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Reaction of 1,2-Diketones with *N,N*-Dimethylcyanamide in the Presence of Titanium(IV) chloride

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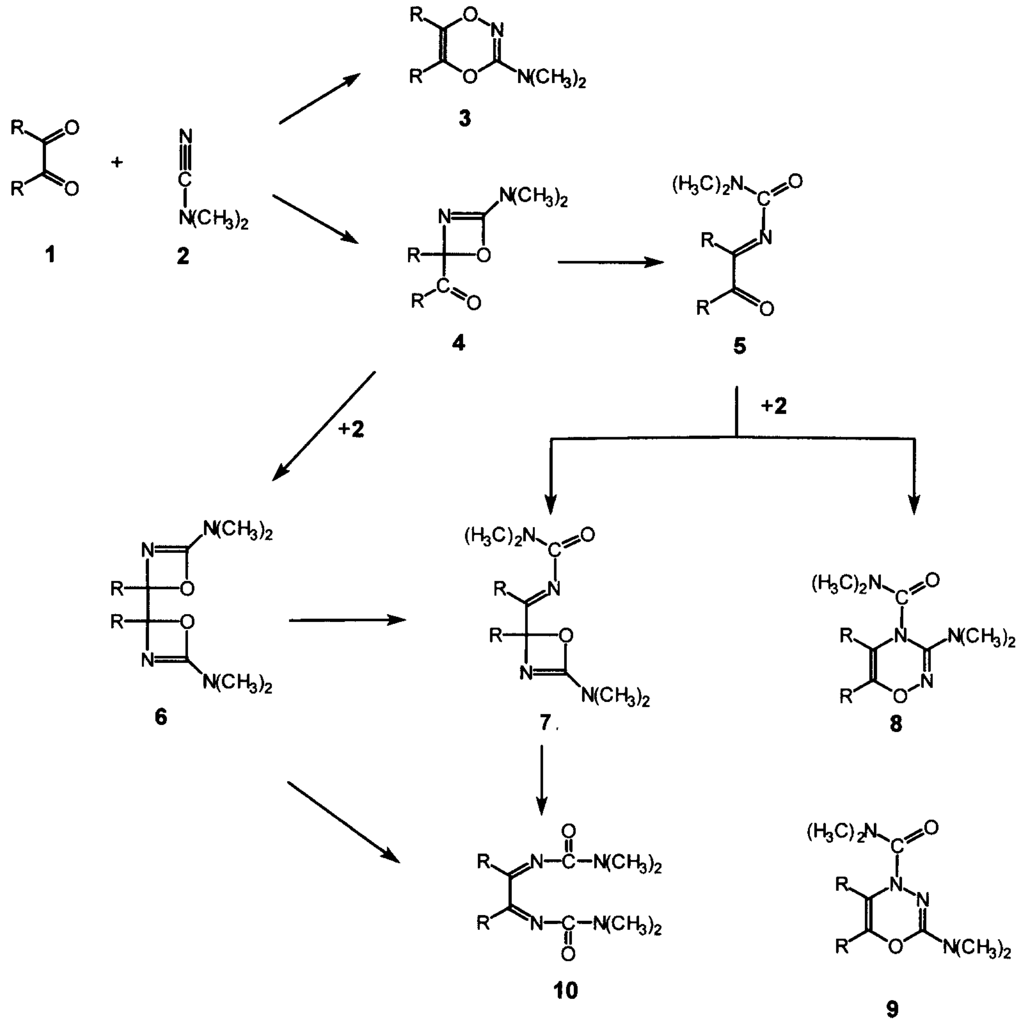
Abstract: In the presence of titanium(IV) chloride 1,2-diketones undergo [2+2] cycloaddition to *N,N*-dimethylcyanamide with subsequent ring opening to 4-*N,N*-dimethylcarbamoyl-2,3-disubstituted-1-oxa-4-aza-1,3-butadienes **5** and 1,4-di-(*N,N*-dimethylcarbamoyl)-2,3-disubstituted-1,4-diaza-1,3-butadienes **10**.

INTRODUCTION

A few [2+2] and [4+2] cycloadditions of 1,2-diketones as heterodienes have been reported in the literature.[1-5] Among these the thermal and photochemical [4+2] cycloadditions of *o*-quinones to a variety of CC-dienophiles have been investigated most thoroughly.[5] The aromatization of the *o*-quinoidal system seems to be the driving force for the reaction.[5] The electrophilic character of the 1,2-dicarbonyl system as 1,3-diene is demonstrated by the exclusive reaction of π-donor olefins such as *E*-1,2-dimethoxy- and tetraethoxyethylene with dimethyl-2,3-dioxosuccinate.[4] The retention of the stereochemistry of *E*-1,2-dimethoxyethylene in this cycloaddition suggests a concerted process. In the case of ethylvinyl ether the nucleophilic β-C-atom attacks a carbonyl C-atom of the 1,2-diketo system leading to a bicyclic structure in a multistep reaction.[4] In addition, the same reaction mode may lead to the formation of [2+2] cycloadducts as demonstrated by Baccer, Scheeren, and Nivard [2] and Mattay and Runsink.[3] Neither [2+2] nor [4+2] cycloadditions of 1,2-diketones to heterodienophiles have been reported so far. Here we report on the reaction of 1,2-diketones with *N,N*-dimethylcyanamide in the presence of a Lewis acid.

RESULTS

The reaction of 1,2-diketones with *N,N*-disubstituted cyanamides may yield three different types of cycloaddition products: 1,4,2-dioxazines **3**, *4H*-1,3-oxazetes **4**, and bis-*4H*-1,3-oxazetes **6** (scheme 1).
Benzil **1a**, substituted derivatives of benzil **1b-1d**, and diacetyl **1e** were treated in a 1:1 molar ratio with *N,N*-dimethylcyanamide in benzene at 75 °C in the presence of titanium(IV) chloride. Within 3-4 hours the products were formed. The presence of equimolar amounts of Lewis acid is essential for the reaction. Among the Lewis acid tested, e.g. $TiCl_4$, $BF_3 \cdot Et_2O$, and $ZnCl_2$, titanium(IV) chloride gave the best results. No reaction took place in the presence of $ZnCl_2$. All products were obtained as stable titanium complexes which were hydrolyzed in aqueous alkaline solution, extracted with chloroform, and finally purified by column chromatography, by preparative TLC, or by crystallization. In general a mixture of two compounds was obtained which was separated by chromatography. It was shown by elemental analysis and mass



1a: R= C_6H_5
1b: R= p-CH_3-C_6H_4
1c: R= m-OCH_3-C_6H_4
1d: R= p-OCH_3-C_6H_4
1e: R= CH_3

5a, 10a: R= C_6H_5
5b, 10b: R= p-CH_3-C_6H_4
5c, 10c: R= m-OCH_3-C_6H_4
5d, 10d: R= p-OCH_3-C_6H_4
5e, 10e: R= CH_3

Scheme 1

spectrometry that the 1,2-diketones had formed 1:1 and 1:2 adducts with *N,N*-dimethylcyanamide. In order to see how the product yields are influenced by the ratio of the educts experiments were also carried out in a ratio of 1:2 of 1,2-diketone and *N,N*-dimethylcyanamide. The results are collected in Table 1.

The identification of the products was carried out by spectroscopic methods. One type of compound, finally identified as **5** (scheme 1), shows characteristic IR absorptions at 1600-1650 cm^{-1} (C=N, conjugated

Table 1. Yields of Products in the Reaction of 1,2-Diketones **1** with *N,N*-Dimethylcyanamide **2**.

1,2-Diketones	Ratio **1**:**2**	Yield of 1:1 adduct (%)	Yield of 1:2 adduct (%)
1a	1 : 1	29	23
	1 : 2	9	55
1b	1 : 1	10	30
	1 : 2	4	65
1c	1 : 1	32	24
	1 : 2	11	60
1d	1 : 1	a)	35
	1 : 2	-	65
1e	1 : 1	30	35
	1 : 2	-	a)

a) Traces of these compounds were observed by GLC/MS.

C=O, N-C=O). The M^+ peaks of 280 (**5a**), 308 (**5b**), 340 (**5c**, **5d**) and 156 (**5e**) confirm the 1:1 ratio of the educts. The signal at ca. 162 ppm in the ^{13}C NMR spectra of **5a-c** is assigned to the C-atom of the CN-double bond, the signal at ca. 172 ppm to the C-atom of the amide carbonyl group, and the signal at ca. 197 ppm to the carbonyl C-atom. The hydrogen atoms of the dimethylamino group appear in the ^1H NMR spectrum (room temperature) as two signals at ca. 2.94 and 3.15 ppm. The absence of a υ_{CO} vibration >1700 cm^{-1} and a ^{13}C-chemical shift of <160 ppm which would be expected for the sp^3 C-atom of **4** excludes the oxazete structure. The 1,4,2-dioxazine structure **3** is also not in agreement with the spectroscopic data. Thus, after an initial [2+2] cycloaddition an electrocyclic ring opening to 4-*N,N*-dimethylcarbamoyl-2,3-disubstituted-4-aza-1-oxa-1,3-butadienes **5** (*N,N*-dimethyl-*N'*-(1,2-diphenyl-2-oxa-ethylidene)-urea) takes place. Depending on the reaction conditions the isolated yields range from 4% (ratio of the educts 1:2) to 32%.

The 1:1 adduct of diacetyl and *N,N*-dimethylcyanamide is a special case as it has two methyl groups bonded to a carbonyl and an imino group in **5**. Besides **5e** (scheme 1) a tautomeric form **5'e** can be written. The ^1H and ^{13}C NMR spectra of this product indicate that it exists as 3-*N,N*-dimethylcarbamoylamino-2-methyl-1-oxa-1,3-butadiene **5'e** (scheme 2).

5e **5'e**

Scheme 2

The ^1H NMR spectrum of **5e** displays five singlets. The singlets at 2.40 ppm and at 2.97 ppm, in an intensity ratio of 1:2, are assigned to the methyl group at the CO and the methyl groups of the dimethylamino substituent, respectively. Two methylene protons are observed as singlets at 5.60 and 6.62 ppm. These two protons are bound to the same C-atom as shown by a CH-correlation spectrum. A broad singlet at 7.45 ppm is assigned to NH-group. The ^{13}C NMR spectrum displays six signals at 23.80, 36.15, 106.73, 139.08, 155.18 and 195.43 ppm. The signals at 23.80 and 36.15 are assigned to the C-atoms of the methyl group and the dimethylamino group. The olefinic carbon atoms appear at 106.73 and 139.08 ppm, the amide carbonyl carbon atom at 155.18, and the second carbonyl C-atom at 195.45 ppm.

The second type of reaction product, the 1:2 adduct of compounds **1** and **2**, might either have a bis-*4H*-1,3-oxazete structure **6** formed from **4** in a second [2+2] cycloaddition, or might also possess structures **7**-**10** (see scheme 1). As no final decision could be made on the basis of the spectroscopic data a X-ray analysis was done for the product from benzil and *N,N*-dimethylcyanamide. Figure 1 shows that ring opening after a second [2+2] cycloaddition leads to 1,4-di-(*N,N*-dimethylcarbamoyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene **10a**. As shown in scheme 1 it can not be decided which of the two pathways has been followed to generate **10**. Having established the structure of **10a** by X-ray analysis it is also possible to assign the NMR data. The symetrical structure follows from the number of ^{13}C NMR signals. The C-atom of the imino group shows up at 162.11 ppm. Because of the quadrupol effect the amide carbonyl C-atom appears as broad peak at 171.70 ppm, which can only be observed after long measuring times. The similarity of the spectroscopic data of all 1:2 adducts confirms their uniform structure.

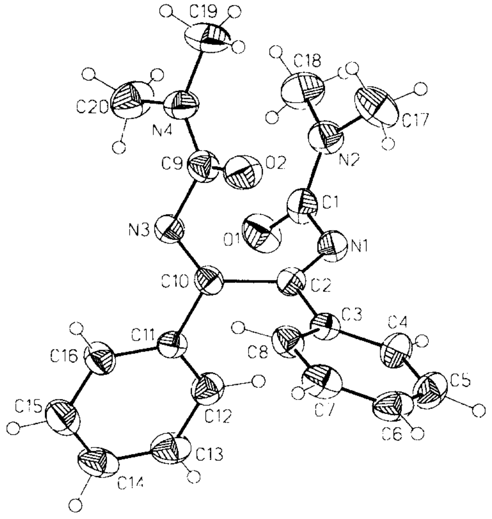


Figure 1. ORTEP Representation of **10a** according to the X-ray analysis.

Although no optimization of the experimental conditions was done several modifications were tried. Replacement of titanium(IV) chloride by other Lewis acids as mentioned above did not show positive effects. $ZnCl_2$ was not effective at all and $BF_3{\cdot}Et_2O$ provided only the 1:1 adduct of benzil and *N,N*-dimethylcyanamide, however in lower yield (19%) than with titanium(IV) chloride. A lowering of the reaction temperature to 25-30 °C, in order to possibly isolate oxazetes, led only to longer reaction times (36 h) and poorer product yields, e.g. only 2% of **5a** and **10a** in the reaction of **1a** and **2** (molar ratio 1:1). At these temperatures it was necessary to replace benzene by dichloromethane for solubility reasons. If less than an equimolar amount of titanium(IV) chloride is used the yields of reaction products drop, e.g. only 10% **5a** was isolated when the reaction of **1a** with **2** was done in the presence of 0.2 M equivalents of $TiCl_4$.

An interesting observation which is presently explored in detail was made when a molar ratio of 1:2:2 of diketone **1**, *N,N*-dimethylcyanamide **2**, and titanium(IV) chloride was chosen. It did not increase the yield of **10**, but the formation of an additional 1:2 adduct took place. Recorded by preliminary structure determination the oxadiazines **8** or **9** are suggested as possible candidates.

DISCUSSION

The attempt to observe [4+2] cycloadditions of 1,2-diketones to *N,N*-dimethylcyanamide was unsuccessful. Instead an initial [2+2] cycloaddition, either once or twice, is followed by electrocyclic ring opening to *N'*-alkylidene-*N,N*-disubstituted urea derivatives. On the bassis of our results it is not possible to decide whether **10** is generated via **6** or **7**. The results open up a new pathway to 4-*N,N*-dimethylcarbamoyl-2,3-disubstituted-4-aza-1-oxa-1,3-butadienes **5** and 1,4-di-(*N,N*-dimethylcarbamoyl)-2,3-disubstituted-1,4-diaza-1,3-butadienes **10**. Literature reports on the preparation of such *N'*-alkylidene-*N,N*-disubstituted ureas involve the reactions of 1-bromo isocyanates with amines,[6] the reactions of 1-chloroalkyl isocyanates with thiourethanes,[7] *N,N'*-dimethylurea,[8] *N*-substituted amides of carboxylic acids [9] or *N*-monosilylated carbodiimides,[10] the conversion of *N*-(1-acyloxyalkyl) carbodiimides,[11,12] the reactions of acyl imines of hexafluoroacetone and perfluoroalkyl isocyanates with methylenebis(dimethylamine),[13] the basic decomposition of pyridinium *N*-acyloxyhydroxylamine-O-sulfonates,[14] the thermolysis of *3H*-1,2,4-oxathiazol-2-oxides,[15] and the thermolysis of 2-dimethylamino-4-alkenyl-1,3-oxazin-6-ones.[16] *N,N'*-Bis(alkylidene) ureas were prepared by the reaction of 1-chloro-isocyanates with ketimines [17] and by the reaction of phosgene with ketimines.[18]

N,N-Dimethylcyanamide can be considered as a molecule having a CN triple bond which is rendered electron rich by the dimethylamino group. Thus, there might be an analogy to the reactivity of electron rich alkynes towards ketones. Indeed, a similar reaction course was observed earlier in the reaction of ketones with alkynes. Ketones react with 1-alkynyl ethers [19,20,21], phenylethyne [22] and ynamines [23], forming the four-membered ring (oxete derivatives), which then ring open to give the esters of α,β-unsaturated acids, α,β-unsaturated ketones and amides of α,β-unsaturated acids, respectively. The oxete intermediates were too unstable to be isolated.

Similar to the oxete system 1,3-oxazetes seem to be unstable with respect to an electrocyclic ring opening. Such ring system have been described as intermediates in the thermal reactions of perhaloketones with cyanamides, giving 1,3,5-oxadiazine derivatives.[24,25] Two literature reports on the synthesis of 1,3-oxazete derivatives involve the thermolysis of the products of the cleavage of the sulfur-sulfur bond in a dithiocyano-hexafluoroacetone adduct [26] and a synthesis from acyl isothiocyanates.[27]

EXPERIMENTAL

IR spectra were recorded on a Perkin- Elmer FT-IR 1600 spectrometer. ^{1}H and ^{13}C NMR spectra were measured using a Varian Gemini 200 and a Bruker AMX 300 spectrometer in $CDCl_3$ solution, with tetramethylsilane as an internal standard. Mass spectra were obtained with a Fisons VG Prospec 3000 and a Hewlett Packard HP 5971A MSD spectrometer. Thin layer chromatography was carried out on silica gel 60 F_{254} (Merck) thin layer chromatography plates. The preparative TLC method was performed using silica gel as the stationary phase (Merck Kieselgel 60 F_{254} plates 1 mm thick) and a benzene-ethyl acetate mixture (3:1 v/v) as the mobile phase. Column chromatography was carried out on 70-230 mesh silica gel 60 (Fluka) using benzene-ethyl acetate mixture (3:1 v/v) as the mobile phase. Melting points are uncorrected. The educts are commercially available.

General procedure for the synthesis of 4-N,N-dimethylcarbamoyl-2,3-disubstituted-4-aza-1-oxa-1,3-butadienes (**5**) *and 1,4-di-(N,N-dimethylcarbamoyl)-2,3-disubstituted-1,4-diaza-1,3-butadienes* (**10**): A solution of $TiCl_4$ (1.9 g, 0.01 mol) in 20 ml of anhydrous benzene was added dropwise to a well-stirred and cooled mixture of the 1,2–diketone (0.01 mol) and *N,N*-dimethylcyanamide (0.7 g, 0.01 mol or 1.4 g, 0.02 mol) in 30 ml of anhydrous benzene. After the addition was completed, the mixture was heated at 75 °C for 3 h, cooled to room temperature, and the benzene was evaporated. About 50 ml of water was added to the residue, the resulting solution was alkalized with 20% NaOH solution and extracted with chloroform. The mixture of products **5** and **10** was separated by column chromatography or by preparative TLC. Compounds **10** can be crystallized from a chloroform-diethyl ether (1:10) mixture.

4-N,N-Dimethylcarbamoyl-2,3-diphenyl-4-aza-1-oxa-1,3-butadiene (**5a**): M.p.100-101°C. ^{1}H NMR: 2.94 (3H, s, NCH$_3$), 3.18 (3H, s, NCH$_3$), 7.39-7.91 (10 H$_{Arom}$, m). ^{13}C NMR: 35.89 (NCH$_3$), 37.56 (NCH$_3$), 128.83, 128.86, 128.94, 129.05, 129.17, 129.93, 132.79, 133.62, 133.96, 135.04, 161.94 (C=N), 172.00 (O=*C*-N(CH$_3$)$_2$), 197.91 (C=O). IR(KBr): 2922, 1655, 1633, 1445, 1201, 1100 cm^{-1}. MS m/z (rel.int.%): 280 (M$^+$, 3), 237(2), 208 (4), 180 (1), 177 (12), 105 (27), 72 (100), 44 (1). $C_{17}H_{16}N_2O_2$ Calcd.280.1210 found 280.1208. Elemental analysis: C 72.55, H 5.85, N 9.97, calcd. C 72.84, H 5.75, N 9.99. R$_f$ 0.37. Yield 29%.

4-N,N-Dimethycarbamoyl-2,3-di(4-methylphenyl)-4-aza-1-oxa-1,3-butadiene (**5b**): M.p.94-95°C. ^{1}H NMR: 2.37 (6H, s, p-CH$_3$), 2.92 (3H, s, NCH$_3$), 3.14 (3H, s, NCH$_3$), 7.18-7.90 (8H$_{Arom}$, m). ^{13}C NMR: 21.69 (p-CH$_3$), 21.87 (p-CH$_3$), 35.85 (NCH$_3$), 37.52 (NCH$_3$), 128.95, 129.44, 129.53, 129.58, 129.72, 130.05, 131.13, 132.76, 143.57, 145.04, 162.21 (C=N), 171.67 ((O=*C*-N(CH$_3$)$_2$)), 197.46 (C=O). IR (KBr): 2915, 1655, 1606, 1389, 1233, 1178, 1150, 922 cm^{-1}. MS m/z (rel.int.%): 308 (M$^+$, 1), 266 (0.5), 236 (2), 189 (8), 119 (56), 91 (20), 72 (100), 65 (10), 44 (1). $C_{19}H_{20}N_2O_2$ Calcd.308.1524 found 308.1567. Elemental analysis: C 74.20, H 6.30, N 9.00 calcd. C 74.00, H 6.54, N 9.08. R$_f$ 0.38. Yield 10%.

4-N,N-Dimethylcarbamoyl-2,3-di-(3-methoxyphenyl)-4-aza-1-oxa-1,3-butadiene (**5c**): Oil. ^{1}H NMR: 2.94 (3H, s, NCH$_3$), 3.17 (3H, s, NCH$_3$), 3.82 (3H, s, OCH$_3$), 3.84 (3H, s, OCH$_3$), 7.04-7.55 (8H$_{Arom}$, m). ^{13}C-NMR: 35.90 (NCH$_3$), 37.57 (NCH$_3$), 55.41 (OCH$_3$), 55.44 (OCH$_3$), 112.00, 112.83, 119.09, 120.92, 121.94, 122.11, 122.69, 123.26, 129.85, 130.06, 134.99, 136.26, 159.81, 159.89, 161.83 (C=N), 171.76 ((O=*C*-N(CH$_3$)$_2$)), 197.38 (C=O). IR (nujol): 2920, 1661, 1577, 1489, 1261, 1150, 1033 cm^{-1}. MS m/z (rel.int.%): 340 (M$^+$, 6), 268 (0.5), 207 (8), 135 (35), 107 (6), 72 (100). $C_{19}H_{20}N_2O_4$ Calcd. 340.1422 found 340.1482. Elemental analysis: C 67.23, H 5.90, N 8.17, calcd. C 67.05, H 5.92, N 8.23. R$_f$ 0.36. Yield 32%.

4-N,N-Dimethylcarbamoyl-2,3-di-(4-methoxyphenyl)-1-oxa-4-aza-1,3-butadiene (**5d**): MS m/z (rel.int.%): 340 (M$^+$, 7), 262 (1), 207 (10), 148 (2), 135 (32), 107 (4), 92 (1), 72 (100), 28 (3).

3-N,N-Dimethylcarbamoylamino-2methyl-1-oxa-1,3-butadiene (**5e**): M.p. 56-57 °C. ^{1}H NMR: 2.40 (3H, s, CH$_3$), 2.96 (6H, s, NCH$_3$), 5.59 (1H, s, H-CH), 6.60 (1H, s, H-CH), 7.44 (1H, wide s, NH). ^{13}C NMR: 23.80 (CH$_3$), 36.15 (N(CH$_3$)$_2$), 106.73 (H$_2$*C*=C), 139.08 (H$_2$C=*C*-NH), 155 ((O=*C*-N(CH$_3$)$_2$)), 195 (C=O). IR (KBr): 3389, 2911, 1655, 1522, 1378, 1289, 1194, 894 cm^{-1}. MS m/z (rel.int.%): 156 (M$^+$, 31), 141 (2), 113 (12), 72 (100), 56 (2), 44 (8), 28 (2). $C_7H_{12}N_2O_2$ Calcd. 156.0898 found 156.0884. Elemental analysis: C 53.60, H 7.68, N 18.00 calcd. C 53.82, H 7.75, N 17.94. R$_f$ 0.18. Yield 35%.

1,4-Di-(N,N-dimethylcarbamoyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene (**10a**): M.p.170-170.5°C. ^{1}H NMR: 2.96 (6H, s, NCH$_3$), 3.02 (6H, s, NCH$_3$), 7.32-7.80 (10H$_{Arom}$, m). ^{13}C NMR: 35.79 (NCH$_3$), 37.24 (NCH$_3$), 128.57, 128.96, 132.02, 135.11, 162.11(C=N), 171.70 ((O=*C*-N(CH$_3$)$_2$)). IR (KBr): 2933, 1654, 1616, 1490, 1447, 1398, 1164, 989 cm^{-1}; MS m/z (rel.int.%): 350 (M$^+$, 1), 306 (41), 262 (16), 234 (3), 206 (1), 193 (0.4), 165 (1), 103 (7), 44 (3). $C_{20}H_{22}N_4O_2$ Calcd.350.350.1741, found 350.1780. Elemental analysis: C 68.28, H 6.23, N 15.98 calcd. C 68.55, H 6.33, N 15.98. R$_f$ 0.10. Yield 23% (mol ratio **1a**:**2**=1:1). Yield 55% (mol ratio **1a**:**2**=1:2).

1,4-Di-(N,N-dimethylcarbamoyl)-2,3-di-(4-methylphenyl)-1,4-diaza-1,3-butadiene (**10b**): M.p.152-153°C. ^{1}H NMR: 2.32 (6H, s, p-CH$_3$), 2.94 (6H, s, NCH$_3$), 3.00 (6H, s, NCH$_3$), 7.12-7.18 (4H$_{Arom}$), 7.69-7.75 (4H$_{Arom}$). ^{13}C NMR: 21.58 (p-CH$_3$), 35.75 (NCH$_3$), 37.19 (NCH$_3$), 128.98, 129.30, 132.65, 142.65, 162.30 (C=N), 171.23 ((O=*C*-N(CH$_3$)$_2$)). IR (KBr): 2929, 1652, 1600, 1397, 1267, 1161, 940 cm^{-1}. MS m/z (rel.int.%): 378 (M$^+$, 1), 334 (25), 306 (0.1), 290 (15), 262 (1), 247 (0.4), 217 (1), 207 (1), 189 (2), 117 (6), 72 (100), 44 (4); $C_{22}H_{26}N_4O_2$ Calcd. 378.2054 found 378.2091. Elemental analysis: C 70.20, H 6.89, N 14.77, calcd. C 69.82, H 6.92, N 14.80. R$_f$ 0.13. Yield 30% (mol ratio **1b**:**2**= 1:1). Yield 65% (mol ratio **1b**:**2**= 1:2).

1,4-Di-(N,N-dimethylcarbamoyl)-2,3-di-(3-methoxyphenyl)-1,4-diaza-1,3-butadiene (**10c**): M.p. 147-148°C. ^{1}H NMR: 2.95 (6H, s, NCH_3), 3.02 (6H, s, NCH_3), 3.78 (6H, s, OCH_3), 6.95-7.50 ($8H_{Arom}$, m). ^{13}C NMR: 35.78 (NCH_3), 37.24 (NCH_3), 55.29 (OCH_3), 112.78, 118.35, 122.29, 129.58, 136.44, 159.57 (*C*-OCH_3), 161.09 (C=N), 171.30 ((O=*C*-$N(CH_3)_2$)). IR (KBr): 2933, 1661, 1622, 1577, 1478, 1433, 1395, 1317, 1289, 1267, 1161, 1044, 989, 694 cm^{-1}. MS m/z (rel. int.%): 410 (M^+,7), 366 (40), 322 (13), 296 (1), 205 (1), 133 (7), 103 (2), 72 (100), 44 (3). $C_{22}H_{26}N_4O_4$ Calcd. 410.1952 found 410.2013. Elemental analysis: C 64.62, H 6.59, N 13.60 calcd. C 64.38, H 6.38, N 13.65. R_f 0.10. Yield 24% (mol ratio **1c**:**2**= 1:1). Yield 60% (mol ratio **1c**:**2**=1:2).

1,4-Di-(N,N-dimethylcarbamoyl)-2,3-di-(4-methoxyphenyl)-1,4-diaza-1,3-butadiene (**10d**): M.p.175-175.5°C. ^{1}H NMR: 2.94 (6H, s, NCH_3), 3.00 (6H, s, NCH_3), 3.78 (6H, s, OCH_3), 6.79-7.87, 7.73-7.81 ($8H_{Arom}$,m). ^{13}C NMR: 35.79 (NCH_3), 37.22 (NCH_3), 55.38 (OCH_3), 113.96, 128.15, 131.00, 162.41 (*C*-OCH_3), 162.67 (C=N), 171.50 ((O=*C*-$N(CH_3)_2$)). IR (KBr): 2922, 1644, 1600, 1572, 1505, 1389, 1244, 1155, 1017, 833, 633 cm^{-1}. MS m/z (rel.int.%): 410 (M^+ ,8), 366 (42), 322 (13), 205 (1), 133 (79, 103 (2), 72 (100), 44 (4). $C_{22}H_{26}N_4O_4$ Calcd. 410.1952 found 410.1865. Elemental analysis:C 64.75, H 6.53, N 13.58 calcd. C 64.38, H 638, N 13.65. R_f 0.11. Yield 35% (mol ratio **1d**:**2**=1:1). Yield 65% (mol ratio **1d**:**2**=1:2).

1:2 Adducts of compounds **1e** *and* **2**. MS m/z (rel.int.%): 226 (M^+, 24), 212 (2), 183 (11), 169 (1), 154 (5), 140 (21), 124 (2), 113 (8), 99 (1), 72 (100), 56 (2), 44 (3), 43 (7), 28 (7), 15 (1).

X-RAY CRYSTALLOGRAPHIC ANALYSIS

The data of a crystal of **10a** with the approximate dimensions 0.38 x 0.31 x 0.23 Å^3 were obtained with a Nicolet R3m/V four circle diffractometer (MoK_α-radiation, graphite-monochromator) at 293 K. Cell dimensions were refined from diffractometer angles of 50 reflections in the 2Θ-range 20-25°. Cell constants: $a = b = 9.280(1)$, $c = 19.321(1)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$. Volume V = 1441.5(3) Å^3, space group $P\,3_1$ (Nr. 144), formula units per cell Z = 3, density $\rho_{ber} = 1.213$ g/cm^3, absorption coefficient $\mu = 0.081$ mm^{-1}, $2\Theta_{max} = 45°$, 2105 unique intensities, of which 1917 ($F_o \geq 4\sigma(F_o)$) were observed, measured in 2Θ :ω-scan technique. The structure was solved using Direct Methods and refined on F using SHELXTL-Plus (Vers.4.2). 212 parameters, phenyl groups refined with idealized geometries, an anisotropic displacement parameters for all atoms except hydrogen atoms, groupewise isotropic displacement parameters all hydrogen atoms, treated as rigid groups. R = 0.0477, $R_w = 0.0554$, $w^{-1} = \sigma^2(F_o) + 0.005357 \cdot F_o^2$, maximum residual electon density 0.29 e/Å^3. Bond lengths and bond angles are given in Tables 2-3. Further details of the crystal structure investigations are available on request from Cambridge Crystallographic Data Center.

Table 2. Bond Lengths (Å).

N (1)-C (1)	1.406 (4)	N (1)-C (2)	1.275 (6)
N (2)-C (1)	1.336 (7)	N (2)-C (17)	1.465 (8)
N (2)-C (18)	1.455 (5)	N (3)-C (9)	1.433 (7)
N (3)-C (10)	1.263 (5)	N (4)-C (9)	1.316 (6)
N (4)-C (19)	1.458 (10)	N (4)-C (20)	1.471 (6)
O (1)-C (1)	1.226 (6)	O (2)-C (9)	1.232 (5)
C (2)-C (3)	1.477 (4)	C (2)-C (10)	1.512 (5)
C (10)-C (11)	1.486 (6)		

Table 3. Bond Angles (°).

C (1)-N (1)-C (2)	120.9 (3)	C (1)-N (2)-C (17)	122.3 (4)
C (1)-N (2)-C (18)	120.2 (4)	C (17)-N (2)-C (18)	117.5 (5)
C (9)-N (3)-C (10)	120.0 (3)	C (9)-N (4)-C (19)	119.9 (4)
C (9)-N (4)-C (20)	123.2 (5)	C (19)-N (4)-C (20)	116.8 (4)
N (1)-C (1)-N (2)	114.2 (4)	N (1)-C (1)-O (1)	121.8 (5)
N (2)-C (1)-O (1)	123.8 (4)	N (1)-C (2)-C (3)	119.0 (3)
N (1)-C (2)-C (10)	123.6 (3)	C (3)-C (2)-C(10)	117.4 (3)
C (2)-C (3)-C (4)	119.4 (2)	C (2)-C (3)-C (8)	120.6 (2)
N (3)-C (9)-N (4)	114.3 (3)	N (3)-C (9)-O (2)	120.7 (5)
N (4)-C (9)-O (2)	124.8 (6)	N (3)-C (10)-C (2)	124.8 (4)
N (3)-C (10)-C (11)	118.2 (3)	C (2)-C (10)-C (11)	116.9 (3)
C (10)-C (11)- C (12)	120.6 (2)	C (10)-C (11)-C (16)	119.3 (2)

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