3-dipole).

RESULTS AND DISCUSSION

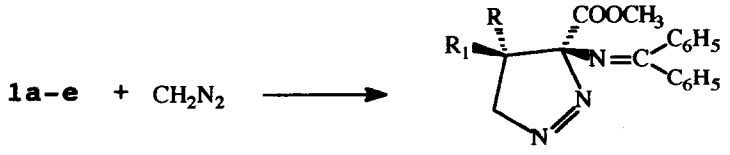
In our earlier study the cycloadditions of nitrile oxides to 1,1-diphenyl-3-carboxymethyl-2-aza-1,3-butadienes **1a-e** were carried out under different reaction conditions in order to achieve the best possible yields of cycloadducts. In consideration of the difficulties in carrying out kinetic experiments in reactions yielding secondary products, we decided to obtain qualitative information on the effects of the structure and geometry of the substituents on C4 by submitting compounds **1a-e** to cycloadditions with 4-nitrobenzonitrile oxide **2** (4-NO_2-BNO) under the following standard conditions: 1,0.01 Mol; 2,0.02 Mol; diethylether-dichloromethane 4:1 (150 mL) /r.t./ 48 hrs. Worth noting is the relatively long half-life of 4-NO_2-BNO (about one month at room temperature in diethylether).[11] The results are summarized in Scheme 1.



1,3	R	R_1	Yields % of 3
a	H	H	50
b	CH_3	H	85
c	H	CH_3	53
d	C_6H_5	H	61
e	H	C_6H_5	0[12]

Scheme 1

Compounds **1a-e** were also submitted to cycloadditions with diazomethane: in all of these cases, regio and siteselective cycloadditions to the C=C bond were observed, as outlined in Scheme 2.



4a-e

4	R	R_1	Yields %
a	H	H	>90
b	CH_3	H	80
c	H	CH_3	45
d	C_6H_5	H	37
e	H	C_6H_5	22

Scheme 2

The yields are referred to the amounts of homogeneous compounds obtained from the chromatographic columns ; unreacted azadienes were recovered in almost stoichiometric amounts from the reactions showing a low conversion ratio, together with small quantities of by-products such as benzophenone, and 4-NO_2-BNO cyclodimer from the reactions of Scheme 1.

With regard to the reactions with 4-NO_2-BNO, we observed that 2-azadiene **1a** reacted exclusively to the terminal C=C bond, giving 2-isoxazoline **3a** in a 50% yield; the (E)-4-methyl derivative **1b** completed the reaction within 6 hrs giving the oxadiazole **3b** (80% yield), whereas its (Z) isomer **1c** was much less reactive (53% yield after 48 hrs). The same trend was observed for the 4-phenyl substituted compounds (E)**1d** and (Z)**1e**: the latter was recovered unchanged after 48 hrs. Oxadiazole cycloadduct **3e** was obtained from **1e** in poor yield (29%) after a 48 hrs reflux in $CHCl_3$ in the presence of six equivalents of 2.

The structure of **3a** was determined both by means of MS and NMR spectroscopy and chemically, obtaining benzophenone from the acid-catalyzed hydrolysis of this compound; the structures of compounds **3b-e** were confirmed comparing their MS and NMR profiles with those of the 4-Cl-phenyl analogues of **3b**, the structure of which had been previously determined by X-Ray Crystallography.[10]

The results as a whole agree with those previously observed in the reactions of **1a-e** with BNO.[10] The C4 substituents switch the siteselectivity of 4-NO_2-BNO cycloadditions from the C=C (**1a**) to the N=C (**1b-e**) double bond. The formation rates of the 2-oxadiazolines were clearly influenced by the geometry of the C4 substituents, since the (E) isomers reacted faster than the (Z) ones.

The cycloaddition reactions of diazomethane with **1a-e** occurred at the C=C bond giving the substituted Δ^1-pyrazolines **4a-e** as single isomers, with yields which were from good to low (90-22%), but almost quantitative if calculated on the unrecovered starting material.

The reaction of **1a** went rapidly to completion after 6 hrs standing at 0°C in dichloromethane. The 4-substituted terms were less reactive: 72 hrs of standing in dichloromethane at r.t. and a four-fold excess of diazomethane were necessary in order to obtain **4b-e**. The diazomethane additions to the (E) isomers proceeded better than those to the (Z) analogues, thus confirming the trend of reactivity outlined by the nitrile oxide additions.

The structures of pyrazolines **4a-e** were assigned both by means of NMR spectroscopy and chemically by photochemical, stereospecific N_2 extrusion to the corresponding known 1-amino-cyclopropancarboxylic acids.[13]

A qualitative explanation for the reactivity pattern described here can be found in the presence of the 3-carbomethoxy substituent, which should confer the characteristics of an acrylate double bond to the C=C double bonds of **1a-e**. It is known from Huisgen's work[14] that methyl acrylate reacts 8.3 times faster than ethylene in cycloaddition reactions with benzonitrile oxide, and that methyl crotonate is 101 times less reactive than methyl acrylate. These data may account for the siteselective addition of 4-NO_2-BNO to the terminal C=C bond of **1a**, turning into site selective additions to N=C double bonds when there are substituents on the C4 position.

It has been reported[15] that in case of cycloaddition reactions of diazomethane to substituted ethylenes there is a great change in reaction rates on passing from ethylene to acrylate and crotonate: ethyl acrylate reacts 175 times faster than methyl crotonate and 5600 times faster than ethylene. Accordingly, the reactions of **1a-e** with diazomethane occurred exclusively to the C=C bonds. Both steric and electronic effects may account for the different behaviour of 4-NO_2-BNO with respect to diazomethane. In fact, substitutions at C4 will give larger steric repulsive interactions in the cycloadditions of the bulky nitrile oxide than in the reactions with diazomethane, which is characterized by small dimensions. Moreover, we can assume from the FMO theory that the 3-carbomethoxy group should be more effective in increasing the reaction rate of the diazomethane reactions, $HOMO_{(dipole)}$-$LUMO_{(dipolarophile)}$ controlled cycloadditions, than in nitrile oxides reactions, where both frontier orbital interactions gain importance.

The reported reactions also show high regioselectivity, and the direction of the 1,3-dipole attack is in accordance with known experimental data and with rationalization based on FMO theory.[1,16]

Unfortunately in compounds such as 1 highly conjugated non-frontier interactions are not negligible making FMO analysis poorly significant.

AM1 calculations[17] carried out on compounds **1a,b,d**, while confirming the above statement, allowed us to study the conformational profile of these molecules

Conformations **A** and **B** of compound **1a** are reported in Figure 1.

Selected geometrical parameters (Table 1) and the relative total energies of **B** with respect to **A** for **1a,b,d** and respective φ angles (Table 2) are reported as well. The azadiene system in compounds **1a,b,d** is not planar, and the deviation from planarity is measured by the torsional angle φ=C1-N2-C3-C4. The most stable conformation is in all cases a *cisoid* gauche (**A**), while the *transoid* gauche conformation (**B**) is a local minimum.

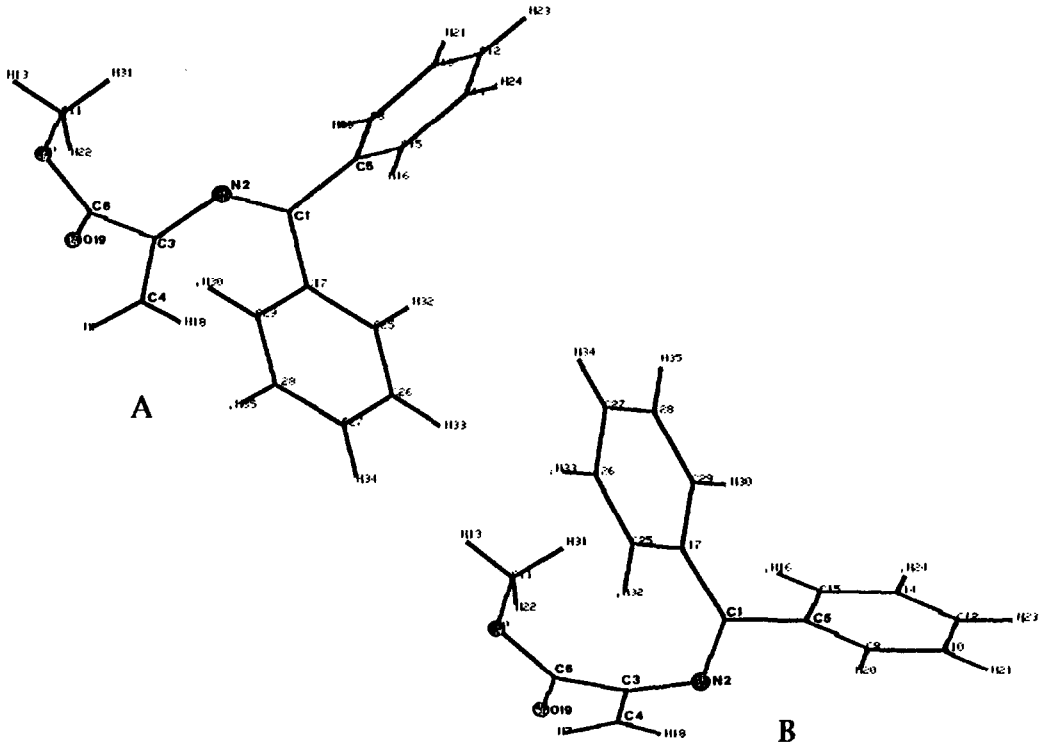


Figure 1. Global (A) and Local (B) Minimum for 1a.

	A	B
Bond Angles (degree)		
(C1-N2-C3)	125.7	124.0
(N2-C3-C4)	121.1	127.4
Bond length (Å)		
(C1-N2)	1.293	1.295
(N2-C3)	1.406	1.406
(C3-C4)	1.350	1.346

Table 1. Selected Structural Parameters of the Conformers A and B of 1a.

	A			B		
Compd.	ΔE^b	φ^a	α^c	ΔE	φ	α
1a	0.0	49.13	-81.46	+3.0	138.34	-116.75
1b	0.0	74.07	-79.98	+4.18	160.57	-72.63
1d	0.0	72.41	-81.23	+2.37	110.35	-77.14
2-NB[d]	+1.23	54.75	---	0.0	180.0	---

a) φ =(C1-N2-C3-C4) b) Relatives Total Energies in kcal·mol^{-1} c) α =(O19-C6-C3-C4) d) Ref.18

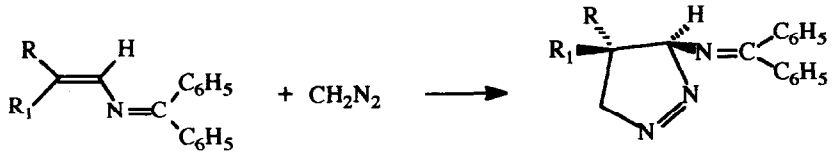
Table 2. Selected Torsional Angles and Relative Total Energies (kcal·mol^{-1}) of the Conformers A and B of **1a,b,d** and 2-Aza-1,3-Butadiene (2-NB).

Bond lengths and angles calculated for compound **1a** (as well as **1b** and **1d**) are consistent with those reported by others for the 2-azabutadiene itself on the basis of an MP2/6-31G*//HF/6-31G* calculation.[18] Conversely, in this compound a global minimum was found for $\varphi = \pm 180°$ (*s-trans* conformer) and a non planar gauche conformation (φ =54.75°), similar to structure A, was found as a local minimum with an energy of only 1.23 kcal ·mol^{-1} above the global minimum (see last row table 2). This difference could be traced back to the lower level of our calculation but could also be due to the presence of substituents on C1 and C3, which should destabilize the *s-trans* conformation.

The most relevant information we obtained from the computer model of **1a** regards the geometry of the C=O double bond of the 3-carbomethoxy group, which in both conformers A and B is out of the plane of the C3=C4 double bond: these geometries are incompatible with a satisfactory conjugation between the π electrons of the C=O and the C=C double bonds. From such a result the question of the effective role of $COOCH_3$ in determining siteselectivity arises. In order to find an experimental answer to the above question, we extended our investigation to the study of 2-aza-1,3-butadienes **1** lacking the 3-carbomethoxy substituent.

Therefore, 1,1-diphenyl-2-aza-1,3-butadiene (**1f**), the (E)-1,1,4-triphenyl-2-aza-1,3-butadiene (**1g**) and the 1,1,4,4-tetraphenyl-2-aza-1,3-butadiene (**1h**) were submitted to cycloaddition with diazomethane (Scheme 3) and 4-NO_2-BNO (Scheme 4). Under the same reaction conditions used for **1a** (0°, 6hr), terminal azadiene **1f** gave the pyrazoline cycloadduct to the terminal double bond (**4f**) in 73% yield, a figure very similar to that obtained from **1a** (90%).

Using the same reaction conditions adopted for **1d** only a 19% yield of pyrazoline **4g** was obtained from **1g**. In both cases, the reactions were site and regiospecific and unreacted **1g** was recovered in stoichiometric amounts. Under the same conditions the tetraphenyl derivative **1h** did not react at all.

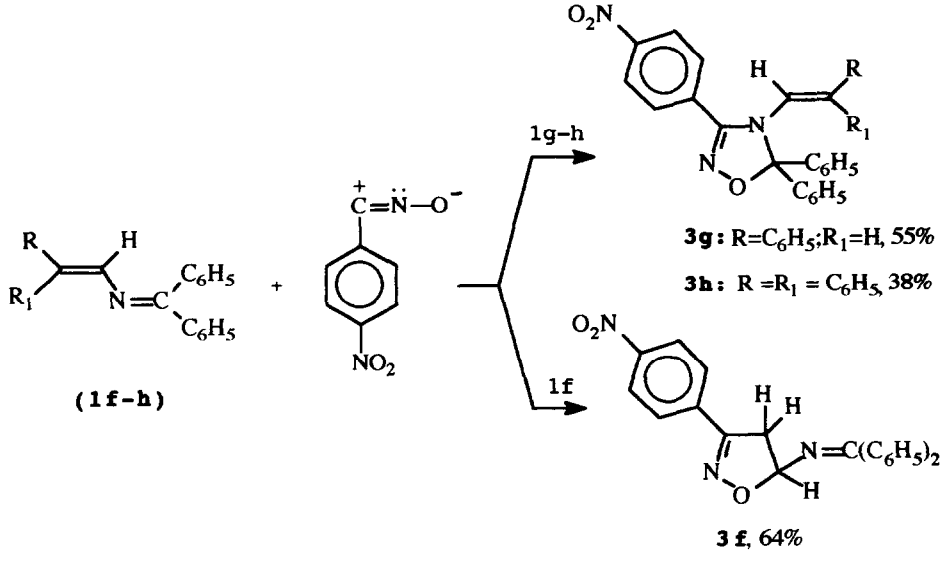


1f-h **4f-h**

1,4	R	R_1	Yields %
f	H	H	73
g	C_6H_5	H	19
h	C_6H_5	C_6H_5	0

Scheme 3

Scheme 4 outlines the results of the reactions of compounds **1f-h** with 4-NO_2-BNO. From terminal diene **1f** we obtained the isoxazoline cycloadducts to the C=C bond (**3f**, 64%) while the C=N cycloadducts **3g,h** from the tri- and tetraphenyl derivatives **1g,h** were obtained in 55[12] and 38% yields, respectively.



(1f-h)

Scheme 4

Therefore, phenylazadienes **1f-h** underwent 1,3-dipolar cycloadditions in a manner similar to those of the 3-carboxymethoxy substituted compounds **1a-e**, although with lower yields.
If we consider that the cycloaddition reactions of compounds **1f-h** were carried out under the same conditions used for compounds **1a-e**,[12] the higher yields observed in the latter may be traced back to the activation of the $COOCH_3$. However, even in the absence of this group the C=C double bond is more reactive than the N=C bond, at least towards diazomethane, and in the case of **1f** toward 4-NO_2-BNO as well.
In addition to the hypothesis of an activation due to the 3-carbomethoxy, it is necessary to consider that phenyl groups on C1 may reduce the N=C reactivity; this effect should be higher when the partner is diazomethane instead of 4-NO_2-BNO.[2,15] Accordingly, the tetraphenyl-2-azabutadiene **1h**, which reacts with 4-NO_2-BNO to the N=C bond, is unreactive with diazomethane.

In summary, yields and siteselectivity of the studied 1,3-dipolar cycloadditions to 1,1-diphenyl-2-aza-1,3-butadiene derivatives depend on the nature of the 1,3-dipolar reagent and of the C4 substituents. The low reactivity of the (Z)-isomers in general and of (Z)-4-phenyl derivative **1e** in particular is in accordance with the general behaviour of *trans* dipolarophiles *versus cis* ones, attributed to steric and electronic factors.[19]
The moderate and not general effects of $COOCH_3$ found in the reactions of **1a-e** when compared with those of compounds **1f-h**, along with some limits and incoherence of the results of our experimental and computed approaches, prevent us from ascribing a decisive role to $COOCH_3$ in determining the siteselectivity observed in the 1,3-dipolar cycloaddition reported here.

EXPERIMENTAL

Melting points were determined on a Büchi SPM-510 open capillary apparatus and are uncorrected. Infrared spectra were obtained from a Perkin Elmer 257 spectrometer. NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200; the chemical shifts are reported in parts per million (δ) and are referenced to the deuterium look signal from the sample solvent; coupling constants were measured in Hertz. MS spectra (EI, 70 eV) were obtained on a GC-MS HP5995 instrument and microanalysis for C, H and N on a Perkin-Elmer CHN analyzer 240 C.
Dichloromethane was distilled over calcium hydride; all the other solvents and reagents were the highest grade commercially available (Aldrich) and were used without additional purification. Evaporations *in vacuo* were conducted on a Büchi rotavapor at water aspirator pressure. Column chromatography purifications were performed under flash conditions using Merck 230-400 Mesh silica gel. Analytical thin layer chromatography was performed using pre-coated plates (Merck Kieselgel 60 F_{254}) visualized by UV lamp at 254 nm. The compounds **1a-e**[20], **1f**[21] and **1h**[22] were prepared as previously described.

Semiempirical calculations:
The compounds reported in Scheme 1 have been built and minimized with the use of Chem-X-Jul91[17] force field and then submitted to systematic search. The resulting conformations have

been fully optimized with the use of AM1 Hamiltonian implemented in MOPAC 5.0[23] and the key-word PRECISE has been used.

Cycloadditions of 4-nitrobenzonitrile oxide (2) with 2-azadienes 1a-h.

The 4-nitrobenzonitrile oxide was prepared according to the following method:
a suspension of 4-nitro-clorobenzaldoxime[24] (20 mmol) in 40 ml of water was treated under stirring at 0°C with NaOH 14% (60 mmol). After 10 minutes the mixture was extracted twice with 60 mL of Et_2O (**1g**[12], $CHCl_3$).
The etheral solution containing some indissolved nitrile oxide was added at room temperature to a solution of **1a-h** (10 mmol) in 30 ml of CH_2Cl_2 (**1g**, $CHCl_3$) and the stirring was continued at r.t. for 48 hrs. In the case of **1b**, the time-course TLC controls revealed a complete disappearance of the starting compounds after 6 hrs. The reaction mixture was washed with water (2x50 mL), dried over sodium sulphate, and evaporated. The crude product was purified by column flash-chromatography (cyclohexane-ethyl acetate 85-15). The chromatographic fractions were furtherly purified by crystallization.

3a: mp 142 °C (Et_2O/light petroleum); IR (nujol) 1730, 1620 cm^{-1}; ^1H NMR 3.51, 4.18 (2d,2H,CH_2), 3.60 (s,3H, OCH_3), 7.06-8.36 (m,14Harom); ms:(m/z) 429(M^+),370, 208, 180 (100), 103, 77. Found: C, 66,86; H, 4,08; N, 9,52% $C_{24}H_{19}N_3O_5$ requires C, 67,13; H, 4,46 ; N, 9,79%.

3b: mp 176 °C (Et_2O/light petroleum); IR (nujol) 1715, 1600 cm^{-1}; ^1H NMR 1.69 (d,3H,CH_3), 3.43 (s,3H, OCH_3), 5.98 (q,1H,=CH-CH_3), 7.20-8.40 (m,14Harom); ms:(m/z) 443(M^+),336, 261, 202, 182, 105 (100), 77. Found: C, 67,68; H, 5,10 ; N, 9,85% $C_{25}H_{21}N_3O_5$ requires C, 67,71; H, 4,77; N, 9,48%.

3c: am solid; IR (nujol) 1715, 1605 cm^{-1}; ^1H NMR 1.63 (d,3H,CH_3), 3.60 (s,3H,OCH_3), 6.56 (q,1H,=CH-CH_3), 7.20-8.40 (m,14Harom); ms:(m/z) 443(M^+), 366, 261, 202, 182, 105 (100), 77. Found: C, 67,41; H, 4,61; N, 9,53% $C_{25}H_{21}N_3O_5$ requires C, 67,71; H, 4,77; N, 9,48%.

3d: mp 169 °C (Et_2O/light petroleum); IR ($CHCl_3$) 1715, 1605 cm^{-1}; ^1H NMR 3.13 (s,3H,OCH_3), 6.46(s,1H, =CH-Ph), 6.63-8.53 (m,19Harom); ms:(m/z) 505(M^+), 428, 323 (100), 264, 182, 105, 77. Found: C, 71,20; H, 4,85; N, 8,23% $C_{30}H_{23}N_3O_5$ requires C, 71,28; H, 4,59; N, 8,31%.

3e: mp 205 °C (Et_2O/light petroleum); IR (nujol) 1715, 1600 cm^{-1}; ^1H NMR 3.65 (s,3H,OCH_3), 7,05 (s,1H, =CH-Ph), 7.10-8.31(m,19Harom); ms:(m/z) 505(M^+), 428, 323 (100), 264, 182, 105, 77. Found: C, 71,48; H, 4,51; N, 8,37% $C_{30}H_{23}N_3O_5$ requires C, 71,28; H, 4,59; N, 8,31%.

3f: mp 204 °C (CH_2Cl_2/Et_2O); IR ($CHCl_3$) 1610, 1595 cm^{-1}; ^1H NMR 3.39 (m,2H,CH_2), 5.92 (m,1H, CH), 7.15-8.31 (m,14Harom); ms:(m/z) 371(M^+), 191, 180 (100), 77. Found: C, 71,00; H, 4,97; N, 11,31% $C_{22}H_{17}N_3O_3$ requires C, 71,15; H, 4,61; N, 11,31%.

3g: mp 161 °C (Et_2O/light petroleum); IR ($CHCl_3$) 1570 cm^{-1}; ^1H NMR 5.53 (d,1H,=CH), 6.59

(d,1H=CH), 6.84-8.37 (m,19Harom); ms:(m/z) 447(M^+), 282, 265, 264, 218, 165 (100), 117. Found: C, 74,76; H, 4,89; N, 9,71% $C_{28}H_{21}N_3O_3$ requires C, 75,15; H, 4,73; N, 9,39%.

3h: mp 225 °C (Et_2O/light petroleum); IR (nujol) 1600 cm^{-1}; ^1H NMR 6.23 (s,1H,=CH), 6.27-7.98 (m,24Harom); ms:(m/z) 523(M^+), 359, 341 (100), 165, 105. Found: C, 77,66; H, 5,17; N, 8,17% $C_{34}H_{25}N_3O_3$ requires C, 77,99; H, 4;81; N, 8,03%.

Diazomethane cycloadditions to 1,1-diphenyl-2-aza-1,3 butadiene derivatives 1a-g.

A solution of compounds **1a-g** (5 mmol) in dichloromethane (15 mL) was treated with an etheral solution of diazomethane [25] (from 2.5 g of N-methyl-N-nitrosourea in 15 mL of ether) in a flask stoppered and protected from light. The mixture was allowed to stand at room temperature (0°C for **4a** and **4f**) for 3 days (6h for **4a** and **4f**), then treated with anhydrous $CaCl_2$ to destroy excess diazomethane, and finally filtered and concentrated *in vacuo*.
The resultant yellow oils were triturated with ether to give Δ^1-pyrazolines **4a** and **4f** as white solids, or filtered through a silica-gel column (cyclohexane/ethyl acetate 9:1 as eluent) to separate pyrazolines **4b-e** and **4g** from unreacted starting materials **1b-e** and **1g**.

4a: mp 70-72°C (dec.); Lit = oil; IR and ^1H-NMR data are identical with those of the literature.[26]

4b: oil; IR ($CHCl_3$) 1735, 1615 cm^{-1}; ^1H NMR 0.82 (d,3H,CH_3), 2.60-2.90 (m, 1H,H-4), 3.30 (s,3H,OCH_3), 4.10-4.95 (m,2H,H-5), 7.15-7.70 (m,10Harom). Found: C, 71,15; H, 5,73; N, 13,44% $C_{19}H_{19}N_3O_2$ requires C, 71,01; H, 5,96; N, 13,07%.

4c: oil; IR ($CHCl_3$) 1730, 1610 cm^{-1}; ^1H NMR 1.23 (d,3H,CH_3), 2.00-2.46 (m, 1H,H-4), 3.27 (s,3H,OCH_3), 4.01-4.92 (m,2H,H-5), 7.20-7.70 (m,10Harom). Found: C, 70,78; H, 5,74; N, 13,11% $C_{19}H_{19}N_3O_2$ requires C, 71,01; H, 5,96; N, 13,07%.

4d: mp 129-132 °C; IR ($CHCl_3$) 1720, 1600 cm^{-1}; ^1H NMR 2.73 (s,3H,OCH_3), 3.93 (t,1H,H-4), 4.98 (d,2H,H-5), 6.80-7.73 (m,15Harom). Found: C, 75,24; H, 5,76; N, 10,90% $C_{24}H_{21}N_3O_2$ requires C, 75,18; H, 5,52; N, 10,96%.

4e: mp 131-135 °C; IR ($CHCl_3$) 1715, 1615 cm^{-1}; ^1H NMR 3.36 (s,3H,OCH_3), 3.52 (t,1H,H-4), 4.80-5.10 (m,2H,H-5), 7.10-7.85 (m,15Harom). Found: C, 74,83; H, 5,35; N, 10,86% $C_{24}H_{21}N_3O_2$ requires C, 75,18; H, 5,52; N, 10,96%.

4f: mp 78-80 °C; IR ($CHCl_3$) 1615, 1595 cm^{-1}; ^1H NMR 1.33-1.76 (m,2H,CH_2), 3.83-5.00 (m,2H,CH_2), 5.43-5.76 (m,1H,CH), 7.00-7.73 (m,10Harom). Found: C, 77,40; H, 6,04; N, 17,14% $C_{16}H_{15}N_3$ requires C, 77,08; H, 6,06; N, 16,,85%.

4g mp 71-74 °C; IR ($CHCl_3$) 1610,1595 cm^{-1}; ^1H NMR 3.34 (m,1H,H-4),4.55 (m,1H,H-5) 5.27 (m,1H,H-5), 5.76 (m,1H, H-3), 6.92-7.69 (m,15Harom). Found: C, 81,00; H, 5,67; N, 12,55% $C_{22}H_{19}N_3$ requires

C, 81,20; H, 5,89; N, 12,91%.

(E,Z)-1,1-(diphenyl)-2-aza-4-phenyl-1,3-butadiene.

A solution of 2-diphenylmethylenamino-1-phenylethanol[27](3.01 g, 10 mmol) and pyridine (8 mL) in dry dichloromethane (20 mL) was added dropwise to a solution of [(diethylamino) sulphur trifluoride] (1.3 mL, 10 mmol) in dichloromethane (20 mL) at 0 °C. The reaction solution was stirred for 5h at 0 °C. The organic phase was washed with a sat. aq. solution of NH_4Cl, then with 5% $NaHCO_3$ and finally with water. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give a residue containing a mixture of both E and Z desired diastereoisomers in almost equimolecular amounts. The diastereoisomers were separated by flash-chromatography on silica gel (cyclohexane/EtOAc 85:15).

E-isomer (1g): mp 61 °C (EtOH); IR (nujol) 1625 cm^{-1}; ^1H NMR 7.08 (d,1H,=CH, J=13.35 Hz), 7.24-7.78 (m,15Harom, 1H,=CH). Found: C, 89,15; H, 6,18; N, 4,66% $C_{21}H_{17}N$ requires C, 89,01; H, 6,05; N, 4,94%.
Z-isomer: mp 79 °C (EtOH), Lit= 76 °C (EtOH)[28]; IR (nujol) 1620 cm^{-1}; ^1H NMR 6.10 (d,1H,=CH, J=8.6 Hz), 6.86 (d,1H,=CH, J=8.6 Hz), 7.27-8.01 (m,15Harom)

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12. In our standard conditions, probably for reasons of solubility, the reactions of **1e** and **1g** did not occurr. Otherwise in trichloromethane the yield of **3e** was 29% (6 equivalents of **2**, 48 hrs, reflux) and the yield of **3g** was 55% (2 equivalents of **2**, 48 hrs, r.t.).

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