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Heterocycles from Heterocycles. 1,3-Diaryl-4,5-imidazolidinediones from 1,3,5-Triarylhexahydro-1,3,5-triazines and Oxalyl Chloride

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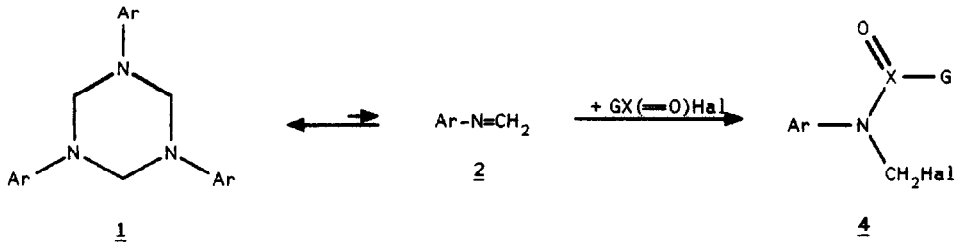
Abstract: 1,3-Diaryl-4,5-imidazolidinediones (6) are easily synthesized from 1,3,5-triarylhexahydro-1,3,5-triazines (1) and oxalyl chloride (5) in a reaction not likely to involve the zwitterionic intermediate (3) of the N-methylenearylamine dimer, but viewing the sequential pick up of two units of the monomer (2) by oxalyl chloride (5) The essential role of ethyl alcohol added to the reaction mixture is recognized Reaction conditions have been optimized and some ten imidazolidinediones (6) were prepared in good to excellent yields Geometric parameters of 6 were obtained by X-ray diffraction analysis all the nuclei are found almost in one plane except for a small twist of the phenyl rings about the C-N bond

INTRODUCTION

1,3,5-Triarylhexahydro-1,3,5-triazines (1), the cyclic trimers[1] of the elusive N-methylenearylamines[2] (2) may be induced to react as 2 or the dimeric zwitterion[3] 3 by interaction with substrates with strongly polarized bonds.[4] It is not clear in most cases whether depolymerization occurs first, either thermally or induced by an added catalyst or whether the substrate attacks 1 directly, causing a reaction sequence all the way down to the observed products.

The employment of 1 to yield heterocycles has been recorded in the literature for the patented preparation of 1,3-diaryl-1,3-(5-thiadiazine)-6-thiones from the reaction of 1 with carbon disulphide.[5] On a different front, the reaction of 1 with G-X(=O)Hal is documented,[6] but not that with bifunctional compounds of the type $G(X[=O]Hal)_2$.



1 2 4

Most of the pertinent work has appeared in the form of patents and 4 were usually poorly characterized intermediates of processes leading to other final products.

RESULTS AND DISCUSSION

The reaction between 1 and oxalyl chloride 5 has now been investigated and developed into a very convenient way of obtaining N,N'-diaryl-4,5-imidazolidinediones (6) (Table 1), a class of compounds so far unreported.

Table 1. 1,3-Diaryl-4,5-imidazolidinediones (6) Prepared.

Triazine (Ar)	Product	Yield[a] (%)	mp (°C)	Crystallization solvent
1a (C_6H_5)	6a	83	269	ethyl acetate
1b (3-Me-C_6H_4)	6b	80	217	ethyl acetate/dichloromethane
1c (4-Me-C_6H_4)	6c	90	>290	ethyl acetate/dichloromethane
1d (4-^{t}Bu-C_6H_4)	6d	55	261	ethyl acetate
1f (2-F-C_6H_4)	6f	60	182	ethyl acetate/trichloromethane
1g (3-F-C_6H_4)	6g	90	251[b]	ethyl acetate/dichloromethane
1h (4-F-C_6H_4)	6h	80	266	ethyle acetate/dichloromethane
1i (3-Cl-C_6H_4)	6i	93	247	ethyl acetate/dichloromethane
1j (4-Cl-C_6H_4)	6j	90	267	ethyl acetate/dichloromethane
1k (3-Br-C_6H_4)	6k	67	268	ethyl acetate/dichloromethane

[a]Yield of recrystallized product [b]Decomposition temperature.

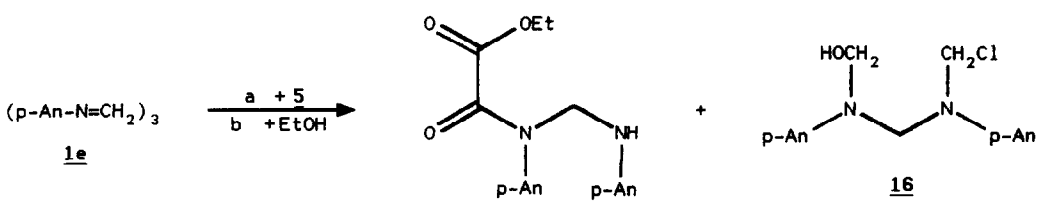
The parent molecule itself, an isomer of the well known compound hydantoin (imidazolidine-2,3-dione), is not known and only two 1,3-derivatives, namely 1,3-dimethyl--4,5-imidazolidinedione[7] and 1,3-dibenzoyl-4,5-imidazolidinedione,[8] were described to date.

Our synthetic procedure calls for the portionwise addition of 5 to an equimolecular amount of 1 in diethyl ether at 0°C, immediately followed by a necessary termination of the reaction with ethanol. Two different courses may be envisaged to rationalize the outcome. If the monomer (2), either in fast equilibrium with the trimer or originating from the induced decomposition of 1 is to be involved, pathway A should be at work (Scheme 1) On the other hand, the dimeric zwitterionic species 3 may be active, thus facilitating pathway B.

Headspace analysis ruled out the presence of CH_2Cl_2, but both diethoxymethane (7) and ethoxymethylchloride (8) were detected, the former coming from ethanolysis of the latter in solution. This observation pointed to an essential role of the alcohol in carrying out the reaction and ruled out the initial intervention of 3 In fact, it is conceivable that 9, if formed, would rapidly evolve to 10, in turn bound to undergo fast reaction with the naked chloride ion to produce 6: but, beside the absence of CH_2Cl_2, ethanol was found to play an essential role

The monomer 2 is, on the other hand, expected to react promptly with 5 to form the intermediate 11 and furthermore to give 12, which, apparently unable to undergo ring closure to 10, survives until ethanol is added and the key intermediate 13 is generated. This, in turn, either undergoes ring closure to **6a-k** or further competitive ethanolysis to the constantly observed by-product oxalamides **14a-k**.

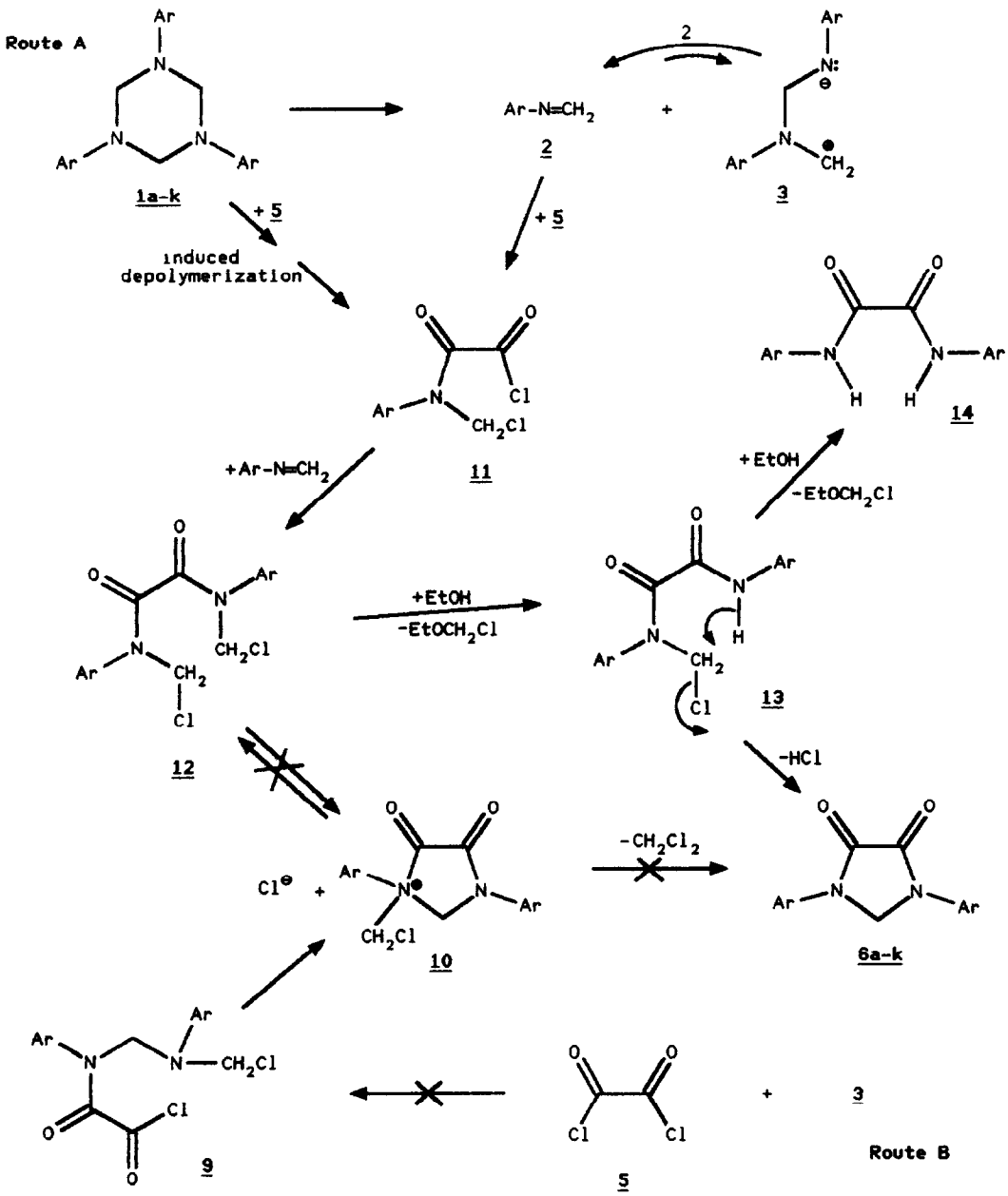
Indirect support for this hypothesis was offered by the reaction between 1,3,5--tri(4-anisyl)hexahydro-1,3,5-triazine (1e) and oxalyl chloride 5 in its devious behaviour: enhanced stabilization of 3 sparked route B, which did not lead to 6e, but to N-ethoxy-oxalyl-di(4-anisylamino)methane (15), detected by direct inlet MS analysis on the reaction mixture, together with another side product, tentatively identified as N-chloromethyl-N'--hydroxymethyl-di(4-anisylamino)methane (16)



1e 15 16

It is possible that for aliphatic 1 to react, decomposition must be induced by direct attack of 3

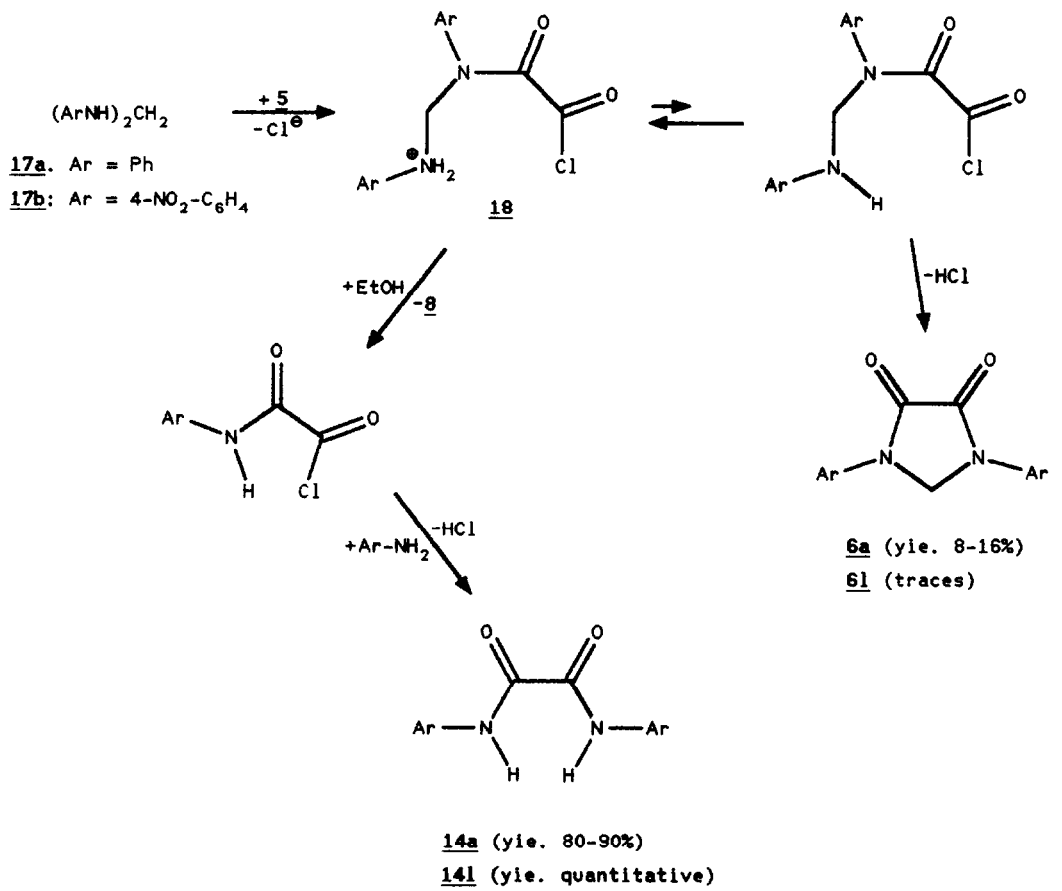
Scheme 1


Route A
1a-k
+ 5
induced depolymerization
Ar-N=CH2
2
3
11
14
+Ar-N=CH2
+EtOH
-EtOCH2Cl
12
13
-HCl
Cl⊖ +
10
-CH2Cl2
6a-k
9
5
Route B

No systematic work was carried out to optimize the yield of 6 in the reactions between 1a and 5, but a few useful experimental observations were made in adjusting the conditions for the reaction of 1a, which were essentially applied to the other substrates. Good solvents for 1, like dioxane and chloroform, were detrimental; the best results were obtained when 1 was added to 5. The use of anhydrous solvents and absolute ethanol gave better yields

An alternate route to 6 was attempted by reaction of aminal N,N'-diphenylaminomethane (17a) with 5 under a variety of experimental conditions, but in all instances the oxamide 14a was by far the main product, accompanied by much lower yields of 6a (Scheme 2).

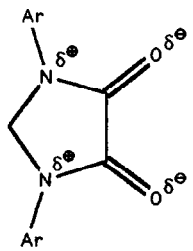
Scheme 2



In the above scheme the cause for the low yields is to be found in the production of acidity which ties up the intermediate (18) in an unreactive form. In fact, we found that practically all of 6a was formed in this reaction before alcohol addition.

All the products 6a–k showed insolubility in most common solvents and exceptionally high melting points which are also indicative of their extraordinary thermal stability

The steadfastness of the crystal structure points to strong intermolecular polar interactions· in fact, the isolated molecules present two sides of opposite polarities



In view of the novelty of the molecules and these properties of the solids, we undertook an X-ray crystal structure determination of 6a.

Worth noticing are the following features of 6a (Figure 1, mean values are quoted)

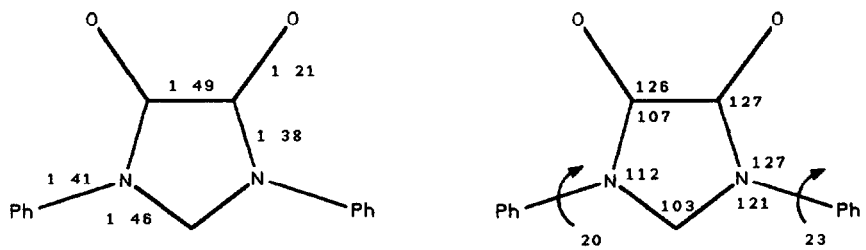
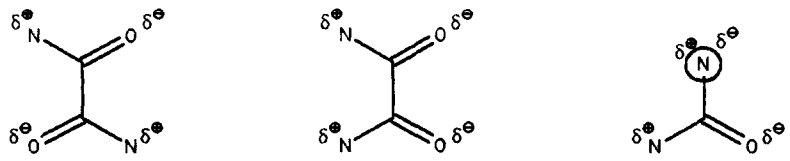


Figure 1. Average values of molecular dimensions and bond angles of 6a.

The slight twisting in the same direction of the phenyl groups, placing them almost on the same plane with respect to the heterocyclic ring, would not inhibit some conjugation as indicated by the Ar–N distance (1 41 Å), above that (1 39 Å) found for a perfectly planar arylamine,[9] and definitively larger than for less conventional amides of this type (1 36 Å) [10] The angle at the saturated carbon is smaller than that expected for a pure sp^3 hybridization, leaving a larger *s* contribution for the bonds with the hydrogens A comparison with open chain oxamides[11,12] has to take into account that these systems show a torsional angle of about 90° around the OC–CO axis which is extraordinarily elongated (*ca* 1 54 Å), the result of the likely charged oxygen, carbon and nitrogen repulsions (Figure 2)

The only possible response of 6a is the widening of the OCC bond angles to a value of 126° against 117° for the open chain case which would cause a quite short O-O distance As a consequence the ring NCC bond angles are squeezed to a meager value of 107° from 117° observed in the open chain cases.



I II III

Figure 2. Conformations of open oxamides

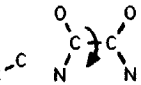
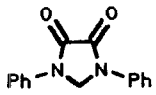
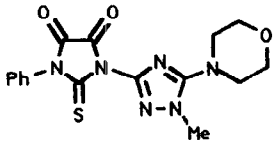
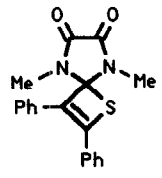
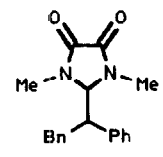
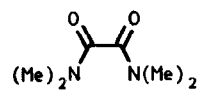
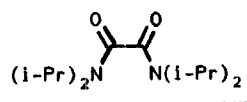
Planar ring enclosed oxamides, like 6a, can only exist in the high energy form II, where likely charges are the closest. Different steric requirements in open oxamides may allow for perpendicular geometries III more or less approaching the ideal lowest electrostatic energy configuration I Entropic factors play a role in the equilibrium positions.

Literature structural data for the heterocyclic system present in 6a are few and some were collected for more substituted derivatives (Table 2) Noteworthy is the contraction by *ca.* 0 04 Å of the C_1-C_2 bond (Figure 3 and Table·2) found in 6a in comparison with all other similar cases [13] Similarly the CCO angle is strongly widened by the oxygen repulsion to a value of 126° in all these systems as well as in 6a. The N-CO bond of 6a is some 0 02 Å larger than in formamide[14] and *ca.* 0.04 Å larger than that of the 1,2,3-trisubstituted 1,3-imidazolidine-4,5-diones investigated,[15] differences which are too small to evince any special conclusion. The practically invariant C=O distance, actually coincident with that of formaldehyde,[16] though, point to an imperfect NCO amide conjugation. Oddly enough, the N-atom seems to be more conjugated with the ring. But, as we shall see, the ^{1}H NMR data will introduce a contradiction here

The nature of the obtained products 6 was confirmed by elemental analysis and their MS and spectroscopic properties. Mass spectra of 6a-k exhibited parent ions of medium intensity with the exception of the low intensity observed for the chloro-derivatives 6i and 6j. The common features of the ion decompositions are shown in scheme 3, which specifically refers to the ion derived from 6a; the composition of the ion at m/z 105 was secured by high resolution mass spectrometry which ruled out the presence of $PhCO^{\oplus}$

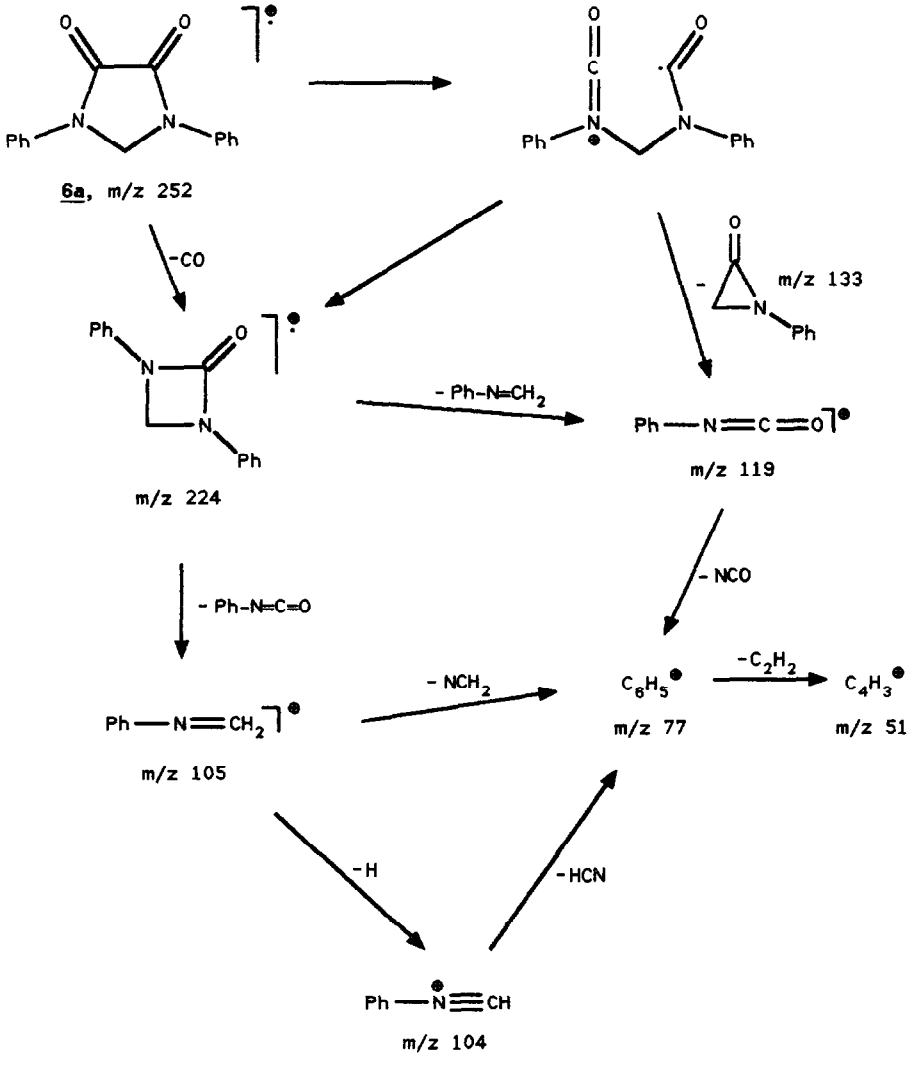
The peak formally ascribed to the N-methylenearylamine radical cation was consistently the base peak in all spectra of 6a-k. Of interest is the formal loss of an aziridone (133 mu) from the parent ion of 6a to produce what is likely the molecular ion of an arylisocyanate molecule (Table 3)

Table 2

Compound \ Molecular parameters	N-C (Å)	N-exoC (Å)	N-CO (Å)	C=O (Å)	OC-CO (Å)	N-C-N (°)	C-N-C (°)	N-C-C (°)	N-C-O (°)	O-C-C (°)	 (°)	Ref
6a 	1.46	1.41	1.38	1.21	1.49	103 0	112.0	107 0	127 0	126 0	0	this work[a]
	1 39	1.44	1.38	1.19	1 52	106.2	111 6	105.3	127 5	127 3	0	13a[b]
	1 43	1 45	1.35	1 22	1.52	102.8	112 6	105 8	127 5	126 7	0	13b
	1 45	1 45	1 34	1 22	1.51	101 3	113.2	106 0	127.3	126 7	0	13b
		1.46	1.32	1.23	1.53		112.0	118 0	124 0	118 0	114 0	11
		1 51	1.34	1.22	1.53		112 0	117.0	125.5	117.5	92 0	12

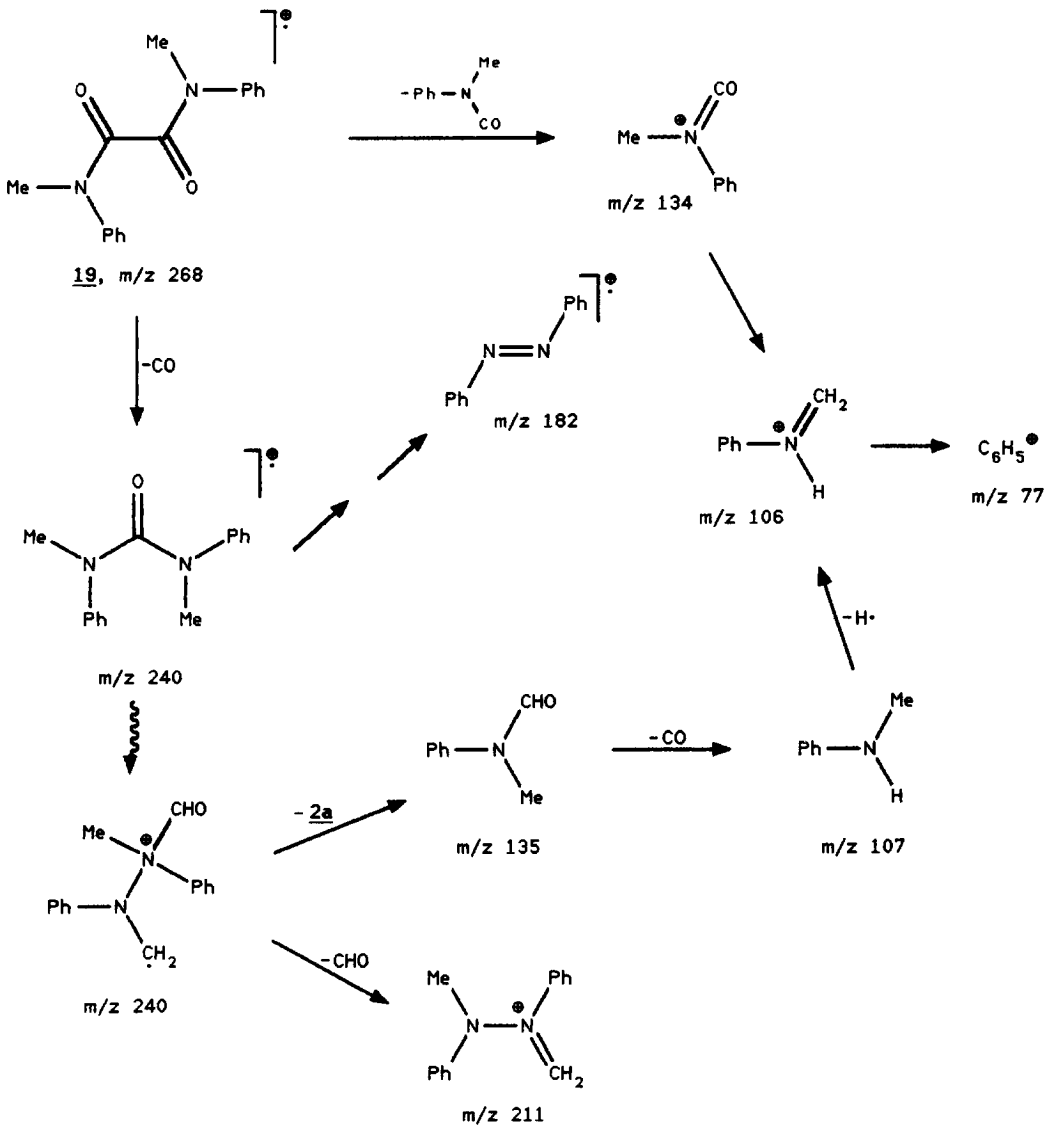
[a]Average values between **6a'** and **6a"** [b]Reported values refer to S=C-N(Ph)-CO-CO system

Scheme 3



Comparison of this spectral pattern with the fragmentation of the closely related open oxamide N,N'-dimethyl-N,N'-diphenyloxamide (19) indicated that the trigger for all of the observed fragments is the cleavage of the sigma bond between the two carbonyls (Scheme 4)

Scheme 4



The crystals of 6a, made up of two independent molecules 6a' and 6a'' with slightly different geometric parameters (Table 4 and Figure 3), exhibited a very compact packing, as indicated by their high density (1 36 g/ml)

Table 3 Properties of 1,3-Diaryl-4,5-imidazolidinediones (6)

Compound	IR[a] (cm^{-1})	^1H NMR[b] (δ, ppm; J, Hz)	MS[c] (m/z, rel%)
6a	1725vs, 1590s, 1490vs, 1455s, 1405vs, 1290s, 1275s, 745vs, 680s	5.66(s, 2H), 7.27-7.35(m, 2H), 7.47-7.57(m, 4H), 7.93(d, 4H, J=8.00)	252(M^+, 23), 119(6), 106(7), 105(100), 77(38), 64(4), 51(16)
6b	1715vs, 1485s, 1400vs, 1290s, 1180m, 790m, 685m	2.43(s, 6H), 5.46(s, 2H), 7.10-7.63(8H, m)	280(M^+, 69), 133(13), 120(22), 119(100), 118(57), 104(6), 91(60), 77(8), 65(21), 51(6)
6c	1735vs, 1610s, 1510s, 1400s, 1300s, 1280s, 815s	2.36(s, 6H), 5.40(s, 2H), 7.27(d, 4H J=9.00), 7.65(d, 4H, J=9.00)	280(M^+, 60), 133(21), 120(22), 119(100), 104(7), 91(70), 77(8), 65(23), 51(8)
6d	2930m, 1725vs, 1510m, 1430m, 1385s, 1300m, 1270m, 830s	1.33(s, 18H), 5.44(s, 2H), 7.48(d, 4H, J=9.00), 7.68(d, 4H, J=9.00)	364(M^+, 32), 349(42), 175(9), 167(20), 161(47), 160(80), 146(100), 132(18), 118(19), 106(6), 91(7), 77(7), 44(21)
6f	1740vs, 1500vs, 1460s, 1410vs, 1310s, 1270s, 1230s, 810s, 755vs	5.48(s, 2H), 7.19-7.45(m, 6H), 7.70-7.80(m, 2H)	288(M^+, 59), 137(11), 124(17), 123(100), 122(85), 109(7), 95(38), 75(18), 57(5)
6g	1730vs, 1610s, 1590s, 1490vs, 1460s, 1420s, 1400s, 1190s, 770s	5.49(s, 2H), 6.99-7.12(m, 2H), 7.40-7.55(m, 4H), 7.66-7,75(m, 2H)	288(M^+, 31), 137(6), 123(100), 122(45), 96(5), 95(29), 75(10)
6h	1730vs, 1710vs, 1500s, 1400s, 1240vs, 1160m, 1090m, 830s	5.47(s, 2H), 7.15-7.30(m, 4H), 7.70-7.85(m, 4H)	288(M^+, 26), 137(9), 123(100), 122(47), 95(29), 75(9), 57(3)

(continued)

Table 3. (continuation)

Compound	IR[a] (cm^{-1})	^1H NMR[b] (δ, ppm; J, Hz)	MS[c] (m/z, rel%)
6i	1725vs, 1590s, 1470s, 1410s, 1270m, 1105m, 870m, 775s, 670m	5.49(s, 2H), 7.25-7.48(m, 4H), 7.70-7.81(m, 4H)	324(M^+, 1), 322(M^+, 8), 320 (M^+, 14), 155(1), 153(5), 141(32), 139(100),138(31), 111(21), 77(7), 75(12), 51 (7)
6j	1735vs, 1495s, 1395vs, 1270m, 1090m, 825vs, 810m	5.48(s, 2H), 7.47(d, 4H, J=9.00), 7.72-7.80(d, 4H, J=9.00)	324(M^+, 3), 322(M^+, 17), 320 (M^+, 27), 155(5), 153(15), 141(42), 139(100), 138(45), 111(27), 77(6), 75(15)
6k	1725vs, 1580s, 1470vs, 1415s, 1400vs, 1305s, 1260s, 1090s, 760vs, 665s	5.50(s, 2H), 7.32-7.47(m, 4H), 7.75-7.93(m, 4H)(M^+, 10), 199(5),	412(M^+, 9), 410(M^+, 21), 408 197(5), 185(99), 183(100),157(19), 155(19), 90(13), 77(26), 51 (17)

[a]Spectra were recorded in KBr. [c]Spectra recorded in $CDCl_3$ solution using TMS as internal standard.
[d]Spectra recorded via direct inlet.

Table 4. Most Significant Geometrical Characteristics of the Refined Molecules

Bond Lengths (Å)

O(1) - C(1)	1.203(7)	N(2) - C(10)	1 396(9)
O(2) - C(2)	1.216(7)	N(3) - C(16)	1.375(8)
O(3) - C(16)	1 222(7)	N(3) - C(18)	1 458(7)
O(4) - C(17)	1 205(8)	N(3) - C(19)	1 409(8)
N(1) - C(1)	1.377(8)	N(4) - C(25)	1 424(8)
N(1) - C(4)	1 422(8)	N(4) - C(18)	1 452(7)
N(1) - C(3)	1.458(7)	N(4) - C(17)	1 380(8)
N(2) - C(2)	1.379(8)	C(16) - C(17)	1.502(9)
N(2) - C(3)	1.467(8)	C(1) - C(2)	1.485(8)

Bond Angles (°)

C(4) - N(1) - C(3)	119.8(5)	O(2) - C(2) - C(1)	126.3(6)
C(1) - N(1) - C(3)	111 7(5)	O(2) - C(2) - N(2)	127 5(5)
C(1) - N(1) - C(4)	128.6(5)	N(3) - C(18) - N(4)	102 7(4)
C(3) - N(2) - C(10)	120.8(5)	N(4) - C(17) - C(16)	105.2(5)
C(2) - N(2) - C(10)	127.1(5)	O(4) - C(17) - C(16)	126.2(6)
C(2) - N(2) - C(3)	112.1(5)	O(4) - C(17) - N(4)	128.6(6)
C(18) - N(3) - C(19)	121.1(5)	N(1) - C(4) - C(9)	121.3(6)
C(16) - N(3) - C(19)	127.3(5)	N(1) - C(4) - C(5)	117.9(5)
C(16) - N(3) - C(18)	111.6(5)	N(1) - C(3) - N(2)	102.6(4)
C(18) - N(4) - C(17)	112.9(5)	N(3) - C(19) - C(24)	119.1(5)
C(25) - N(4) - C(17)	126.8(5)	N(3) - C(19) - C(20)	121.1(5)
C(25) - N(4) - C(18)	120.3(5)	N(2) - C(10) - C(15)	120.1(6)
O(3) - C(16) - N(3)	127.5(5)	N(2) - C(10) - C(11)	122.2(6)
N(3) - C(16) - C(17)	107.3(5)		
O(3) - C(16) - C(17)	125.2(6)		
N(4) - C(25) - C(30)	119.9(6)	Selected Torsion Angles (°)	
N(4) - C(26) - C(26)	120.4(6)		
O(1) - C(1) - N(1)	126.5(6)	C(1) - N(1) - C(4) - C(5)	21.0(9)
N(1) - C(1) - C(2)	107 4(5)	C(3) - N(2) - C(10) - C(15)	-24.0(9)
O(1) - C(1) - C(2)	126.2(6)	C(18) - N(3) - C(19) - C(24)	19.3(8)
N(2) - C(2) - C(1)	106.2(5)	C(18) - N(4) - C(25) - C(30)	-22.0(8)

The molecules are stacked in the crystals like parallel columns; the columns, contacting each other by a slight overlapping of the *meta*-position of a phenyl ring and the *para*-position of a phenyl ring of the adjacent column, are made up of piles of alternating molecules 6a' and 6a'', where the heterocyclic ring of one is almost parallel to the second phenyl ring of the other. The relative positions of these molecular sections are indicative of some electrostatic interaction between the negatively charged oxygens and the electron impoverished phenyl ring.

^{1}H NMR spectra of 6 in $CDCl_3$ showed the expected pattern with a sharp singlet for the methylene group localized at δ values between 5.40 and 5.66 ppm from the standard tetramethylsilane (Table 3). Whereas the aryl protons appeared in three well separated regions, *para*-substituted 6 showed two types of resonances: all of them were located at between 7.10 and 8.00 ppm (Table 3), positions definitively at lower field than for aniline,[17] N,N-dimethylaniline[18] and N-methyl-N-formylaniline[19] and their corresponding derivatives These data are an indication of a somewhat strong electron depletion away

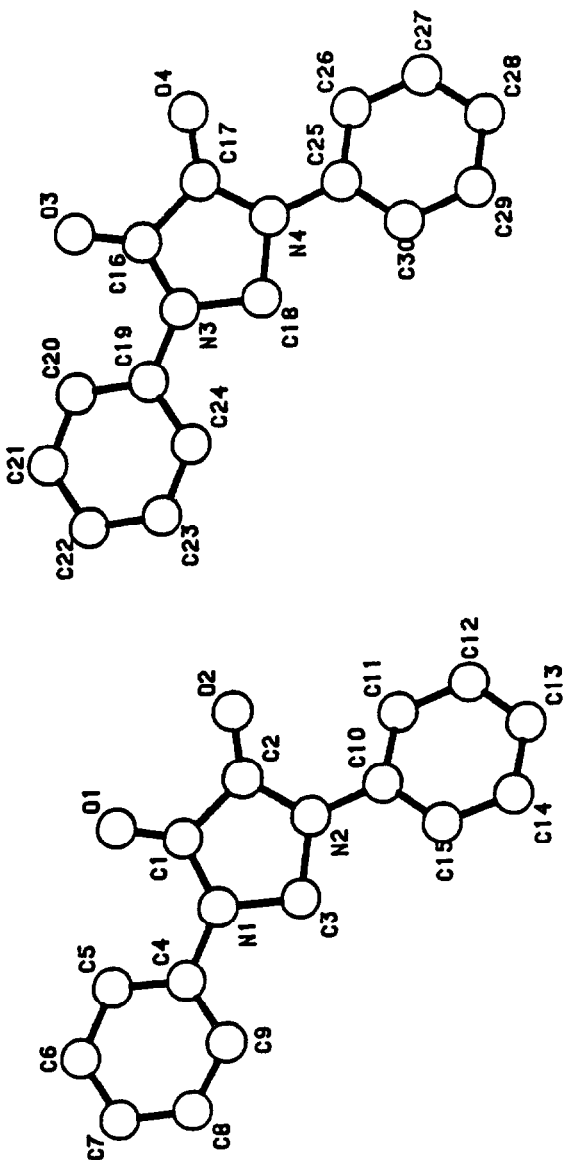


Figure 3. Two independent molecules with the numbering scheme viwed along the normal to the five membered ring

from the aromatic ring into the amide function.

An indirect confirmation of the positive polarization of thr aromatic rings came from the packing of the molecules 6a' and 6a'' in the crystals with the oxygens of one just on top of the carbons of phenyl ring, two such interaction being active for every single molecule with slightly different positionings This appears to be due to the strong polar intermolecular attraction playing an important part in holding the molecules together in the crystals.

A full view of the crystal packing is offered by figure 4a and 4b, where a side by side columnar packing of the stacked molecules, with any two columns barely "touching" with the free phenyls, is evidenced. The closest distance between the phenyl ring of one molecule 6a' and the related heterocyclic ring of the other (6a'') was found to be 3 6 Å, well beyond any charge transfer interaction.

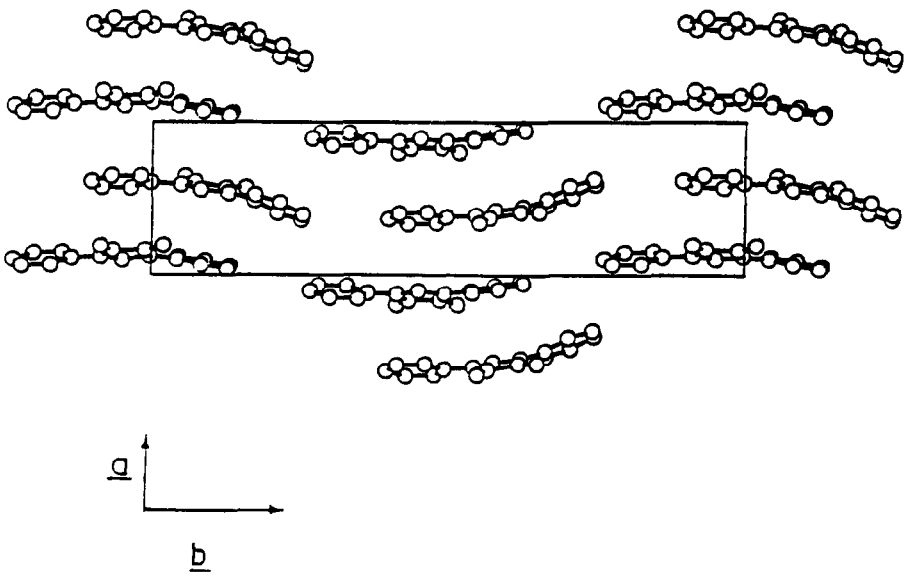


Figure 4a. General view of crystal packing of 6a.

The huge hypsochromic shift of the carbonyl stretching frequency (1725 cm^{-1}) of 6a and the range 1715-1740 cm^{-1} for 6b-k (Table 3) compared with the pratically coincidental values for N-methylacetamide (20) (1656 cm^{-1}) and N,N'-dimethyl-N,N'--diphenyloxamide (19) (1650-1665, doublet) is due to the combined effect of enhanced carbonyl character and, therefore lesser delocalization of electrons from the nitrogen atom, and ring strain [20]

This may be simply a descreening effect by the nitrogen lone pairs or an overwhelming field electron withdrawing σ-effect. This effect overlaps with some much less effective π-electron transfer from the nitrogen to the ring.

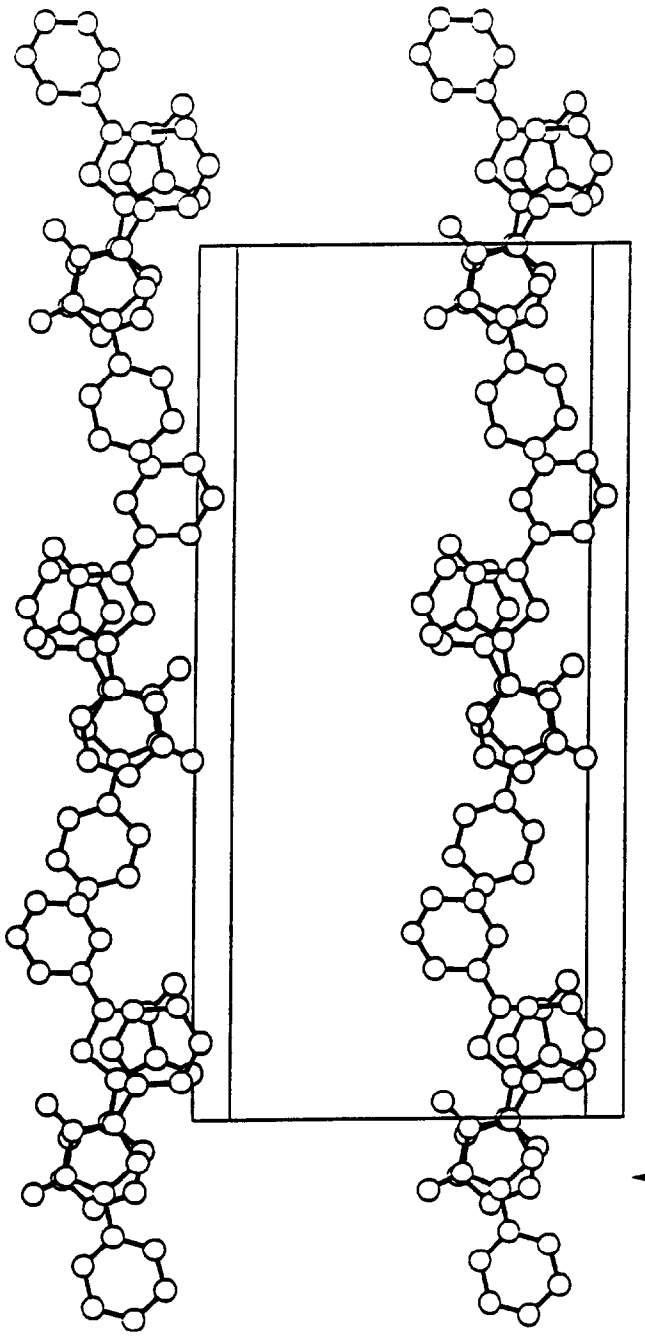


Figure 4b. Detailed view of crystal packing of 6a.

EXPERIMENTAL SECTION

Materials. Oxalyl chloride (5) and primary aromatic amines (2) were commercially available (Aldrich, Milano, Italy)· they were conveniently purified before use and used to prepare the 1,3,5-triarylhexahydro-1,3,5-triazines (1) according to the amine paraformaldehyde method.[1a] Diarylaminomethanes (17) were prepared according to a described procedure.[1b] Dry solvents were obtained following standard procedures.[21] TLC plates (neutral alumina on aluminium plates) were obtained from Merk, Italy.

Equipment. High pressure liquid chromatography analyses were performed with a Waters Millipore instrument, equipped with an inverse phase C_{18} Bondapak column (lengh 30 cm, i.d 3.9 mm) and a fixed wavelength (240 nm) uv detector. The system uses two independent pumps and a processing unit enabling eluent composition control. Water–acetonitrile mixtures were found suitable for our analyses operating at a flow rate of *ca.* 1 ml/min.

Infrared spectra were recorded with a Jasco Mod. DS-702G spectrophotometer by the KBr pellet technique

Electron impact (70 eV) mass spectra were obtained from a Finnigan MAT 1020 with automatic continuous data recording. During direct inlet vaporization of the whole sample into the ion source, the full recording was carefully inspected in order to detect any side product and check sample purity. Headspace analyses were performed by injecting the vapours over the solutions kept in inert atmosphere into a gaschromatograph prior to the electron impact with continuous ms monitoring of the eluate for the detection of gaseous products. The most intense peaks with their relative intensity (%) are reported for each product.

^{1}H NMR data were secured from a Bruker Mod. AC-F 200 spectrometer using tetramethylsilane as internal standard. The high insolubility of 6a-k presented a practical difficulty in recording of the ^{13}C NMR spectra.

Elemental analyses were obtained with a Carlo Erba Mod. 1106 elemental analyzer for all isolated compounds and were satisfactory.

X-ray diffraction analyses were obtained from a crystal of 6a *ca.* 0.2 × 0.2 × 0.5 mm that was mounted on a CAD-4 single crystal diffractometer with graphite monochromatized Mo Kα radiation, 25 reflections with ϑ in range $10 \leq \vartheta \leq 16°$ used for measuring lattice constants (Table 5).

For data collection $3 \leq \vartheta \leq 26°$ ($-8 \leq h \leq 8$, $0 \leq k \leq 32$, $0 \leq 1 \leq 14$), $\omega - 2\vartheta$ scans, ω-scan width (0.80 + 0.35 tanϑ); intensities of three reflections monitored every 2h of exposure time showed no significant variation 4537 unique reflections were collected; 1095 with $I \geq 3\sigma(I)$. The structure was solved with MULTAN 80[22] in default setting and refined with SHELX 76.[23] At convergence R = 0.059 for 1095 observed data. Hydrogen atoms were located at calculated positions. Atomic scattering factors were

taken from Cromer & Mann.[24]

Table 5. Crystal Data and Experimental Details

Formula	$C_{15}H_{12}O_2N_2$	Cryst. size /mm	0.2 x 0 2 x 0.5
M W.	252.3	Θ range /°	3.26
Space Group	$P2_1/c$	h range	-8.8
a/Å	7.259(3)	k range	0.32
b/Å	27.466(2)	l range	0 14
c/Å	12.525(2)	scan mode	Θ - 2Θ
β/°	99.23(3)	Measd. Reflections	2402
V/Å^3	2464.8(8)	Solution of Structure	MULTAN80
Z	8	Refinement	SHELX76
D_{calc}/g cm^{-3}	1.36	Final R factor	0.058
λ(Mo Kα)Å	0.71069	Final R_w factor	0.059
μ/cm^{-1}	0.86	Room temperature	
F(000)	1024		

General Procedure for the Preparation of 6*a-k*. A suspension of the appropriate 1,3,5-triarylhexahydro-1,3,5-triazine (1, 10 mmol) in anhydrous ether (*ca*. 50 ml) was slowly added to neat oxalyl chloride (5, 30 mmol) kept at 0°C under efficient stirring in an atmosphere of Argon. About 10 minutes after the end of the addition anhydrous ethanol (30 ml) is added at 0°C slowly, while hydrogen chloride is evolved and a solid separates. The precipitation is completed at room temperature by addition of ether. The precipitate, separated by filtration, is recrystallized from a suitable solvent. Headspace analysis was performed in the case of the synthesis of 6a, by sampling the atmosphere over the reaction mixture after the addition of ethanol and analysing it by GC-MS. The procedure with inverted order of addition of the initial reagents or not using ethanol to end the process yielded products 6 in substantially lower yields

The above procedure is in part the result of the study of the variation of a number of reaction parameters, when 1a was used as a substrate (Table 6)

*Reaction between N,N'-Diarylaminomethane (*17*) and* 5. The reaction was carried out according to the optimal procedure described for the preparation of 6. When 17a was the substrate only *ca* 10% yield of 6a was obtained; N,N'-diphenyloxalamide (14a) being the other observed product.

A similar result was obtained when N,N'-di(4-nitrophenyl)aminomethane (17b) was used, but the cyclic product 6l was not present at all.

Table 6

mol 5/mol 1a	Reaction time	Quenching reagent[a]	Reaction solvent[a]	Yield (%)
6	10 min	Et_2O[b]	--	50[c]
3	10 min	EtOH	--	40[d]
12	10 min	EtOH	--	25[d]
1	10 min	EtOH	Et_2O	45
3	10 min	EtOH	Et_2O	75[c]
6	10 min	EtOH	Et_2O	58
3	10 min	EtOH	Dioxane	mix[e]
3	10 min	EtOH	$CHCl_3$	mix[e]
6	16 hours	EtOH	Hexane	65

[a]Anhydrous materials were used. [b]Commercial diethyl ether was used as received [c]DI-MS analysis of mother liquors obtained after filtration of 6a showed the presence of N,N'-diphenyloxamide [14a; MS (m/z): 240 ($M^{\oplus}$, 43), 121(30), 120(31), 105(12), 93(100), 92(22), 77(58)] [d]DI-MS analysis of mother liquours obtained after filtration of 6a showed the presence of 14a and bis(N-ethoxyoxalyl-N-phenyl)diaminomethane [MS (m/e)· 398($M^{\oplus}$, 1), 325(18), 252(4), 206(28), 178(100), 134(8), 120(10), 106(83), 93(34), 77(38)]. [e]A very complex mixture was obtained which was not worked up.

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