Thermal Reactions of Aryl Azides with *trans*-1,2-Dibenzoyl- and *trans*-1,2-Diacetyl-ethylene. Reactivity of 4,5-Dibenzoyl- and 4,5-Diacetyl-1-aryltriazolines

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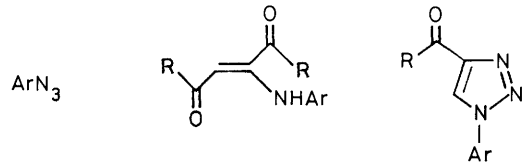
Thermal reactions of 4-substituted phenyl azides (**1**) with *trans*-1,2-dibenzoyl- (DBE) and *trans*-1,2-diacetyl-ethylene (DAE) have been investigated in benzene solution at room temperature and at 110 °C. These reactions lead to decomposition products of unstable 4,5-diacyl-1-aryltriazolines (**14A** and **B**) which have generally escaped isolation except in one case. At room temperature triazolines (**14A** and **B**) undergo formal elimination of an aldehyde moiety to give 4-acyltriazoles (**3A** and **B**), isomerization to diazo diones (**15A** and **B**) from which 1-arylamino-1,2-diacylethylenes (**2A** and **B**) are eventually formed, and oxidation to diacyltriazoles (**10A** and **B**). At 110 °C 1-arylamino-2,2-diacylethylenes (**12A** and **B**) and *N*-aryl-*N*-vinylamides (**13A** and **B**), the rearrangement products occurring *via* acyl-group migration, are preferentially produced. Under these conditions varying amounts of pyrrolidines (**11A** and **B**) also occur. These compounds (**11A** and **B**) are ascribed to cycloaddition reactions of azomethine ylides resulting from ring opening of intermediate aziridines (**16A** and **B**) with DBE or DAE. However, decomposition of triazolines (**14A** and **B**) in the presence of triethylamine leads exclusively to the enamines (**2A** and **B**). The possible reaction mechanisms involved in the formation of the observed products are discussed.

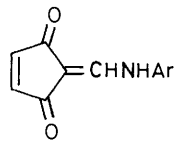
During a previous study of the thermal reactions of aryl azides with furans[1] we found that the aryl azides (**1c** and **d**) reacted smoothly at 110 °C with (*E*)-1,2-dibenzoylethylene (DBE) or (*E*)-1,2-diacetylethylene (DAE) to give the 1-anilino-2,2-diacylethylenes (**12Ac**) and (**12Bc** and **d**), in addition to the 4-acyltriazoles (**3Ac**) and (**3Bc** and **d**) and the (*Z*)-enamines (**2Ac**) and (**2Bc**) presumably by rearrangement of the intermediate triazolines (**14Ac**) and (**14Bc** and **d**). These findings prompted



(1) (2) (3)

A, R = Ph; **B**, R = Me; **a**, Ar = Ph; **b**, Ar = C_6H_4OMe-*p*; **c**, Ar = $C_6H_4NO_2$-*p*; **d**, Ar = C_6H_4Cl-*p*

us to investigate the reactions of the 4-substituted phenyl azides (**1a**—**d**) with DBE and DAE both at room temperature and 110 °C in order to explore the possible effects of 1-aryl substituents and temperature on the chemical reactivity of the diacyltriazolines (**14A**,**B**). In fact, despite the fact that these compounds were first discovered by Wolff and collaborators in 1912 during their studies on the action of organic azides on 1,4-benzoquinone and 1,4-naphthoquinone,[2] little was known about the chemistry of 4,5-diacyl-substituted triazolines and the available data were rather conflicting. Thermal reactions of aryl azides with benzoquinone and naphthoquinone have been reported to give enamines (**4**) and (**5**), the ring-contraction products arising from presumed intermediate triazolines *via* 1,2-acyl migration.[3] Intermediacy of 4,5-dibenzoyl-1-aryltriazolines (**14A**) has been proposed by L'Abbé and co-workers for the formation of 1-anilino-1,2-dibenzoylethylenes (**2A**) produced in the reactions of aryl azides (**1**)



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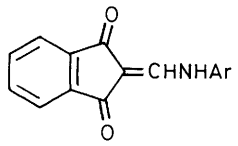
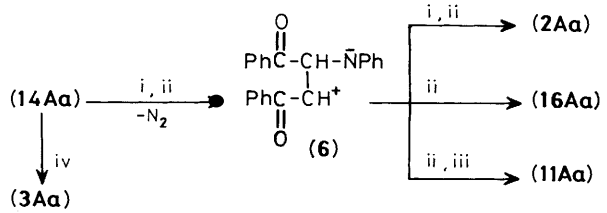


(5)

with phenacylidenesulphuranes ($PhCOCH{=}SR_2$) at room temperature.[4]

Later the enamine (**2Aa**) and the benzoyltriazole (**3Aa**) were reported by Kadaba[5] to be the exclusive products obtained by reaction of phenyl azide (**1a**) with (*E*)-1,2-dibenzoylethylene in benzene at room temperature. When the same reaction was carried out in refluxing methanol a mixture of the enamine (**2Aa**) and the pyrrolidine (**11Aa**) was obtained. Under these circumstances the aziridine (**16Aa**) was claimed to be also obtained as a minor product.

A 1,3-zwitterionic intermediate (**6**), resulting from the intermediate dibenzoyltriazoline (**14Aa**), was believed to be respon-



Scheme 1. *Reagents and conditions:* i, benzene, 25 °C; ii, methanol, 65 °C; iii, DBE; iv, −PhCHO, benzene, 25 °C

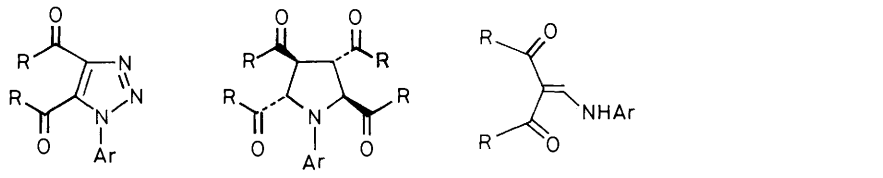
sible for the thermolysis products (**2Aa**), (**16Aa**), and (**11Aa**) (Scheme 1).

Recently Schultz and McMahon[6] showed that the thermolyses of 2-(azidopropyl)-1,4-benzoquinones (and naphtho-

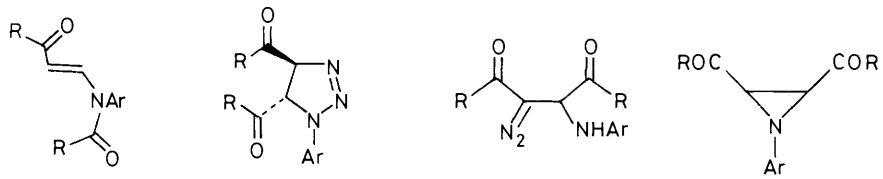
Table 1. Product yields (%)[a] for reactions of aryl azides (**1**) with dibenzoyl- and diacetyl-ethylene at room temperature[b]

Entry	Aryl azide	Diacylethylene	1,2-Diacyl enamine	Acyltriazole	Diacyltriazole	Other products
1	(**1b**)	DBE				35 (**14Ab**)[c]
2	(**1c**)	DBE	10 (**2Ac**)	30 (**3Ac**)		29 (**15Ac**)
3	(**1d**)	DBE	32 (**2Ad**)	28 (**3Ad**)	14 (**10Ad**)	9 (**12Ad**), 3 (**11Ad**), 6 (**13Ad**)
4	(**1b**)	DAE	45 (**2Bb**)	22 (**3Bb**)	4 (**10Bb**)	1 (**12Bb**)
5	(**1d**)	DAE	50 (**2Bd**)	25 (**3Bd**)		3 (**12Bd**)

[a] Isolated yields based on consumed azide (**1**) (75—90%). [b] Reactions run in benzene solution in the presence of 1 mol equiv. of DBE or DAE. [c] Isolated yield based on azide (**1b**) initially used.

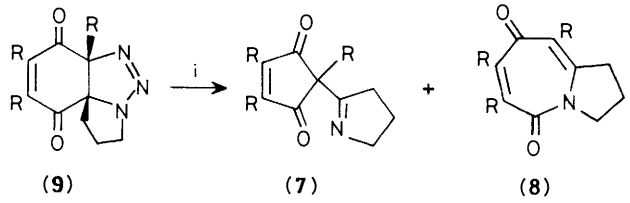


(10) (11) (12)



(13) (14) (15) (16)

A, R = Ph; **B**, R = Me; **a**, Ar = Ph; **b**, Ar = C_6H_4OMe-*p*; **c**, Ar = $C_6H_4NO_2$-*p*; **d**, Ar = C_6H_4Cl-*p*



(9) (7) (8)

Scheme 2. *Conditions:* i, $-N_2$, refluxing benzene

quinones) essentially lead to products of ring contraction and expansion, *i.e.* (**7**) and (**8**), *via* rearrangement of intermediate triazolines (**9**) produced by intramolecular azide–olefin cycloadditon (Scheme 2).

Results and Discussion

Reaction of 4-methoxyphenyl azide (**1b**) with equimolar amounts of DBE in benzene at room temperature led, after *ca.* 8 days, to the isolation of the *trans*-dibenzoyltriazoline (**14Ab**), which separated as a pale-yellow solid from the reaction mixture, in moderate yield (Table 1, entry 1). After this time t.l.c. analysis of the crude reaction mixture showed that the triazoline (**14Ab**) was accompanied to some extent by its decomposition products (*vide infra*), whereas noticeable amounts of unchanged azide (**1b**) and DBE were still present. Our attempts to improve the yield of isolable triazoline (**14Ab**) by suitably prolonging (or decreasing) the reaction time always led to less satisfactory results. Structural assignment of the compound (**14Ab**) was readily made on the basis of spectral analysis (see Experimental section) in addition to chemical evidence. To our knowledge this triazoline (**14Ab**) represents the first instance of an isolated 4,5-diacyl-substituted triazoline. The triazoline (**14Ab**) was found to undergo complete decomposition in benzene, at room temperature, within *ca.* 10 days. The (*Z*)-enamine (**2Ab**), the 4-benzoyltriazole (**3Ab**), the dibenzoyltriazole (**10Ab**), and the formanilide (**21**) (3%), were the only identifiable products obtained after column chromatography (Table 2, entry 1).

Upon elution through a silica gel column the triazoline (**14Ab**) rearranged mainly to the diazo dione (**15Ab**) and, to a minor extent, to the enamine (**2Ab**) (Table 2, entry 2).* Moreover, in benzene at room temperature it was essentially converted into the diazo dione (**15Ab**) upon treatment with an excess of aniline, whereas in the presence of triethylamine (TEA) it underwent rapid and complete decomposition to the enamine (**2Ab**) (Table 2, entries 3 and 4).

The diazo dione (**15Ab**) was found in turn to rearrange slowly to (**2Ab**) in benzene at room temperature, but instantaneously in the presence of TEA (see Experimental section).

4-Nitrophenyl (**1c**) and 4-chlorophenyl azide (**1d**) reacted in benzene with DBE at room temperature at much slower rate than the azide (**1b**). These reactions did not lead to isolable triazolines (**14Ac** and **d**). The azide (**1c**) led to the benzoyltriazole (**3Ac**) and the diazo compound (**15Ac**) along with minor amounts of the (*Z*)-enamine (**2Ac**) (Table 1, entry 2). Analogously to the diazo compound (**15Ab**), (**15Ac**) was found to be instantaneously decomposed by TEA to the enamine (**2Ac**), but in the absence of the base such a process occurred much more slowly than with (**15Ab**).

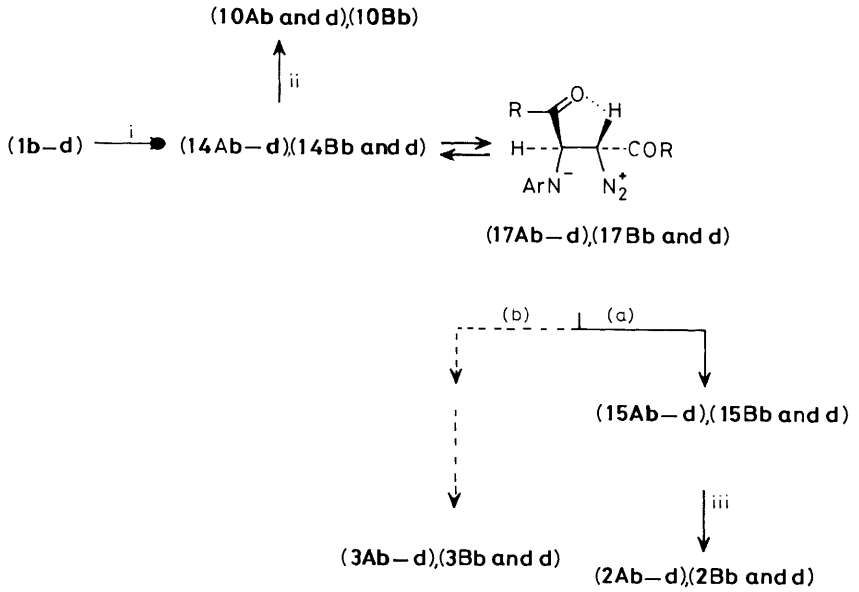
The azide (**1d**) gave major amounts of the (*Z*)-enamine (**2Ad**) and the benzoyltriazole (**3Ad**) in addition to minor amounts of the dibenzoyltriazole (**10Ad**), the enamine (**12Ad**), and the enamide (**13Ad**) (Table 1, entry 3). Under analogous conditions, the azides (**1b** and **d**) reacted with DAE to afford the corre-

* For a related acid-promoted isomerization of a diacyltriazoline see ref. 6.

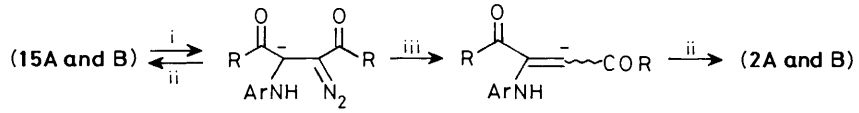
Table 2. Decomposition of 4,5-dibenzoyl-1-(4-methoxyphenyl)-4,5-dihydro-1,2,3-triazole (**14Ab**)[a]

		Products[b]						
Entry	Conditions	Enamine (**2Ab**)	Enamine (**12Ab**)	Benzoyltriazole (**3Ab**)	Dibenzoyltriazole (**10Ab**)	Enamide (**13Ab**)	Diazo dione (**15Ab**)	Pyrrolidine
1	25 °C; 10 days	39		21	13			
2	SiO_2; 25 °C[c]	10					90	
3	$PnNH_2$; 25 °C; 2 h	10					90	
4	$(Et)_3N$; 25 °C; few min	100						
5	110 °C; 5 h		50			17		
6	110 °C; DBE;[d] 5 h		40			19		20 (**11Ab**)
7	110 °C; DAE;[e] 5 h		48			23		28 (**20**)

[a] In benzene solution, unless stated otherwise. [b] Isolated yields based on consumed triazoline (%). [c] Rapid elution through a silica gel column. [d] Dibenzoylethylene (1 mol equiv.). [e] Diacetylethylene (5 mol equiv.).



Scheme 3. *Reagents and conditions:* i, DAE and/or DBE, benzene, room temperature; ii, oxygen; iii, $-N_2$



Scheme 4. *Reagents and conditions:* i, $-H^+$; ii, H^+; iii, $-N_2$

sponding (*Z*)-enamines (**2Bb** and **d**) along with the 4-acetyltriazoles (**3Bb** and **d**) as main products (Table 1, entries 4,5).

Our findings indicate that the reaction of aryl azides with DBE and DAE leads to reaction products ascribable to intermediate diacyltriazolines which are not generally isolable owing to their low stability and the long reaction times involved. The enamines (**2A** and **B**) would result from the corresponding diacyltriazolines (**14A** and **B**) probably *via* intermediacy of diazo diones (**15A** and **B**). Spontaneous (or base-promoted) isomerization of the triazolines (**14A** and **B**) to the diazo compounds (**15A** and **B**) *via* heterolytic ring opening to the diazonium betaines (**17A** and **B**) and subsequent C–N proton transfer is expected in the light of the behaviour exhibited by triazolines bearing an electron-withdrawing group at C-4 along with a free hydrogen (Scheme 3, path a).[2,7] Occurrence of heterolytic ring cleavage is consistent with our observation that the stability of diacyltriazoline is apparently enhanced by electron-releasing anilino substituents. Thermal conversion of diazo compounds into enamines is well documented; this is generally believed to involve carbene-like intermediates.[2,7] However, with diazo diones (**15A** and **B**) such a process is base-catalysed, as evidenced by the fact that in the presence of TEA the diazo diones (**15Ab** and **c**) underwent instantaneous decomposition to the corresponding enamines (**2Ab** and **c**). A plausible mechanism is depicted in Scheme 4. In the absence of external base, the arylamino substituent of the diazo dione itself would act as the basic catalyst. Thus, the much greater stability exhibited by the diazo compound (**15Ac**) with respect to (**15Ab**) would reflect the difference in basicity between the 4-nitro- and 4-methoxy-anilino groups.

The reaction path apparently involved in the formation of the enamines (**2A** and **B**), while being consistent with previously related findings,[4] does not agree with that suggested by Kadaba for the formation of the enamine (**2Aa**) from (**14Aa**) (Scheme 1).[5]

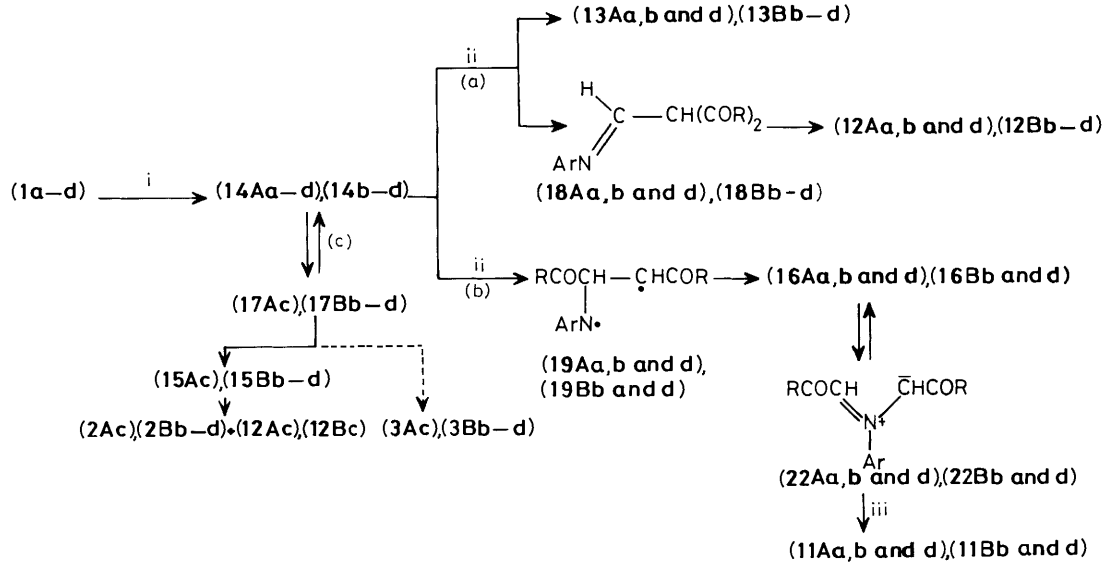
The observed aromatization of the triazolines (**14A** and **B**) to the acyltriazoles (**3A** and **B**) by formal elimination of a molecule of aldehyde [first observed by Kadaba[5a] with (**14Aa**)] is noteworthy, though several instances of triazole formation from 5-substituted triazolines bearing a free hydrogen in the 4-position are known.[2,7]

In all cases examined we failed to find any evidence for the actual fragment liberated in these aromatizations. Possible

Table 3. Product yields (%)[a] for reactions of aryl azides (**1**) with dibenzoyl- and diacetyl-ethylene at 110 °C[b]

Entry	Aryl azide	Diacylethylene	1,2-Diacyl enamine	Acyltriazole	Pyrrolidine	2,2-Diacyl enamine	Enamide
1	(**1a**)	DBE			5 (**11Aa**)	45 (**12Aa**)	16 (**13Aa**)
2	(**1b**)	DBE		1 (**3Ab**)	27 (**11Ab**)	38 (**12Ab**)	25 (**13Ab**)
3	(**1b**)[c]	DBE	20 (**2Ab**)	12 (**3Ab**)	13 (**11Ab**)	22 (**12Ab**)	5 (**13Ab**)
4	(**1b**)[d]	DBE	9 (**2Ab**)	6 (**3Ab**)	16 (**11Ab**)	27 (**12Ab**)	20 (**13Ab**)
5	(**1c**)	DBE	37 (**2Ac**)	42 (**3Ac**)		9 (**12Ac**)	
6	(**1d**)	DBE			11 (**11Ad**)	49 (**12Ad**)	18 (**13Ad**)
7	(**1b**)	DAE	8 (**2Bb**)	18 (**3Bb**)	9 (**11Ab**)	48 (**12Bb**)	6 (**13Bb**)
8	(**1c**)	DAE	10 (**2Bc**)	36 (**3Bc**)		48 (**12Bc**)	4 (**13Bc**)
9	(**1d**)	DAE	4 (**2Bd**)	9 (**3Bd**)	6 (**11Bd**)	50 (**12Bd**)	12 (**13Bd**)

[a] Isolated yields *based on consumed* azide (**1**) (56—96%). [b] Reactions were generally carried out in benzene solutions for *ca.* 5 h in the presence of 1 mol equiv. of DBE or DAE, unless stated otherwise. [c] Reaction carried out in benzonitrile. [d] Reaction carried out in nitromethane.



Scheme 5. *Reagents and conditions:* i, DAE and/or DBE, benzene, 110 °C; ii, $-N_2$; iii, DBE or DAE

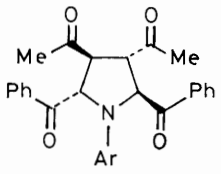
occurrence of the triazoles (**3A** and **B**) from reaction of the triazolines (**14A** and **B**) with oxygen was ruled out by our observation that the decomposition of the triazoline (**14Ab**) in oxygen-saturated benzene led to an enhancement of the dibenzoyltriazole (**10Ab**) at the expense of both the 4-benzoyltriazole (**3Ab**) and the enamine (**2Ab**). Moreover, our attempts to find further mechanistic information by treating the azides (**1b** and **c**) with (*Z*)-1,2-dibenzoylethylene at room temperature were unsuccessful, since no reaction occurred in either case. The actual mechanism leading to the acyltriazoles (**3A** and **B**) still remains unclear.

When 4-methoxyphenyl azide (**1b**) was allowed to react with an equimolar amount of DBE in benzene at 110 °C for *ca.* 5 h, the enamino-1,3-dione (**12Ab**), the (*E*)-enamide (**13Ab**), and the *trans,trans,trans*-pyrrolidine (**11Ab**) were isolated by column chromatography of the reaction mixture (Table 3, entry 2).

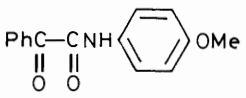
Structural elucidation of the new compounds (**12Ab**), (**13Ab**), and (**11Ab**) was accomplished by i.r., n.m.r., and mass spectral analysis (see Experimental section). In particular the stereochemistry of the pyrrolidine (**11Ab**) was established on the basis of ^{1}H n.m.r. spectral evidence. The pyrrolidine ring protons appeared as an AA′XX′ system with J_{AX} *ca.* 3 Hz, which is as expected for vicinal *trans*-coupling.[8] Similar findings were obtained on treating the azides (**1a**) and (**1d**) with DBE under the same conditions. In such cases also, the corresponding enamines (**12Aa** and **d**), the (*E*)-enamides (**13Aa** and **d**), and the pyrrolidines (**11Aa** and **d**) were obtained as the only identifiable products (Table 3, entries 1 and 6).

The observed occurrence of the pyrrolidines (**11Aa,b**, and **d**) can be explained by assuming that at 110 °C the diacyltriazolines (**14Aa,b**, and **d**) undergo homolytic fragmentation to the corresponding aziridines (**16Aa,b**, and **d**) through intermediacy of the singlet 1,3-diradicals (**19Aa,b**, and **d**). In fact, 1,3-diradicals are commonly accepted as the intermediates in aziridine formation from thermolysis of 1-aryltriazolines, especially when electron-withdrawing groups are present on the 4-carbon.[2,7] Moreover, aziridines are well known to undergo thermal ring-opening to form equilibrium mixtures with azomethine ylides, which can be suitably trapped by alkene or alkyne dipolarophiles.[8] In our cases, trapping of the azomethine ylides (**22Aa,b**, and **d**), in equilibrium with the corresponding aziridines (**16Aa,b**, and **d**), by DBE would give the pyrrolidines (**11Aa,b**, and **d**) (Scheme 5, path b).

Support for our suggestion came from independent experiments. The triazoline (**14Ab**) was found to decompose at 110 °C in benzene solution to give the enamino dione (**12Ab**) and the enamide (**13Ab**) in addition to small amounts of the formanilide (**21**) (6%) as the only identifiable products (Table 2, entry 5). The compounds (**12Ab**) and (**13Ab**) were accompanied by the pyrrolidine (**11Ab**) when the decomposition of (**14Ab**) was carried out in the presence of DBE, and by the *trans,trans,trans*-pyrrolidine (**20**) in the presence of DAE (Table 2, entries 6 and 7). The occurrence of the pyrrolidine (**20**) is clearly consistent with the intermediacy of the azomethine ylide (**22Ab**). Further support came from thermal decomposition of the previously reported *cis*-2,3-dibenzoyl-1-phenylaziridine



(20) Ar = C_6H_4OMe-*p*



(21)

(**16Aa**),[8] which gave unidentified products in benzene at 110 °C, but mainly the pyrrolidine (**11Aa**) in the presence of DBE.

In the light of our findings, the previously suggested[5a] involvement of the 1,3-zwitterionic intermediate (**6**) in the formation of the pyrrolidine (**11Aa**) (Scheme 1) appears to be excluded. Moreover, we note that the solid compound, m.p. 231—232 °C, which was previously assigned by Kadaba[5] the dibenzoylaziridine structure (**16Aa**) is not actually the *cis*- (nor the *trans*-)aziridine (**16Aa**).[8] This unknown compound, which we could isolate by treating the azide (**1a**) with DBE under Kadaba's conditions, was found to remain unchanged at 110 °C in benzene (8 h) both in the absence and in the presence of DBE. Moreover its ^1H n.m.r. spectrum exhibited no signal in the aliphatic region expected for the aziridine ring protons.[8] As for the rearrangement of the triazolines (**14Aa,b**, and **d**) to the enamines (**12Aa,b**, and **d**) and enamides (**13Aa,b**, and **d**), it presumably results from migration of the 5-acyl group to the adjacent nitrogen (with elimination of nitrogen) and/or acyl migration to the adjacent carbon followed by isomerization of the resulting imine (**18Aa,b**, and **d**) by 1,3-shift of the acyl group and/or hydrogen (Scheme 5, path a).[6,9]

In principle, the 1,3-diradicals (**19Aa,b**, and **d**) might be the intermediates involved in these rearrangements, although to our knowledge 1,2-migrations of acyl groups in 1,3-diradicals are unknown. We believe that the involvement of radicals (**19Aa,b**, and **d**) is unlikely on the basis of the observed lack of any product ascribable to migration of hydrogen. 1,2-Migrations of hydrogen in 1,3-diradicals are known to occur effectively.[2,7,10] Moreover, the observed occurrence of significant amounts of the enamide (**13Ad**) and the enamino dione (**12Ad**) in the decomposition of the triazoline (**14Ad**) at room temperature is not reasonably ascribable to homolytic fragmentation of the triazoline itself (Table 1, entry 3). Intervention of the diazo diones (**15Aa,b**, and **d**) might be possible,[6] but it appears to be ruled out by our findings that in benzene at 110 °C the diazo compound (**15Ab**) gave no rearranged products (**12Ab**) and (**13Ab**), but led mainly to the (*Z*)-enamine (**2Ab**). Intermediacy of the diazonium betaines (**17Aa,b**, and **d**) would appear conceivable. These might lead to the imines (**18Aa,b**, and **d**) [and then to (**13Aa,b**, and **d**) and (**12Aa,b**, and **d**)] by anionotropic acyl migration to carbon with loss of nitrogen.[2,7,11] 1,2-Migrations of acyl groups toward electron-deficient centres are well documented and are known to be preferred over hydrogen migrations.[12] However, possible intermediacy of the betaines (**17Aa,b**, and **d**) is not consistent with the evidence provided by the reaction of the azide (**1b**) with DBE at 110 °C in benzonitrile or nitromethane. In these polar solvents such reactions led to the formation of significant amounts of the (*Z*)-enamine (**2Ab**) and the benzoyltriazole (**3Ab**) at the expense of the rearranged products (**12Ab**) and (**13Ab**) and the pyrrolidine (**11Ab**), which occurred in ratios roughly comparable to that observed for the corresponding reaction in benzene (Table 3, entries 2—4). These findings are consistent with the involvement of the diazonium betaine (**17Ab**) in the formation of the enamine (**2Ab**) and the triazole (**3Ab**), not of the compounds (**12Ab**) and (**13Ab**). On this basis, we assume that the rearrangement of triazolines (**14Aa,b**, and **d**) to the enamides (**13Aa,b**, and **d**) and the enamino diones (**12Aa,b**. and **d**) occurs *via* concerted acyl migration and loss of nitrogen (Scheme 5, path a). The chemical reactivity trend exhibited by the triazoline (**14Ac**) at 110 °C is essentially identical to that observed at room temperature. In fact, the reaction of 4-nitrophenyl azide (**1c**) with DBE at 110 °C led mainly to the 4-benzoyltriazole (**3Ac**) and the (*Z*)-enamine (**2Ac**) in addition to small amounts of the enamino dione (**12Ac**) (Table 3, entry 5). No pyrrolidine (**11Ac**) could be observed. Moreover, an independent experiment showed that the (*Z*)-enamine (**2Ac**) and, to a lesser extent, the enamino dione (**12Ac**) resulted from decomposition of the diazo dione (**15Ac**) under the same conditions. Thus, the strongly electron-withdrawing nitro substituent would largely favour heterolytic cleavage of the triazoline (**14Ac**), irrespective of the reaction temperature (Scheme 5, path c). Our results obtained from the reactions of the azides (**1b** and **d**) with diacetylethylene at 110 °C lead substantially to the same conclusions as those drawn from the corresponding reactions with DBE. However, in these cases significant occurrence of acyltriazoles (**3Bb** and **d**) and (*Z*)-enamines (**2Bb** and **d**) was observed, thus suggesting that with the diacetyltriazolines (**14Bb** and **d**) heterolytic N–N bond cleavage may still occur to a relevant extent at 110 °C (Table 3, entries 7,9; Scheme 5, paths a—c). Finally, the evidence provided by our reaction of 4-nitrophenyl azide (**1c**) with DAE (Table 3, entry 8) suggests that the chemical behaviour of the resulting triazoline (**14Bc**) be comparable to that of the triazoline (**14Ac**). However, it appears that (**14Bc**), differently from (**14Ac**), can also undergo concerted rearrangement to enamino dione (**12Bc**) and enamide (**13Bc**) to a significant extent (Scheme 5, paths a and c).

Interestingly the azides (**1a—d**) reacted with DAE and/or DBE at 110 °C in the presence of TEA leading to the corresponding (*Z*)-enamines (**2A** and **B**) in almost quantitative yields (Scheme 6). Under these conditions base-promoted isomerization of the resulting triazolines (**14A** and **B**) to the ring-opened diazo compounds (**15A** and **B**) and subsequent fragmentation to (**2A** and **B**) would exclusively occur. These reactions therefore offer a new effective route to the (*Z*)-enamines (**2A** and **B**) which are useful intermediates in organic synthesis.[5b,9]

(**1a—d**) $\xrightarrow{i}$ (**14Aa—d**), (**14Bb—d**) $\xrightarrow{ii}$ (**2Aa—d**), (**2Bb—d**)

Scheme 6. *Reagents and conditions:* i, DAE and/or DBE, benzene, 110 °C: ii, Et_3N

In conclusion, we have shown that 1-aryl-4,5-diacyltriazolines (**14**) exhibit three major decomposition paths to an extent dependent upon the reaction conditions and the nature of the 1-aryl substituent: (i) heterolytic N–N bond cleavage ultimately leading to 4-acyltriazoles (**3**), diazo diones (**15**), and/or enamines (**2**); (ii) homolytic fragmentation affording elusive diacylaziridines (**16**); and (iii) rearrangement to enamides (**13**) and enamino diones (**12**) *via* acyl-group migration with concomitant loss of nitrogen. The chemical reactivity trend exhibited by these triazolines is consistent with that expected for triazolines bearing an electron-withdrawing group at the 4-position, though a peculiar behaviour results from the great migratory aptitude of the acyl group at the 5-position.

Experimental

The aryl azides (**1a—d**)[13] were prepared from the corresponding anilines by procedure A of Smith and Brown, and (*E*)-1,2-diacetylethylene (DAE)[14] as previously reported; (*E*)-1,2-dibenzoylethylene (DBE) was commercially available. Reaction products such as the 1-arylamino-1,2-diacylethylenes (**2Ab** and

d),[15a] (**2Aa**),[5] (**2Ac**),[4] and (**2Bc**),[15b] the triazoles (**3Aa**),[5a] (**3Ac**),[16] and (**3Bc** and **d**),[1] and the 1-arylamino-2,2-diacetylethylenes (**12Bc** and **d**)[1] where each identified by spectral comparison with authentic specimens. Column chromatography was carried out on Merck silica gel (0.040—0.063 particle size) by gradual elution with light petroleum (b.p. 40—70 °C), diethyl ether–light petroleum mixtures (up to 100% diethyl ether), and finally with chloroform. All m.p.s (Köfler melting point apparatus) are uncorrected. ^{1}H N.m.r. spectra were measured in $CDCl_3$ with $SiMe_4$ as internal standard and recorded on a Varian T60 (60 MHz) or a Brucker AM300 (300 MHz) spectrometer. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer. Mass spectra were determined by the electron impact method on a VG 7070 instrument.

Reaction of Aryl Azides (**1**) *with DAE or DBE at Room Temperature. General Procedure.*—A solution of the appropriate aryl azide (**1**) (3 mmol) in benzene (15 ml) containing an equimolar amount of DAE or DBE was kept in the dark at room temperature for the appropriate time. The resulting reaction mixtures were then worked up and the reaction products separated as specified in each case. Yields of identified products are given in Table 1.

(a) *Reaction of* 4-*methoxyphenyl azide* (**1b**) with *DBE*. This reaction was carried out for 8 days. After removal of the solvent under reduced pressure below 20 °C, the residue was dissolved in chloroform (30 ml). Upon subsequent addition of pentane (200 ml) a pale-yellow solid precipitated. This was filtered off and shown to be trans-4,5-*dibenzoyl*-1-(4-*methoxyphenyl*)-4,5-*dihydro*-1,2,3-*triazole* (**14Ab**), m.p. 115—116 °C (decomp.); δ_H(60 MHz) 3.67 (3 H, s), 6.0 (1 H, d, *J* 7 Hz), 6.37 (1 H, d, *J* 7 Hz), 6.73 (2 H, d, *J* 9 Hz), 7.23 (2 H, d, *J* 9 Hz), and 7.22—8.43 (10 H, m); *m/z* 357 (M^+ − 28) 356, 278, 252, 105, 77, and 51 (Found: C, 71.65; H, 4.9; N, 10.95. $C_{23}H_{19}N_3O_3$ requires C, 71.7; H, 4.95; N, 10.9%).

(b) *Reaction of* 4-*nitrophenyl azide* (**1c**) *with DBE*. This reaction was carried out for 8 months. The solid material which had separated after this time was collected and then extracted with diethyl ether (100 ml); the remaining solid was shown to be 4-benzoyl-1-(4-nitrophenyl)-1,2,3-triazole (**3Ac**). Evaporation of the diethyl ether layer under reduced pressure afforded 2-*diazo*-3-(4-*nitroanilino*)-1,4-*diphenylbutane*-1,4-*dione* (**15Ac**) as yellow needles, m.p. 153—155 °C (decomp.); $\nu_{max.}$(CS_2) 3 380 (NH) and 2 080 cm^{-1} (C=N$_2$); δ_H(60 MHz) 6.03 (1 H, br d, *J* 7 Hz), 6.4 (1 H, d, *J* 7 Hz), and 6.63—8.83 (14 H, m); *m/z* 372 (M^+ − 28), 342, 267, 237, 221, 105, 77, and 51 (Found: C, 65.9; H, 4.1; N, 13.95. $C_{22}H_{16}N_4O_4$ requires C, 66.0; H, 4.05; N, 14.0%).

The benzene mother liquor was evaporated and the residue was chromatographed to give (i) 4-nitrophenyl azide (**1c**) (0.66 mmol, 22% recovery), (ii) DBE (2% recovery); (iii) (*Z*)-1,4-diphenyl-2-(4-nitroanilino)but-2-ene-1,4-dione (**2Ac**); (iv) a mixture of unidentified products (260 mg); and (v) tarry material.

(c) *Reaction of* 4-*chlorophenyl azide* (**1d**) *with DBE*. This reaction was carried out for 8 months. The solid which had separated after this time was collected and shown to be 4-*benzoyl*-1-(4-*chlorophenyl*)-1,2,3-*triazole* (**3Ad**), m.p. 219—220 °C; δ_H(60 MHz) 7.23 (2 H, d, *J* 6 Hz), 7.33—8.55 (7 H, m), and 8.61 (1 H, s) (Found: M^+, 283.051 58, $C_{15}H_{10}ClN_3O$ requires *M*, 283.051 24); *m/z* 255, 227, 214, 111, 105, 77, and 51.

The benzene mother liquor was evaporated and the gummy residue was washed with diethyl ether (100 ml) to give a crystalline solid. This was collected by filtration to yield 1,4-diphenyl-2-(4-chloroanilino)but-2-ene-1,4-dione (**2Ad**). The diethyl ether filtrate was evaporated and the resulting residue was subjected to column chromatography to afford (i) unchanged azide (**1d**) (0.12 mmol, 4% recovery; (ii) further (*Z*)-enamine (**2Ad**); (iii) 4,5-*dibenzoyl*-1-(4-*chlorophenyl*)-1,2,3-*triazole* (**10Ad**), m.p. 130—132 °C; δ_H(60 MHz) 7—7.9 (12 H, m) and 8.25—8.6 (2 H, m); *m/z* 387 (M^+), 359, 358, 331. 254, 111, 105, 77, and 51 (Found: C, 68.1; H, 3.65; N, 10.8: Cl, 9.1. $C_{22}H_{14}ClN_3O_2$ requires C, 68.15; H, 3.65; N, 10.85; Cl, 9.15%); (iv) 2-[(4-*chloroanilino*)*methylene*]-1,3-*diphenylpropane*-1,3-*dione* (**12Ad**), m.p. 144—145 °C; $\nu_{max.}$(KBr) 3 140br (NH), 1 650 (C=O), and 1 620 cm^{-1} (C=O); δ_H(60 MHz) 6.76—7.68 (14 H, m), 8.13 (1 H, d, *J* 14 Hz), and 12 (1 H, br d, *J* 14 Hz) (Found: M^+, 361.086 30. $C_{22}H_{16}ClNO_2$ requires *M*, 361.086 96); *m/z* 360, 332, 282, 157, 105, 77, and 51; (v) N-[(E)-2-*benzoylvinyl*]-N-(4-*chlorophenyl*)*benzamide* (**13Ad**), m.p. 144—145 °C; $\nu_{max.}$(solid film) 1 680 (C=O) and 1 660 cm^{-1} (C=O); δ_H(60 MHz) 6.0 (1 H, d, *J* 13.5 Hz), 6.68—7.66 (14 H, m) and 8.13 (1 H, d, *J* 13.5 Hz) (Found: M^+, 361.086 30. $C_{22}H_{16}ClNO_2$ requires *M*, 361.086 96); *m/z* 360, 332, 282, 228, 157, 105, 77, and 51; and (vi) trans, trans, trans-2,3,4,5-*tetrabenzoyl*-1-(4-*chlorophenyl*)-*pyrrolidine* (**11Ad**), m.p. 182—183 °C; $\nu_{max.}$(solid film) 1 690 cm^{-1} (C=O); δ_H(300 MHz) 4.57 (2 H, d, *J* 3 Hz), 6.14 (2 H, d, *J* 3 Hz), 6.41 (2 H, d, *J* 9 Hz), 6.95 (2 H, d, *J* 9 Hz), and 6.95—7.91 (20 H, m) (Found: M^+, 597.171 53. $C_{38}H_{28}ClNO_4$ requires *M*, 597.170 69); *m/z* 492, 388, 105, and 77.

(d) *Reaction of* 4-*methoxyphenyl azide* (**1b**) *with DAE*. This reaction was carried out for 2 months. The residue obtained after removal of the solvent was chromatographed to give (i) unchanged azide (0.54 mmol, 18% recovery); (ii) (Z)-3-(4-*methoxyanilino*)*hex*-3-*ene*-2,5-*dione* (**2Bb**) as yellow plates, m.p. 88—89 °C; $\nu_{max.}$(solid film) 3 210br (NH), 1 720 (C=O), and 1 630 cm^{-1} (C=O); δ_H(60 MHz) 2.0 (3 H, s), 2.17 (3 H, s), 3.73 (3 H, s), 5.33 (1 H, s), 6.6—7.0 (4 H, m), and 11.27 (1 H, s) (Found: M^+, 233.105 62. $C_{13}H_{15}NO_3$ requires *M*, 233.105 19); *m/z* 190, 175, 148, 121, 92, 77, and 43; (iii) 4,5-*diacetyl*-1-(4-*methoxyphenyl*)-1,2,3-*triazole* (**10Bb**), m.p. 109—110 °C; $\nu_{max.}$(solid film) 1 700 (C=O) and 1 690 cm^{-1} (C=O); δ_H(60 MHz) 2.53 (3 H, s), 2.77 (3 H, s), 3.5 (3 H, s), 6.9 (2 H, d, *J* 9 Hz), and 7.3 (2 H, d, *J* 9 Hz) (Found: M^+, 259.095 74. $C_{13}H_{13}N_3O_3$ requires *M*, 259.095 69); *m/z* 231, 216, 189, 174, 147, 146, 132, 107, 92, 77, and 43; (iv) 4-*acetyl*-1-(4-*methoxyphenyl*)-1,2,3-*triazole* (**3Bb**), m.p. 130—132 °C; $\nu_{max.}$(KBr) 1 700 cm^{-1} (C=O); δ_H(60 MHz) 2.73 (3 H, s), 3.9 (3 H, s), 7.07 (2 H, d, *J* 9 Hz), 7.67 (2 H, d, *J* 9 Hz), and 8.4 (1 H, s) (Found: M^+, 217.084 87. $C_{11}H_{11}N_3O_2$ requires *M*, 217.085 13); *m/z* 189, 174, 147, 146, 132, 92, 77, 51, and 43; and (v) 3-[(4-*methoxyanilino*)*methylene*]*pentane*-2,4-*dione* (**12Bb**), m.p. 96—97 °C; $\nu_{max.}$(KBr) 3 160br (NH), 1 660 (C=O), and 1 630 cm^{-1} (C=O); δ_H(60 MHz) 2.33 (3 H, s), 2.57 (3 H, s), 3.8 (3 H, s), 6.8—7.23 (4 H, m), and 8.07 (1 H, d, *J* 13 Hz, collapsing to a singlet upon D_2O shake) (Found: M^+, 233.105 62. $C_{13}H_{15}NO_3$ requires *M*, 233.105 19); *m/z* 218, 200, 190, 176, 112, and 43.

(e) *Reaction of* 4-*chlorophenyl azide* (**1d**) *with DAE*. This reaction was carried out for 2 months. After removal of the solvent, the resultant residue was chromatographed to give (i) unchanged azide (**1d**) (0.75 mmol, 25% recovery); (ii) (Z)-3-(4-*chloroanilino*)*hex*-3-*ene*-2,5-*dione* (**2Bd**), m.p. 60—62 °C; $\nu_{max.}$(CCl_4) 3 240br (NH), 1 720 (C=O), and 1 640 cm^{-1} (C=O); δ_H(60 MHz) 2.1 (3 H, s), 2.2 (3 H, s), 5.48 (1 H, s), 6.87 (2 H, d, *J* 9 Hz), 7.23 (2 H, d, *J* 9 Hz), and 11.4 (1 H, s) (Found: M^+, 237.055 70. $C_{12}H_{12}ClNO_2$ requires *M*, 237.055 66); *m/z* 194, 152, 117, 111, and 43; (iii) 4-acetyl-1-(4-chlorophenyl)-1,2,3-triazole (**3Bd**); and (iv) 3-[(4-chloroanilino)methylene]pentane-2,4-dione (**12Bd**).

Decomposition of 4,5-*Dibenzoyl*-1-(4-*methoxyphenyl*)-4,5-*dihydro*-1,2,3-*triazole* (**14Ab**) (*Yields of identified products are given in Table* 2).—(a) *At room temperature*. A solution of the triazoline (**14Ab**) (0.3 mmol) in benzene (10 ml) was kept in the dark at room temperature for 10 days. Chromatography of the crude mixture obtained by evaporation of the solvent gave (i) *N*-(4-methoxyphenyl)phenylglyoxylamide (**21**) (0.01 mmol, 3%)

identical in all respects with an authentic specimen independently prepared by oxidation of *N*-(4-methoxyphenyl)mandelamide;[17] (ii) the (*Z*)-enamine (**2Ab**); (iii) 4,5-*dibenzoyl*-1-(4-*methoxyphenyl*)-1,2,3-*triazole* (**10Ab**), m.p. 143—144 °C; $\nu_{max.}$(CS_2) 1 680 (C=O) and 1 650 cm^{-1} (C=O); δ_H(60 MHz) 3.73, (3 H, s), 6.83 (2 H, d, *J* 9 Hz), 7.23 (2 H, d, *J* 9 Hz), and 7.22—8.63 (10 H, m); *m/z* 383 (M^+), 355, 354, 327, 326, 105, 77, and 51 (Found: C, 71.8; H, 4.5; N, 11.0. $C_{23}H_{17}N_3O_3$ requires C, 72.05; H, 4.45; N, 10.95%); and (iv) 4-*benzoyl*-1-(4-*methoxyphenyl*)-1,2,3-*triazole* (**3Ab**), m.p. 150—151 °C; δ_H(60 MHz) 3.8 (3 H, s), 6.93 (2 H, d, *J* 9 Hz), 7.17—8.5 (7 H, m), and 8.57 (1 H, s); $\nu_{max.}$(solid film) 1 640 cm^{-1} (C=O) (Found: M^+, 279.100 83. $C_{16}H_{13}N_3O_2$ requires *M*, 279.100 78); *m/z* 251, 236, 105, 77, and 51. This compound (**3Ab**) was independently obtained in 30% yield by treatment of the azide (**1b**) with benzoylacetylene.[18] This reaction also gave the isomeric 5-*benzoyl*-1-(4-*methoxyphenyl*)-1,2,3-*triazole* (20%), m.p. 100—101 °C; δ_H(60 MHz) 3.75 (3 H, s), 6.86 (2 H, d, *J* 9 Hz), 7.3 (2 H, d, *J* 9 Hz), 7.36—7.93 (5 H, m), and 8.0 (1 H, s) (Found: M^+, 279.100 68); *m/z* 251, 236, 220, 174, 105, 77, and 51.

(b) *At room temperature with silica gel.* The triazoline (**14Ab**) (0.3 mmol) was absorbed on a silica gel column (20 cm × 2 cm) and rapidly eluted with diethyl ether to give (i) 2-*diazo*-3-(4-*methoxyanilino*)-1,4-*diphenylbutane*-1,4-*dione* (**15Ab**) as yellow plates, m.p. 98—100 °C; $\nu_{max.}$(CS_2) 3 410 (NH) and 2 100 cm^{-1} (C=N_2); δ_H(60 MHz) 3.67 (3 H, s), 6.27 (1 H, s), 6.63—6.8 (4 H, m), and 7.17—8.23 (10 H, m); *m/z* 357 (M^+ − 28), 252, 251, 235, 105, 77, and 51 (Found: C, 71.9; H, 5.0; N, 11.05. $C_{23}H_{19}N_3O_3$ requires C, 71.7; H, 4.95; N, 10.9%) and (ii) the enamine (**2Ab**). The yield of the enamine (**2Ab**) was found to increase at the expense of the diazo dione (**15Ab**) upon prolonged absorption on silica gel.

(c) *At room temperature in the presence of TEA.* To a stirred solution of the triazoline (**14Ab**) (0.1 mmol) in benzene (10 ml) was added TEA (*ca.* 0.1—0.2 mmol). The resulting reaction mixture was stirred for a few min and then evaporated to give the enamine (**2Ab**) in quantitative yield.

(d) *At room temperature in the presence of aniline.* A 0.1M solution of the triazoline (**14Ab**) in [$^2H_6$]benzene was placed in an n.m.r. tube and treated with a *ca.* five-fold excess of aniline. After 2 h the n.m.r. spectrum (300 MHz) showed the exclusive presence of the diazo dione (**15Ab**), the triazoline (**14Ab**), and the (*Z*)-enamine (**2Ab**) in the proportions 56:38:6, respectively.

(e) *At* 110 °C. A solution of the triazoline (**14Ab**) (0.39 mmol) in benzene (10 ml) was heated at 110 °C for 5 h in a sealed tube. The excess of solvent was evaporated off and the residue was chromatographed to give (i) *N*-(4-methoxyphenyl)phenylglyoxylamide (**21**) (0.02 mmol, 5%); (ii) an unidentified product (18 mg), *m/z* 357, 356, 328, 251, and 105; (iii) 2-[(4-*methoxyanilino*)*methylene*]-1,3-*diphenylpropane*-1,3-*dione* (**12Ab**), m.p. 164—165 °C; $\nu_{max.}$(KBr) 1 680, 1 640, 1 580, and 1 540 cm^{-1} δ_H(60 MHz) 3.77 (3 H, s), 6.7—7.7 (14 H, m), 8.2 (1 H, d, *J* 13.5 Hz), and 12.1 (1 H, d, *J* 13.5 Hz); *m/z* 357 (M^+), 356, 328, 279, 251, 236, 105, 77, and 51 (Found: C, 76.9; H, 5.3; N, 3.85. $C_{23}H_{19}NO_3$ requires C, 77.3; H, 5.35; N, 3.9%); (iv) N-[(E)-2-*benzoylvinyl*]-N-(4-*methoxyphenyl*)*benzamide* (**13Ab**), m.p. 140—142 °C; $\nu_{max.}$(solid film) 1 680, 1 660, 1 600, 1 580, and 1 560 cm^{-1}; δ_H(60 MHz) 3.77 (3 H, s), 6.0 (1 H, d, *J* 13.5 Hz), 6.7—7.8 (14 H, m), and 8.6 (1 H, d, *J* 13.5 Hz); *m/z* 357 (M^+), 356, 252, 105, and 77 (Found: C, 76.85; H, 5.4; N, 4.0. $C_{23}H_{19}NO_3$ requires C, 77.3; H, 5.35; N, 3.9%); and (v) a mixture of unidentified products (10 mg).

(f) *At* 110 °C *in the presence of DBE.* A solution of the triazoline (**14Ab**) (0.26 mmol) and DBE (0.26 mmol) in benzene (7 ml) was heated at 110 °C for 5 h. The solvent was distilled off and the crude mixture was extracted with hot methanol (15 ml); the remaining yellow solid was filtered and shown to be trans,trans,trans-2,3,4,5-*tetrabenzoyl*-1-(4-*methoxyphenyl*)-*pyrrolidine* (**11Ab**), m.p. 200—201 °C; δ_H(300 MHz) 3.60 (3 H, s), 4.62 (2 H, d, *J* 3.5 Hz), 6.1 (2 H, d, *J* 3.5 Hz), 6.57 (4 H, m), 7.17—7.52 (16 H, m), and 7.91 (4 H, m); *m/z* 593 (M^+), 488, 105, and 77 (Found: C, 78.5; H, 5.2; N, 2.3. $C_{39}H_{31}NO_5$ requires C, 78.9; H, 5.25; N, 2.35%). The residue obtained from evaporation of the methanolic filtrate was chromatographed to give (i) unchanged DBE (0.19 mmol, 75%); (ii) the enamino dione (**12Ab**); and (iii) the enamide (**13Ab**).

(g) *At* 110 °C *in the presence of DAE.* A solution of the triazoline (**14Ab**) (0.49 mmol) and DAE (2.47 mmol) in benzene (10 ml) was heated at 110 °C for 5 h. After removal of the solvent the residue was chromatographed to give (i) unchanged DAE; (ii) the enamino dione (**12Ab**); (iii) the enamide (**13Ab**); and (iv) trans,trans,trans-3,4-*diacetyl*-2,5-*dibenzoyl*-1-(4-*methoxyphenyl*)*pyrrolidine* (**20**), m.p. 142—144 °C; δ_H(300 MHz) 2.22 (6 H, s), 3.61 (5 H, br s), 6.02 (2 H, d, *J* 2.9 Hz), 6.46 (2 H, d, *J* 9 Hz), 6.64 (2 H, d, *J* 9 Hz), 7.58—7.7 (6 H, m), and 8.07 (4 H, m) (Found: M^+, 469.189 57. $C_{29}H_{27}NO_5$ requires *M*, 469.188 92); *m/z* 364, 357, 356, 332, 105, 77, and 43.

Reaction of the Aryl Azides (**1a—d**) *with DBE or DAE at* 110 °C. *General Procedure.*—A solution of the appropriate aryl azide (**1**) (3 mmol) in benzene (15 ml) (unless otherwise stated) containing an equimolar amount of DBE or DAE was heated at 110 °C in a sealed tube for 5 h. The solvent was evaporated off and the residue was chromatographed. Yields of identified products are reported in Table 3.

(a) *Reaction of phenyl azide* (**1a**) *with DBE.* Chromatography gave (i) unchanged azide (**1a**) (0.6 mmol, 20% recovery); (ii) a mixture of DBE and an unidentified product (50 mg); (iii) 2-(anilinomethylene)-1,3-diphenylpropane-1,3-dione (**12Aa**),[19] m.p. 129—130 °C; $\nu_{max.}$(CCl_4) 1 650 (C=O) and 1 625 cm^{-1} (C=O); δ_H(60 MHz) 6.83—7.9 (15 H, m), 8.3 (1 H, d, *J* 13.5 Hz), and 12.2 (1 H, d, *J* 13.5 Hz); *m/z* 327 (M^+); (iv) N-[(E)-2-*benzoylvinyl*]-N-*phenylbenzamide* (**13Aa**), m.p. 110—111 °C; $\nu_{max.}$(solid film) 1 680, 1 660, 1 600, 1 590, and 1 580 cm^{-1}; δ_H(60 MHz) 6.07 (1 H, d, *J* 13.5 Hz), 6.8—8.03 (15 H, m), and 8.8 (1 H, d, *J* 13.5 Hz); *m/z* 327 (M^+), 326, 222, 106, 105, and 77 (Found: C, 79.9; H, 5.3; N, 4.25. $C_{22}H_{17}NO_2$ requires C, 80.7; H, 5.25; N, 4.3%); and (v) *trans,trans,trans*-2,3,4,5-tetrabenzoyl-1-phenylpyrrolidine (**11Aa**), m.p. 160—162 °C (lit.,[5a] m.p. 166—167 °C); δ_H(300 MHz) 4.58 (2 H, d, *J* 3 Hz), 6.18 (2 H, d, *J* 3 Hz), 6.43—7.05 (5 H, m), and 7.3—8.0 (20 H, m); *m/z* 563 (M^+), 458, 236, 222, 105, and 77 (Found: C, 80.6; H, 5.15; N, 2.45. Calc. for $C_{38}H_{29}NO_4$: C, 81.0; H, 5.2; N, 2.5%).

(b) *Reaction of* 4-*methoxyphenyl azide* (**1b**) *with DBE.* Chromatography gave (i) unchanged azide (**1b**) (0.6 mmol, 20% recovery); (ii) a mixture (35 mg) of unidentified products; (iii) the 4-benzoyltriazole (**3Ab**); (iv) the enamine (**12Ab**); (v) the (*E*)-enamide (**13Ab**); and (vi) the pyrrolidine (**11Ab**).

(c) *Reaction of* 4-*methoxyphenyl azide* (**1b**) *with DBE in benzonitrile.* Chromatography gave (i) unchanged azide (**1b**) (0.12 mmol, 4% recovery); (ii) DBE (0.06 mmol, 2% recovery); (iii) the formanilide (**21**) (0.08 mmol, 3%); (iv) the (*Z*)-enamine (**2Ab**); (v) trace amounts of the dibenzoyltriazole (**10Ab**); (vi) the 4-benzoyltriazole (**3Ab**); (vii) the enamine (**12Ab**); (viii) the enamide (**13Ab**); (ix) the pyrrolidine (**11Ab**); and (x) an unknown solid compound (50 mg).

(d) *Reaction of* 4-*methoxyphenyl azide* (**1b**) *with DBE in nitromethane.* Chromatography gave (i) unchanged azide (**1b**) (0.2 mmol, 7% recovery); (ii) DBE (0.09 mmol, 3% recovery); (iii) the formanilide (**21**) (0.08 mmol, 3%); (iv) the enamine (**2Ab**); (v) the dibenzoyltriazole (**10Ab**) (0.08 mmol, 3%); (vi) the 4-benzoyltriazole (**3Ab**); (vii) the enamine (**12Ab**); (viii) the enamide (**13Ab**); and (ix) the pyrrolidine (**11Ab**).

(e) *Reaction of* 4-*nitrophenyl azide* (**1c**) *with DBE.* Upon cooling the reaction mixture, a pale-yellow solid separated. This was collected by filtration and triturated with diethyl ether to give the benzoyltriazole (**3Ac**). The benzene mother liquor

was evaporated and the residue was chromatographed to give (i) unchanged azide (**1c**) (0.90 mmol, 30% recovery); (ii) DBE (0.47 mmol, 16% recovery); (iii) the (*Z*)-enamine (**2Ac**); (iv) 2-[(4-*nitroanilino*)*methylene*]-1,3-*diphenylpropane*-1,3-*dione* (**12Ac**), m.p. 182—183 °C; $\nu_{max.}$(KBr) 1 670, 1 650, 1 630, 1 620, 1 600, and 1 580 cm^{-1}; δ_H(60 MHz) 7.03—7.8 (12 H, m), 8.23 (1 H, d, *J* 13 Hz), 8.24 (2 H, d, *J* 9 Hz), and 12.1 (1 H, d, *J* 13 Hz); *m*/*z* 372 (M^+), 371, 343, 105, and 77 (Found: C, 71.2; H, 4.4; N, 7.45. $C_{22}H_{16}N_2O_4$ requires C, 70.95; H, 4.35; N, 7.50%); and (v) the acyltriazole (**3Ac**).

(f) *Reaction of* 4-*chlorophenyl azide* (**1d**) *with DBE.* Chromatography gave (i) unchanged azide (**1d**) (0.43 mmol, 14% recovery); (ii) DBE (0.42 mmol, 4% recovery); (iii) the enamine (**12Ad**); (iv) the enamide (**13Ad**); and (v) the pyrrolidine (**11Ad**).

(g) *Reaction of* 4-*methoxyphenyl azide* (**1b**) *with DAE.* Chromatography gave (i) unchanged azide (**1b**) (0.37 mmol, 12% recovery, (ii) the enamine (**2Bb**); (iii) the diacetyltriazole (**10Bb**) (0.08 mmol, 3%); (iv) the 4-acetyltriazole (**3Bb**); (v) the enamine (**12Bb**) (0.94 mmol, 36%); (vi) an isomeric mixture of the enamine (**12Bb**) and N-[(E)-2-*acetylvinyl*]-N-(4-*methoxyphenyl acetamide* (**13Bb**) (0.47 mmol, 18%) (Found: C, 67.4; H, 6.45; N, 5.95. $C_{13}H_{15}NO_3$ requires C, 66.95; H, 6.5; N, 6.0%). The n.m.r. spectrum (60 MHz) showed, in addition to the signals corresponding to the enamine (**12Bb**), signals at δ_H 1.9 (3 H, s), 2.1 (3 H, s), 3.8 (3 H, s), 5.0 (1 H, d, *J* 14 Hz), 6.6—7.2 (4 H, m), and 8.5 (1 H, d, *J* 14 Hz). Integration showed that the enamine (**12Bb**) and the enamide (**13Bb**) were in the ratio 2:1 respectively; and (vii) trans,trans,trans-2,3,4,5-*tetra-acetyl*-1-(4-*methoxyphenyl*)*pyrrolidine* (**11Bb**), m.p. 130—131 °C; δ_H(60 MHz) 1.95 (6 H, s), 2.27 (6 H, s), 3.7 (5 H, br s), 4.6 (2 H, d, *J* 3 Hz), 6.7 (2 H, d, *J* 9 Hz), and 6.87 (2 H, d, *J* 9 Hz); *m*/*z* 345 (M^+), 302, 260, 242, 216, 174, and 43 (Found: C, 65.8; H, 6.65; N, 4.0. $C_{19}H_{23}NO_5$ requires C, 66.05; H, 6.7; N, 4.05%).

(h) *Reaction of* 4-*nitrophenyl azide* (**1c**) *with DAE.* Chromatography gave (i) unchanged azide (**1c**) (1.31 mmol, 44% recovery), (ii) DAE (mmol 0.76, 19% recovery); (iii) the enamine (**2Bc**); (iv) the 4-acetyltriazole (**3Bc**); (v) the enamine (**12Bc**) (0.77 mmol, 46%); and (vi) an isomeric mixture of the enamine (**12Bc**) and N-[(E)-2-*acetylvinyl*]-N-(4-*nitrophenyl*)*acetamide* (**13Bc**) (0.09 mmol, 6%) (Found: C, 58.15; H, 4.8; N, 11.4. $C_{12}H_{12}N_2O_4$ requires C, 58.05; H, 4.85; N, 11.3%). The n.m.r. spectrum (60 MHz) showed, in addition to the bands due to the enamine (**12Bc**), signals at δ_H 2.07 (3 H, s), 2.22 (3 H, s), 5.37 (1 H, d, *J* 14 Hz), 7.5 (2 H, d, *J* 9 Hz), 8.47 (2 H, d, *J* 9 Hz), and 8.57 (1 H, d, *J* 14 Hz). Integration showed that the compounds (**12Bc**) and (**13Bc**) were present in the ratio 1:2 respectively.

(i) *Reaction of* 4-*chlorophenyl azide* (**1d**) *with DAE.* Chromatography gave (i) unchanged azide (**1d**) (0.29 mmol, 10% recovery); (ii) the enamine (**2Bd**); (iii) the acetyltriazole (**3Bd**); (iv) the enamine (**12Bd**); (v) N-[(E)-2-*acetylvinyl*]-N-(4-*chlorophenyl*)*acetamide* (**13Bd**), m.p. 135—136 °C; δ_H(60 MHz) 2.0 (3 H, s), 2.2 (3 H, s), 5.0 (1 H, d, *J* 14 Hz), 7.03 (2 H, d, *J* 9 Hz), 7.47 (2 H, d, *J* 9 Hz), and 8.43 (1 H, d, *J* 14 Hz); $\nu_{max.}$(solid film) 1 720 (C=O) and 1 680 cm^{-1} (C=O); *m*/*z* 237 (M^+), 195, 194, 180, 117, 111, and 43 (Found: C, 61.0; H, 5.15; Cl, 15.0; N, 5.85. $C_{12}H_{12}ClNO_2$ requires C, 60.65; H, 5.1; Cl, 14.9; N, 5.9%); and (vi) trans,trans,trans-2,3,4,5-*tetra-acetyl*-1-(4-*chlorophenyl*)*pyrrolidine* (**11Bd**), m.p. 102—104 °C; δ_H(60 MHz) 2.06 (6 H, s), 2.43 (6 H, s), 3.77 (2 H, d, *J* 3 Hz), 4.77 (2 H, d, *J* 3 Hz), 6.5 (2 H, d, *J* 9 Hz), and 7.27 (2 H, d, *J* 9 Hz) (Found: M^+, 349.107 94. $C_{18}H_{20}ClNO_4$ requires *M*, 349.108 09); *m*/*z* 306, 264, 220, 204, 178, 143, and 43.

Decomposition of 2-*Diazo*-3-(4-*methoxyanilino*)-1,4-*diphenylbutane*-1,4-*dione* (**15Ab**).—(a) *At room temperature.* A 0.1M solution of the diazo dione (**15Ab**) in [$^2H_6$]benzene was kept at room temperature for 4 days. After this time n.m.r. spectroscopy of the reaction mixture showed exclusive presence of comparable amounts of the starting diazo dione (**15Ab**) and the (*Z*)-enamine (**2Ab**).

When the same solution of the diazo dione (**15Ab**) was treated with TEA (1 mol equiv.) instantaneous conversion into the (*Z*)-enamine (**2Ab**) was shown to occur by n.m.r. spectroscopy.

(b) *At* 110 °C. A 0.1M benzene solution of the diazo dione (**15Ab**) was heated in a sealed tube at 110 °C for 60 min, after which time t.l.c. analysis of the reaction mixture showed the absence of the starting dione (**15Ab**) and the occurrence of the enamine (**2Ab**), as the main product.

Decomposition of 2-*Diazo*-3-(4-*nitroanilino*)-1,4-*diphenylbutane*-1,4-*dione* (**15Ac**).—(a) *At room temperature.* A 0.1M solution of the diazo dione (**15Ac**) in benzene was kept at room temperature for *ca.* 2 months. After this time t.l.c. showed that compound (**15Ac**) had remained largely unchanged, only small amounts of the (*Z*)-enamine (**2Ac**) being detectable. When the same solution of the diazo dione (**15Ac**) in [$^2H_6$]benzene was treated with TEA (1 mol equiv.) instantaneous conversion into the (*Z*)-enamine (**2Ac**) was evidenced by n.m.r. spectroscopy.

(b) *At* 110 °C. A solution of the diazo dione (**15Ac**) (0.25 mmol) in benzene (5 ml) was heated in a sealed tube at 110 °C for 5 h. After removal of the excess of solvent the residue was chromatographed to give (i) the (*Z*)-enamine (**2Ac**) (0.06 mmol, 25%); (ii) a mixture of unidentified products (8 mg); (iii) the enamine (**12Ac**) (0.03 mmol, 12%); and (iv) an unknown solid compound (23 mg).

Decomposition of cis-2,3-*Dibenzoyl*-1-*phenylaziridine* (**16Aa**).—A solution of the aziridine (**16Aa**)[8] (0.19 mmol) and DBE (0.38 mmol) in benzene (10 ml) was heated in a sealed tube at 110 °C for 2 h. The solvent was evaporated off and the residue was chromatographed to give (i) unchanged DBE (0.25 mmol); (ii) the pyrrolidine (**11Aa**) (0.13 mmol, 68%); and (iii) tarry material.

In an independent experiment, the aziridine (**16Aa**) was heated in benzene at 110 °C for 2 h. After this time t.l.c. showed complete absence of the starting aziridine (**16Aa**) and formation of a number of unidentified products.

Reaction of Phenyl Azide (**1a**) *with DBE in Methanol.*—This reaction was carried out by refluxing a solution of phenyl azide (**1a**) (0.015 mol) and DBE (0.01 mol) in methanol (15 ml) according to the procedure described by Kadaba.[5b] The white solid (150 mg) which separated upon cooling the reaction mixture to room temperature was filtered off and had m.p. 230—232 °C (lit.,[5b] m.p. 231—232 °C); *m*/*z* 327 (M^+), 282, 235, 105, 102, 77, and 51; δ_H(Me_2SO; 300 MHz) 6.65—6.85 (3 H, m), 7.03—7.15 (2 H, t), 7.38—7.63 (9 H, m), 7.95—8.05 (2 H, m), and 8.22 (1 H, s). The unknown was found to remain essentially unchanged upon heating in benzene at 110 °C for 8 h both in the absence and in the presence of a two-fold excess of DBE.

Reaction of the Aryl Azides (**1a**—**d**) *with DBE or DAE at* 110 °C *in the Presence of TEA.*—A solution of the appropriate aryl azide (**1**) (3 mmol) in benzene (20 ml) containing DBE or DAE (3 mmol) and TEA (6 mmol) was heated in a sealed tube at 110 °C for 5 h. The resultant reaction mixture was percolated through silica gel to give, after removal of the solvent, the appropriate enamine (**2Aa**—**d**) or (**2Bb**—**d**) in 93—98% yield.

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