Thermal Reactivity of Tricyclic 4,5-Diacyltriazolines Resulting from Addition of Aryl Azides to 1,4-Naphthoquinone and 2-Methyl-1,4-naphthoquinone

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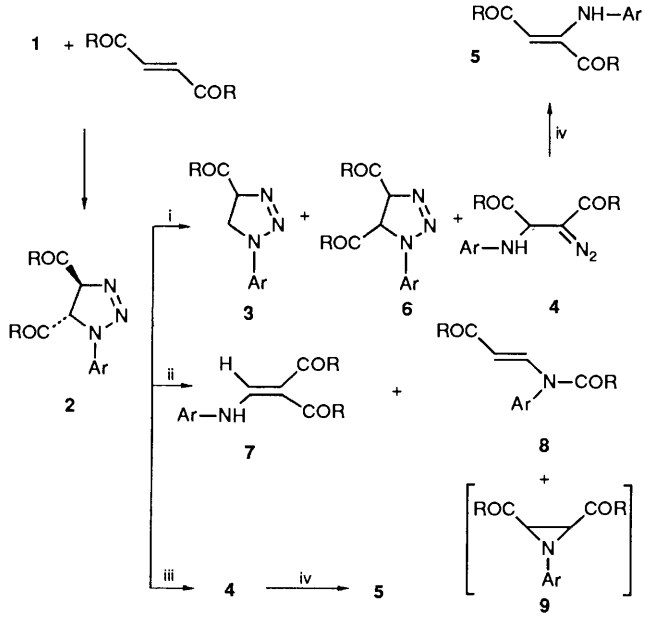
Reaction of 4-methoxyphenyl azide **1a** with 1,4-naphthoquinone **10** at 15–100 °C in benzene, dimethyl sulphoxide, or nitromethane leads mainly to the ring-contracted enamine **18a**, the ring-expanded 2-benzazepine-1,5-dione **20a**, and the aziridine **16a**, the decomposition products of an intermediate triazoline **12a**, to an extent largely independent of the solvent polarity and the temperature employed. However, the triazole **15a** appears to be the main decomposition product of the triazoline **12a** produced in hexamethylphosphoric triamide.

A comparable chemical trend is observed with thermal additions of 4-nitrophenyl azide **1b** to the quinone **10**. Cycloaddition of the azide **1a** to 2-methyl-1,4-naphthoquinone **11** leads regioselectively to the formation of the triazoline adduct **13a**, which undergoes preferential isomerization to an isolable diazo dione **23a**. On the other hand the azide **1b** leads to a mixture of the regioisomeric triazolines **13b** and **14b**. The triazoline **13b**, analogously to **13a**, rearranges to the ring-opened diazo dione **23b**, whereas the triazoline **14b** is converted into a mixture of the ring-contracted and ring-expanded products **24b** and **21b**. The possible reaction mechanisms involved in the decomposition of the triazolines **12a** and **12b**, **13a** and **13b** and **14b** are discussed.

In a previous paper[1] we have shown that the thermal reactions of 4-substituted phenyl azides **1** with (*E*)-1,2-dibenzoyl- and (*E*)-1,2-diacetyl-ethylene lead to unstable *trans*-4,5-diacyl-1-aryl-4,5-dihydro-1,2,3-triazoles **2**, whose decomposition paths are largely dependent upon the reaction conditions and, to a lesser extent, the nature of the 1-aryl substituent. At room temperature, compounds **2** undergo formal elimination of an aldehyde moiety to give 4-acyltriazoles **3** and isomerization to diazo diones **4**, from which 1-arylamino-1,2-diacylethylenes **5** are eventually formed, as well as oxidation to diacyltriazoles **6**, to a small extent. At 110 °C 1-arylamino-2,2-diacylethylenes **7** and *N*-aryl-*N*-vinylamides **8**, the rearrangement products occurring *via* 1,2-migration of the 5-acyl group to carbon and nitrogen, are preferentially formed in addition to varying amounts of elusive diacylaziridines **9**, resulting from homolytic fragmentation (Scheme 1). However, in the presence of triethylamine, these diacyldihydrotriazoles **2** undergo exclusively ring-cleavage isomerization to the diazo diones **4** and subsequent fragmentation to the enamines **5**.



Scheme 1 *Conditions:* i, benzene, room temperature; ii, $-N_2$, benzene, 110 °C; iii, Et_3N, benzene; iv, $-N_2$

In this paper we report our results from a related study of the thermal additions of 4-methoxyphenyl **1a** and 4-nitrophenyl azide **1b** to 1,4-naphthoquinone **10** and its 2-methyl derivative **11**, carried out under various experimental conditions. Our aim was to shed further light on the chemistry of 4,5-diacyl-substituted triazolines by suitable exploration of the thermal reactivity of tricyclic diacyltriazolines which should result from cycloadditions of the azides **1a** and **1b** to the olefin double bond of the quinones **10** and **11**.

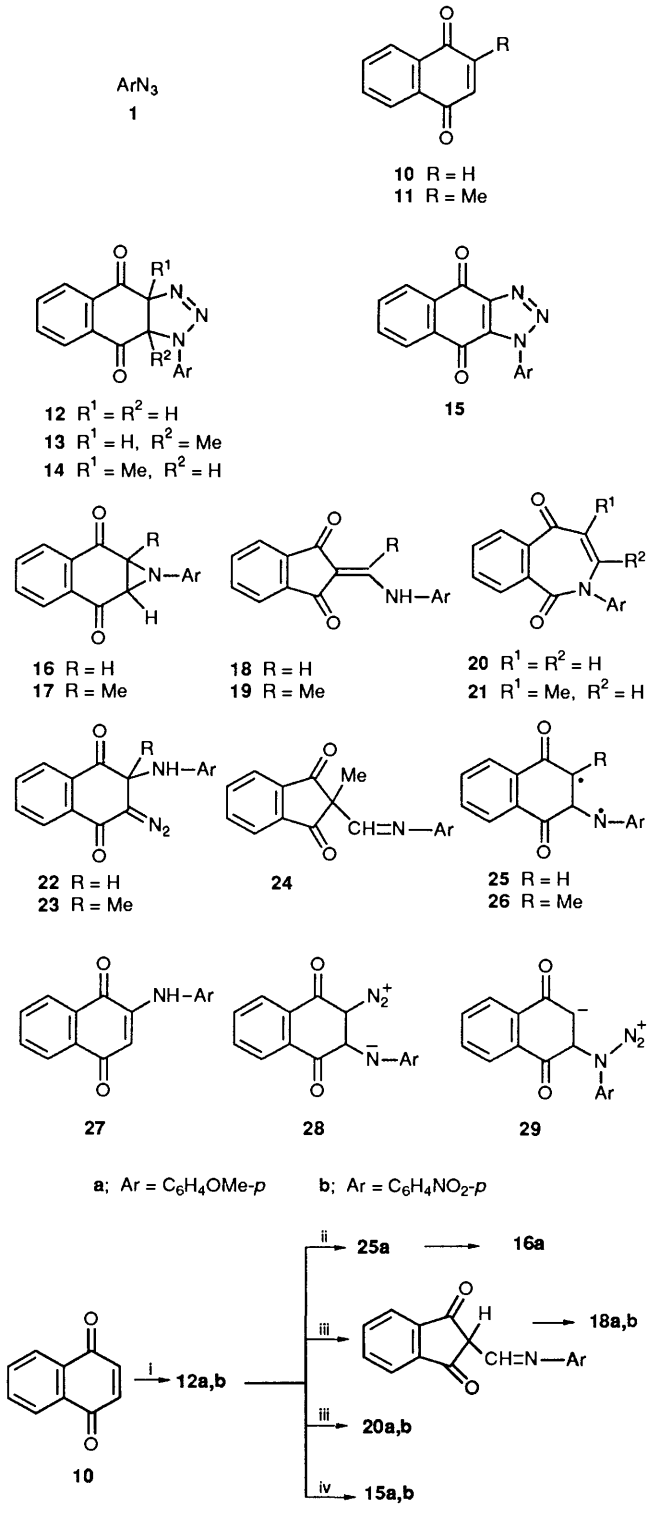
Little is known about the reaction of organic azides with quinones.[2] Thermal reactions of phenyl and 4-nitrophenyl azide with 1,4-naphthoquinone (and 1,4-benzoquinone) have been reported to give only ring-contracted cyclopentene-1,3-diones arising from presumed intermediate triazolines *via* 1,2-acyl migration.[3]

Moreover, thermolyses of 2-(azidoalkyl)-1,4-naphthoquinones (and benzoquinones) have recently been shown[4] to lead to fused ring azepine-1,5-diones and cyclopentene-1,3-diones *via* intermediate diacyltriazolines produced by intramolecular azide–olefin cycloaddition.

Results and Discussion

Reaction of 4-methoxyphenyl azide **1a** with an equimolar amount of 1,4-naphthoquinone **10** in benzene at room temperature (*ca.* 15 °C) led, after *ca.* 60 days, to the isolation of the naphthotriazole **15a** and the ring-contracted enamine **18a** in addition to minor amounts of the aziridine **16a** and the ring-expanded 2-benzazepine-1,5-dione **20a** (Table 1, entry 1 and Scheme 2).

The observed products **15a**, **16a**, **18a** and **20a** can be conceivably ascribed to decomposition of an intermediate triazoline **12a**, but direct evidence for its occurrence could not



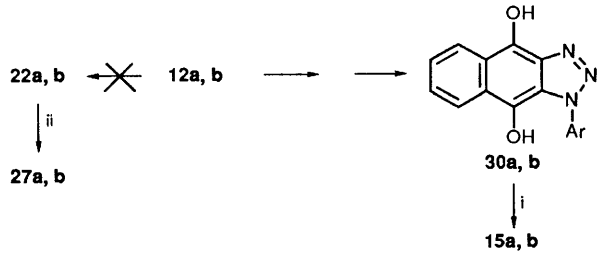
Scheme 2 *Reagents and conditions:* i, **1a** or **1b**, DMSO and/or $MeNO_2$ and/or HMPA and/or PhH, 15–100 °C; ii, **12a**, $-N_2$; iii, $-N_2$; iv, 1,4-naphthoquinone **10** and/or oxygen, −2 H

be achieved, presumably owing to its low stability and very low rate of formation, which is indicated by the fact that the azide **1a** and quinone **10** could be recovered unchanged to a great extent (*ca.* 65%) after the remarkably long reaction time employed. When the above reaction was carried out at 60 or 100 °C for the appropriate time (until TLC showed the starting quinone **10** to have been largely consumed) the occurrence of the triazole **15a** was found to be almost suppressed, in favour of the triazoline-fragmentation products **16a**, **18a** and **20a**, which were produced in proportions roughly comparable to those observed at 15 °C (Table 1, entries 2–4). Thus it appears that the tricyclic triazoline **12a** can, largely irrespectively of the thermal reaction conditions, effectively rearrange to the enamine **18a**, the benzazepinedione **20a**, and the aziridine **16a**.

This would contrast with the situation previously observed[1] with monocyclic diacyltriazolines **2**. These compounds at 110 °C generally led to analogous rearrangement products (**7**, **8** and **9**), but at room temperature mainly suffered aromatization to 4-acryltriazoles **3** and isomerization to diazo diones **4**, eventually affording enamines **5**. Unfortunately the mechanism involved in the noteworthy conversion of the monocyclic triazolines **2** into 4-acyltriazoles **3** is still unknown. Therefore the actual reasons for the observed lack of a similar aromatization process with the tricyclic triazoline **12a** (and also with the triazoline analogues **12b** and **13a** and **13b**, *vide infra*) remain unclear at this stage. Possibly the failure of the triazoline **12a** (and the triazolines **12b**, **13a** and **13b**) to undergo elimination of the 4-hydrogen and the 5-acyl substituent results from unfavourable stereochemical factors.

As for the additional failure of the triazoline **12a** to exhibit a rearrangement to diazo dione **22a** (and/or enamine **27a**) analogous to that observed with the triazolines **2**, it might at first be attributed to a lack of an effective basic promoter.[1] However, this possibility seems to be ruled out by our subsequent results obtained from the above reaction carried out at 60 °C in hexamethylphosphoric triamide (HMPA), a basic and polar solvent. Our initial attempt to ascertain the possible effect of added base by allowing the azide **1a** to react with the quinone **10** in benzene at 60 °C in the presence of a slight excess of triethylamine was frustrated by the fact that under these circumstances a very intractable reaction mixture was produced. We were therefore led to repeat the reaction in neat HMPA, in which solvent 4,5-dibenzoyl-1-(4-methoxyphenyl)-4,5-dihydro-1,2,3-triazole **2**; R = Ph, Ar = C_6H_4OMe-*p* was found to undergo smooth rearrangement to the enamine **5**; R = Ph, Ar = C_6H_4OMe-*p* analogously to that previously encountered in benzene in the presence of triethylamine[1] (see Experimental section). In HMPA the reaction cleanly afforded the triazole **15a** (62%), the ring-contracted enamine **18a** (3%), and 1,4-dihydroxynaphthalene (35%) as the exclusive products (Table 1, entry 5).

It therefore appears that even in basic medium the triazoline **12a** would not be capable of undergoing isomerization to diazo dione **22a**, but would instead suffer dehydrogenation to the triazole **15a** by the starting quinone **10** and presumably the oxygen present.[1] We suggest that base-promoted (or spontaneous) ring-opening isomerization to diazo dione **22a** be essentially prevented owing to the fact that possible keto–enol tautomerization might compete most favourably. This might eventually lead to the dihydroxynaphthotriazole **30a**, resulting in aromatization of both cyclohexenedione and triazoline ring. The ensuing triazole **30a** would then afford the observed naphthotriazole dione **15a** by subsequent dehydrogenation (Scheme 3).



Scheme 3 *Reagents:* i, 1,4-naphthoquinone **10** and/or oxygen, −2 H; ii, $-N_2$

Table 1 Product yields (%)[a] for thermal reactions of 4-methoxyphenyl **1a** and 4-nitrophenyl azide **1b** with 1,4-naphthoquinone **10**[b]

Entry	Azide	Conditions	Enamine	Azepinedione	Aziridine	Naphthotriazole
1	**1a**	PhH, 15 °C, 60 days[c]	37 **18a**	10 **20a**	11 **16a**	33 **15a**
2	**1a**	PhH, 60 °C, 14 days[c]	48 **18a**	14 **20a**	24 **16a**	6 **15a**
3	**1a**	PhH, 60 °C, 5 days	46 **18a**	20 **20a**	31 **16a**	1 **15a**
4	**1a**	PhH, 100 °C, 6 h[c]	49 **18a**	14 **20a**	24 **16a**	3 **15a**
5	**1a**	HMPA, 60 °C, 15 h[d]	3 **18a**			62 **15a**
6	**1a**	$MeNO_2$, 60 °C, 14 days[c]	49 **18a**	19 **20a**	31 **16a**	2 **15a**
7	**1a**	DMSO, 60 °C, 15 h	37 **18a**	10 **20a**	20 **16a**	21 **15a**
8	**1b**	PhH, 15 °C, 70 days[c]	7 **18b**			48 **15b**
9	**1b**	PhH, 60 °C, 60 h	60 **18b**	12 **20b**		15 **15b**
10	**1b**	$MeNO_2$, 60 °C, 65 h	67 **18b**	9 **20b**		21 **15b**
11	**1b**	HMPA, 60 °C, 18 h[e]	4 **18b**			51 **15b**

[a] Isolated yields based on consumed quinone **10** (17–98%). [b] Unless otherwise stated, a three-fold molar excess of starting azide **1** was employed. [c] Equiv. molar amounts of starting azide **1** were employed. [d] 1,4-Dihydroxynaphthalene was also isolated, in 35% yield. [e] 1,4-Dihydroxynaphthalene was also isolated, in 21% yield.

When 4-methoxyphenyl azide **1a** was treated with the quinone **10** in nitromethane at 60 °C, the enamine **18a**, the azepine **20a**, and the aziridine **16a** were obtained in yields strictly comparable to the corresponding ones observed in benzene (Table 1, entries 6, 2 and 3). Similar results were obtained from the same reaction carried out in dimethyl sulphoxide (DMSO), but in this somewhat basic solvent the triazole **15a** was also produced to a significant extent (Table 1, entry 7). It may therefore be inferred that the thermal rearrangement of the triazoline **12a** to products **18a**, **20a** and **16a** is not affected by the solvent polarity. This observation suggests that diazonium betaines such as species **28a**[1,4] and/or **29a**[4] are not likely to be involved in the formation of the compounds **18a** and **20a**, if the reasonable assumption is granted that competing aziridine formation should occur *via* the intermediacy of a singlet 1,3-diradical **25a** (see also below).[1,2,5] Compounds **18a** and **20a** probably result from concerted acyl migration to carbon and nitrogen and loss of nitrogen, in line with our previous suggestion for related diacyltriazoline **2** rearrangements.[1] However, the possibility that homolytic pathways[1] may also be involved in the occurrence of the rearranged products **18a** and **20a** cannot be ruled out on the basis of the fact that the observed ratio of aziridine **16a** to enamine **18a** and to azepinedione **20a** formation was found to remain largely unchanged over the whole range of temperatures examined.

The thermal reactions of the quinone **10** with 4-nitrophenyl azide **1b** in benzene (at room temperature and 60 °C), nitromethane (at 60 °C), and HMPA (at 60 °C) showed a chemical trend comparable to that encountered with the corresponding reactions with the azide **1a**, except that they never led to any aziridine formation. Reaction in benzene or nitromethane at 60 °C gave mainly a mixture of the rearranged products **18b** (60–67%) and **20b** (9–12%) together with minor amounts of the naphthotriazole **15b** (Table 1, entries 8 and 9). On the other hand, in HMPA the triazole **15b** (51%), the ring-contracted enamine **18b** (4%), and 1,4-dihydroxynaphthalene (21%) were the only identifiable products (Table 1, entry 10). Similar results were obtained from the reaction in benzene at room temperature (Table 1, entry 11). On this basis, it may be inferred that the resulting intermediate triazoline **12b** can display a chemical reactivity trend similar to that of the methoxy-substituted analogue **12a** (Schemes 2 and 3). However, the strongly electron-withdrawing nitro substituent would prevent homolytic fragmentation to aziridine, which might have been anticipated in the light of our previous evidence with monocyclic 1-(4-nitrophenyl)-substituted diacyltriazolines.[1]

Our study was subsequently extended to the thermal additions of the azides **1a** and **1b** to 2-methyl-1,4-naphthoquinone **11**, which were expected[2] to lead preferentially to the triazoline adducts **13a** and **13b** over the regioisomeric isomers **14a** and **14b**. Triazolines of type **13** were of interest to us in that, being conceivably hindered from undergoing aromatization to naphthotriazole diones, they should be capable of exhibiting effective isomerization to ring-opened diazo compounds **23**. In fact, reaction of the azide **1a** with 2-methyl-1,4-naphthoquinone **11** in benzene at 40 °C led to the isolation of the diazo dione **23a** (37%) and the aziridine **17a** (10%) as the only identifiable products (Table 2, entry 1). The diazo compound **23a** could be obtained in fairly good yield (59%) along with some aziridine **17a** when the same reaction was carried out in HMPA (Table 2, entry 2). Moreover, the azide **1a** reacted with the quinone **11** in toluene at 100 °C to give the ring-contracted enamine **19a** and minor amounts of the aziridine **17a** (Table 2, entry 3). The diazo dione **23a** was found to decompose rapidly in refluxing toluene to give the enamine **19a**, formally resulting from rearrangement of a carbene intermediate *via* anionotropic acyl migration.* The above results, while suggesting that addition of the azide **1a** to the quinone **11** proceeds in a regioselective fashion leading to the expected triazoline **13a**, also suggest that ring-cleavage isomerization should be the preferred decomposition path for such a triazoline, especially in basic medium and at low temperature (Scheme 4).

At 100 °C 4-nitrophenyl azide **1b** reacted with the quinone **11** in toluene to afford the ring-contraction product **19b** together with comparable amounts of 2-methylindanedione **31** and the formanilide **32** and minor amounts of the azepinedione **21b** (Table 2, entry 5). Similar results were obtained in acetonitrile at 60 °C, but in this case the diazo compound **23b** could be isolated in 11% yield at the expense of the ring-contracted enamine **19b** (Table 2, entry 4). Comparable findings were also obtained in HMPA at 60 °C, except that the triazoline **33** was obtained instead of the indanedione **31** (Table 2, entry 6).

Finally, the diazo dione **23b** was found to occur essentially at the expense of the enamine **19b** when this latter reaction was carried out for a suitably shorter time (Table 2, entry 7). The diazo compound **23b** was independently shown to be converted into the enamine **19b** upon being heated in boiling toluene, analogously to the diazo dione **23a**.

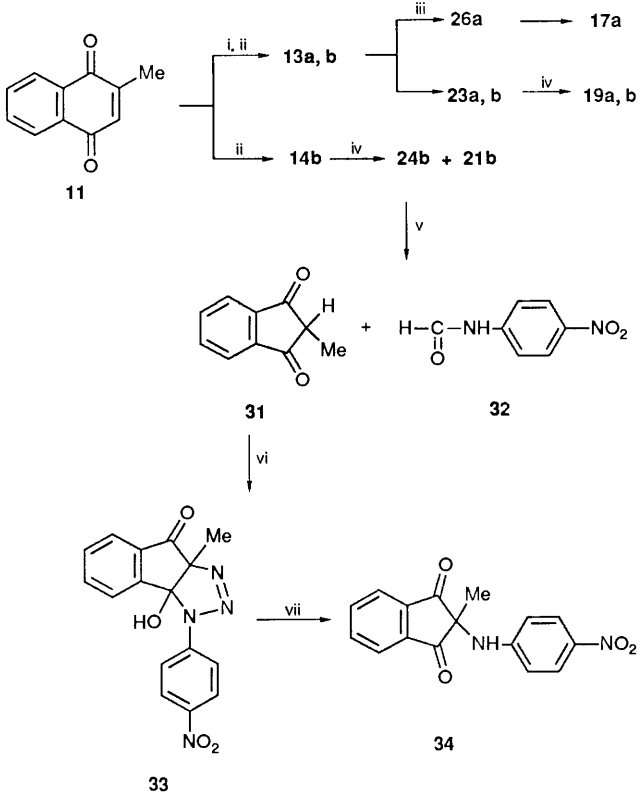
The triazoline **33** produced in HMPA most likely arose from further reaction of indanedione **31** with *p*-nitrophenyl azide **1b**. This was supported by a control experiment which showed that the compound **31** reacted smoothly with the azide **1b** in HMPA to afford the triazoline **33** in high yield.[6] Structural assignment

* For a related thermal rearrangement of a diazo enedione see ref. 4.

Table 2 Product yields (%)[a] for thermal reactions of 4-methoxyphenyl **1a** and 4-nitrophenyl azide **1b** with 2-methyl-1,4-naphthoquinone **11**[b]

Entry	Azide	Conditions	Enamine	Aziridine	Azepinedione	Diazo dione	Triazoline **33**	Indanedione **31**
1	**1a**	PhH, 40 °C, 7 days		10 **17a**		37 **23a**		
2	**1a**	HMPA, 40 °C, 6 days		10 **17a**		59 **23a**		
3	**1a**	PhMe, 100 °C, 5 h	44 **19a**	17 **17a**				
4	**1b**	MeCN, 60 °C, 48 h[c]	32 **19b**		12 **21b**	11 **23b**		40
5	**1b**	PhMe, 100 °C, 17 h[c]	44 **19b**		11 **21b**			39
6	**1b**	HMPA, 60 °C, 10 days[c]	28 **19b**		7 **21b**	1 **23b**	32	
7	**1b**	HMPA, 60 °C, 24 h[c]	5 **19b**		3 **21b**	**20 23b**	16	

[a] Isolated yields based on consumed quinone **11** (27–91%). [b] A three-fold molar excess of starting azide **1** was generally employed. [c] The formanilide **32** was also isolated (see Experimental section).



Scheme 4 *Reagents and conditions:* i, **1a**, PhH (40 °C), HMPA (40 °C), or PhMe (100 °C); ii, **1b**, HMPA (60 °C), MeCN (60 °C), or PhMe (100 °C); iii, **13a**, $-N_2$; iv, $-N_2$; v, water; vi, **1b**, HMPA, 60 °C; vii, $-N_2$, H^+, benzene

of compound **33** was made on the basis of spectral analysis (see Experimental section) and chemical evidence, and was fully confirmed by an X-ray crystal structure determination (details will be reported elsewhere). The triazoline **33** in benzene was quantitatively converted into the indanedione **34** upon treatment with a trace of trifluoroacetic acid (Scheme 4).[6]

The above results lead to the conclusion that the azide **1b**, differently from the more reactive azide **1a**, adds to the quinone **11** to give a mixture of regioisomeric triazolines **13b** and **14b**, to a comparable extent. The triazoline **13b** would give the diazo dione **23b** as the exclusive decomposition product, whereas the regioisomeric triazoline **14b** would rearrange to the azepinedione **21b** and the imine **24b**, from which the indanedione **31** and the formanilide **32** would be eventually produced by subsequent hydrolysis (Scheme 4).

In line with the 1-(4-nitrophenyl)-substituted diacyl-4,5-dihydrotriazole **12b** no homolytic fragmentation to aziridine would be undergone by either triazoline **13b** or **14b**.

In the light of the general evidence provided in the present study by the 1-aryl-substituted triazolines (**12a** and **b**, **13a** and **b** and **14b**) in addition to related evidence obtained with 1-alkyl-substituted analogues[4] it should be concluded that the chemical reactivity of these tricyclic 4,5-diacyl-4,5-dihydrotriazoles, analogously to that of the monocyclic ones, is essentially dominated by the great migratory aptitude of the acyl group at the 5-position and the acidity of the hydrogen atom (if present) at the 4-position.

Rearrangement to ring-expanded 2-benzazepine-1,5-diones and/or ring-contracted indane-1,3-diones *via* 1,2-acyl migration to nitrogen and/or carbon can generally occur irrespective of the thermal reaction conditions. However, if a free hydrogen is present at the 4-position, as well as at the adjacent 5-position, especially at low temperature and/or in basic medium, dehydrogenation to naphthotriazole diones can become (largely) preferred, but if no hydrogen substituent is available at the 5-position isomerization to isolable 2-diazo-2,3-dihydronaphthoquinones is greatly favoured.

Finally, the electronic character of an *N*-aryl substituent can play a significant role. An electron-rich *N*-aryl substituent would, in fact, cause homolytic fragmentation to a tricyclic diacylaziridine to be an additional, important decomposition path.

Experimental

The aryl azides **1a** and **1b**[7] were prepared from the corresponding anilines by procedure A of Smith and Brown; 1,4-naphthoquinone **10** and 2-methyl-1,4-naphthoquinone **11** were commercially available. Reaction products such as 2-methylindane-1,3-dione **31**,[8] 4-nitroformanilide **32**,[9] and 1,4-dihydroxynaphthalene were each identified by spectral comparison with authentic specimens. Column chromatography was carried out on ICN silica 63–200 60A by gradual elution with light petroleum (boiling range 40–70 °C), diethyl ether–light petroleum mixtures (up to 100% diethyl ether), and finally with acetone. All m.p.s (Köfler melting point apparatus) are uncorrected. ^1H NMR spectra were measured in $CDCl_3$ with $SiMe_4$ as internal standard and recorded on a Varian EM 360L (60 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer 257 spectrometer. MS spectra were determined by the electron-impact method (70 eV) on a VG 7070 instrument.

Reactions of Aryl Azides (**1a** *and* **b**) *with* 1,4-*Naphthoquinone* **10**.—*Procedure A*. A solution of the aryl azide **1a** or **1b** (3 mmol) in the appropriate solvent (15 cm^3) containing an equimolar amount of the quinone **10** was kept in a sealed tube, in the dark, at the appropriate temperature for the suitable time (generally until TLC showed the starting quinone **10** to have been largely consumed).

Procedure B. This was analogous to the above procedure A except that the aryl azide **1a** or **1b** (3 mmol) was allowed to react with the quinone **10** (1 mmol) in the appropriate solvent (1 cm^3).

The resulting reaction mixtures were then worked up and the

reaction products separated as specified in each case. Yields of identified products and reaction times are given in Table 1.

Reaction of 4-*Methoxyphenyl Azide* **1a** *with* 1,4-*Naphthoquinone* **10**.—(a) *in benzene at* 15 °C (*procedure A*). After removal of the solvent under reduced pressure below 20 °C, the residue was chromatographed to give (i) substrate 4-methoxyphenyl azide **1a** (1.87 mmol, 62% recovery); (ii) the starting quinone **10** (2.08 mmol, 69% recovery); (iii) 1a,7a-*dihydro*-1-(4-*methoxyphenyl*)-1H-*naphth*[2,3-b]*azirine*-2,7-*dione* **16a**, m.p. 130–131 °C; δ_H(60 MHz) 3.68 (2 H, s), 3.93 (3 H, s), 7.1–7.28 (4 H, m) and 8.08–8.75 (4 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 1695 (C=O) and 1600 (C=O) (Found: M^+, 279.089 44. $C_{17}H_{13}NO_3$ requires M, 279.089 54); *m/z* 278, 264 and 134; (iv) 2-(4-*methoxyphenyl*)-2H-2-*benzazepine*-1,5-*dione* **20a**, m.p. 180–182 °C; δ_H(200 MHz) 3.82 (3 H, s), 5.92 (1 H, d, *J* 10 Hz), 6.98 (3 H, m), 7.23 (2 H, d, *J* 9 Hz) and 7.72–8.48 (4 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 1650 (C=O) (Found: M^+, 279.089 44. $C_{17}H_{13}NO_3$ requires M, 279.089 54); *m/z* 278, 264, 253, 236, 149 and 134; (v) 2-[(4-*methoxyanilino*)*methylene*]*indane*-1,3-*dione* **18a**, m.p. 200–201 °C; δ_H(60 MHz) 3.9 (3 H, s), 7.17 (4 H, m), 7.8 (4 H, m), 8.23 (1 H, d, *J* 14 Hz, collapsing to a singlet upon D_2O shake), and 10.86 (1 H, br d, *J* 14 Hz); $\nu_{max}(CHCl_3)/cm^{-1}$ 1650 (C=O) and 1620 (C=O) (Found: M^+, 279.089 44. $C_{17}H_{13}NO_3$ requires M, 279.089 54); *m/z* 264; and (vi) 1-(4-*methoxyphenyl*)-1H-*naphtho*[2,3-d][1,2,3]*triazole* 4,9-*dione* **15a**, m.p. 223–224 °C; δ_H(60 MHz) 3.85 (3 H, s), 7.0 (2 H, d, *J* 9 Hz), 7.47–7.93 (4 H, m) and 8.0–8.38 (2 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700 (C=O) and 1600 (C=O) (Found: M^+, 305.079 67. $C_{17}H_{11}N_3O_3$ requires M, 305.080 04); *m/z* 277, 262, 234, 233 and 206.

(b) *In benzene at* 60 °C (*procedure A*). The solid material which had separated was collected and shown to be the enamine **18a** (1.07 mmol). The benzene mother liquor was evaporated and the residue was chromatographed to give (i) the naphthoquinone **10** (0.32 mmol, 11% recovery); (ii) the aziridine **16a**; (iii) the azepinedione **20a**; and (iv) additional enamine **18a** (0.17 mmol).

(c) *In benzene at* 60 °C (*procedure B*). The solid material which separated upon addition of diethyl ether (20 cm^3) was filtered off and shown to be the enamine **18a** (0.41 mmol). The filtrate was evaporated and the solid residue was extracted with diethyl ether (50 cm^3); the remaining solid (45 mg) was shown by ^1H NMR spectroscopy to be a mixture of the enamine **18a**, the triazole **15a**, and the azepine **20a** in *ca.* 1:1.7:3.6 proportions. The ether layer was evaporated and the resulting residue was subjected to column chromatography to give (i) unchanged azide **1a**; (ii) unchanged quinone **10** (0.02 mmol, 2% recovery); (iii) the aziridine **16a** (0.24 mmol); (iv) additional azepinedione **20a** (0.01 mmol); (v) additional enamine **18a** (0.03 mmol); and (vi) further triazole **15a** (0.01 mmol).

(d) *In benzene at* 100 °C (*procedure A*). The solid which had separated was collected by filtration to yield the enamine **18a** (0.72 mmol). Chromatography of the residue obtained on evaporation of the benzene mother liquor afforded (i) unchanged azide **1a** (1.02 mmol, 34% recovery); (ii) unchanged quinone **10** (1.20 mmol, 40% recovery); (iii) the aziridine **16a** (0.43 mmol); (iv) the azepinedione **20a** (0.25 mmol); (v) further enamine **18a** (0.16 mmol), and (vi) the triazole **15a** (0.06 mmol).

(e) *In HMPA at* 60 °C (*procedure B*). Filtration of the solid which separated upon addition of diethyl ether (20 cm^3) gave the triazole **15a** (0.49 mmol). Chromatography of the evaporated filtrate gave (i) unchanged azide **1a**; (ii) unchanged quinone **10** (0.14 mmol, 14% recovery); (iii) 1,4-dihydroxynaphthalene (0.30 mmol); (iv) the enamine **18a** (0.03 mmol); and (v) additional triazole **15a** (0.04 mmol).

(f) *In nitromethane at* 60 °C (*procedure A*). The solid material which had separated was filtered off and found to be the enamine **18a** (1.11 mmol). Chromatography of the residue obtained after evaporation of the nitromethane mother liquid yielded (i) unchanged azide **1a** (0.37 mmol, 12% recovery); (ii) unchanged quinone **10** (0.49 mmol, 16% recovery); (iii) the aziridine **16a** (0.78 mmol); (iv) the azepinedione **20a** (0.47 mmol); (v) additional enamine **18a** (0.12 mmol); and (vi) the triazole **15a** (0.06 mmol).

(g) *In DMSO at* 60 °C (*procedure B*). The solid material which separated upon addition of diethyl ether (20 cm^3) was collected by filtration to yield a mixture (116 mg) of the enamine **18a** and the triazole **15a** in *ca.* 1.7:1 ratio, as indicated by ^1H NMR spectroscopy. Chromatography of the residue obtained on evaporation of the filtrate gave (i) unchanged azide **1a**; (ii) unchanged quinone **10** (0.08 mmol, 8% recovery); (iii) the aziridine **16a** (0.18 mmol); (iv) an unidentified red compound (9 mg); (v) the azepinedione **20a** (0.09 mmol); (vi) additional enamine **18a** (0.08 mmol); and (vii) additional triazole **15a** (0.04 mmol).

Reaction of 4-*Nitrophenyl Azide* **1b** *with* 1,4-*Naphthoquinone* **10**.—(a) *In benzene at* 15 °C (*procedure A*). The solid material which had separated was collected by filtration to give 2-[(4-nitroanilino)methylene]indane-1,3-dione **18b** (0.03 mmol), m.p. 347–349 °C (lit.,[3b] ~315 °C); $\delta_H(CF_3CO_2D$; 60 MHz) 7.57 (2 H, d, *J* 9 Hz), 7.8 (4 H, m), 8.33 (2 H, d, *J* 9 Hz), and 8.53 (1 H, s); $\nu_{max}(KBr)/cm^{-1}$ 1 652 (C=O) and 1 634 (C=O) (Found: M^+, 294.064 71. $C_{16}H_{10}N_2O_4$ requires M, 294.064 06); *m/z* 293, 265, 247, 219 and 104.

The benzene mother liquor was evaporated and the resulting solid residue was washed with diethyl ether (30 cm^3); the remaining solid was 1-(4-*nitrophenyl*)-1H-*naphtho*[2,3-d][1,2,3]*triazole*-4,9-*dione* **15b** (0.12 mmol), m.p. 237–238 °C; δ_H(200 MHz) 7.8–7.98 (2 H, m), 8.25 (2 H, d, *J* 9 Hz), 8.19–9.22 (2 H, m) and 8.5 (2 H, d, *J* 9 Hz); $\nu_{max}(CHCl_3)/cm^{-1}$ 1600 (C=O) and 1580 (C=O) (Found: M^+, 320.054 97. $C_{16}H_8N_4O_4$ requires M, 320.054 56); *m/z* 292, 262, 246, 218, 190 and 104. The diethyl ether layer was evaporated and the residue was chromatographed to afford (i) unchanged azide **1b** (2.5 mmol, 83% recovery); (ii) unchanged quinone **10** (2.5 mmol, 83% recovery); and (iii) further triazole **15b** (0.12 mmol).

(b) *In benzene at* 60 °C (*procedure B*). Upon addition of methylene dichloride (10 cm^3) a yellow solid precipitated out. This was filtered off and shown to be the enamine **18b** (0.52 mmol). The organic filtrate was concentrated and the resulting residue was washed with diethyl ether (30 cm^3) to give the triazole **15b** (0.14 mmol). Evaporation of the ether layer under reduced pressure afforded a solid residue, which was chromatographed to yield (i) unchanged azide **1b**; (ii) unchanged quinone **10** (0.14 mmol, 14% recovery); and (iii) 2-(4-*nitrophenyl*)-2H-2-*benzazepine*-1,5-*dione* **20b** (0.1 mmol), m.p. 178–180 °C; δ_H(200 MHz) 6.01 (1 H, d, *J* 11 Hz), 6.86 (1 H, d, *J* 11 Hz), 7.57 (2 H, d, *J* 9 Hz), 7.80 (2 H, m) and 8.18–8.50 (4 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 660 (C=O) and 1 600 (C=O) (Found: M^+, 294.063 83. $C_{16}H_{10}N_2O_4$ requires M, 294.064 06); *m/z* 293, 266, 247, 220, 219, 149, 146 and 105.

(c) *In nitromethane at* 60 °C (*procedure B*). Work-up of the reaction mixture similar to that above described for the corresponding reaction in benzene afforded (i) the enamine **18b** (0.5 mmol) and (ii) the triazole **15b** (0.16 mmol). Chromatography of the resulting residue yielded (i) unchanged azide **1b**; (ii) unchanged quinone **10** (0.26 mmol, 26% recovery); and (iii) the azepinedione **20b** (0.07 mmol).

(d) *In HMPA at* 60 °C (*procedure B*). Upon addition of diethyl ether (100 cm^3) a yellow solid precipitated out. This was collected by filtration and found to be the triazole **15b** (0.31 mmol). Upon partial concentration the organic filtrate precipitated the enamine **18b** (0.03 mmol). Subsequent chromatography of the remaining filtrate gave (i) unchanged

azide **1b**; (ii) unchanged naphthoquinone **10** (0.33 mmol, 33% recovery); (iii) 1,4-dihydroxynaphthalene (0.14 mmol); and (iv) 4-nitroaniline (0.04 mmol).

Reactions of Aryl Azides **1a** *and* **1b** *with* 2-*Methyl*-1,4-*naphthoquinone* **11**.—These were generally carried out according to the procedure B reported above for the corresponding reactions with 1,4-naphthoquinone **10**. Yields of identified products and reaction times are given in Table 2.

Reaction of 4-*Methoxyphenyl Azide* **1a** *with* 2-*Methyl*-1,4-*naphthoquinone* **11**.—(a) *In benzene at* 40 °C. Upon addition of diethyl ether (20 cm^3) an orange solid precipitated out. This was filtered off and found to be 3-*diazo*-2,3-*dihydro*-2-(4-*methoxyanilino*)-2-*methyl*-1,4-*naphthoquinone* **23a** (0.25 mmol), m.p. 125 °C (decomp.); δ_H(200 MHz) 1.77 (3 H, s), 3.7 (3 H, s), 6.6 (2 H, d, *J* 8 Hz), 6.88 (2 H, d, *J* 8 Hz) and 7.7–8.33 (4 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 3410 (NH), 2100 (C=N_2), 1700, 1630 (C=O) and 1600 (C=O); *m/z* 321 (M^+), 293, 292, 278, 123, 122 and 28 (Found: C, 67.45; H, 4.75; N, 13.0. $C_{18}H_{15}N_3O_3$ requires C, 67.3; H, 4.7; N, 13.1%). Upon being heated in refluxing toluene (*ca.* 30 min) this compound was converted almost quantitatively into the enamine **19a** (*vide infra*).

The residue resulting from evaporation of the organic filtrate was chromatographed to give (i) unchanged azide **1a**; (ii) unchanged quinone **11** (0.33 mmol, 33% recovery); and (iii) 1a,7a-*dihydro*-1-(4-*methoxyphenyl*)-1a-*methyl*-1H-*naphtho*[2,3-b]*azirine*-2,7-*dione* **17a** (0.07 mmol), m.p. 115–117 °C; δ_H(60 MHz) 1.33 (3 H, s), 3.35 (1 H, s), 3.75 (3 H, s), 6.77 (4 H, m) and 7.38–8.27 (4 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 1690 (C=O) and 1 600 (C=O) (Found: M^+, 293.105 42. $C_{18}H_{15}NO_3$ requires M, 293.105 19); *m/z* 160, 148 and 134.

(b) *In HMPA at* 40 °C. Upon addition of diethyl ether (20 cm^3) the reaction mixture precipitated the diazo dione **23a** (0.23 mmol). Chromatography of the concentrated filtrate furnished (i) unchanged azide **1a**; (ii) unchanged quinone **11** (0.58 mmol, 58% recovery); (iii) the aziridine **17a** (0.043 mmol); and (iv) additional diazo dione **23a** (0.04 mmol).

(c) *In toluene at* 100 °C. Chromatography yielded (i) unchanged azide **1a**; (ii) unchanged quinone **11** (0.1 mmol, 10% recovery); (iii) the aziridine **17a** (0.16 mmol); (iv) 2-[1-(4-*methoxyanilino*)*ethylidene*]*indane*-1,3-*dione* **19a** (0.04 mmol), m.p. 172–174 °C; δ_H(200 MHz) 2.58 (3 H, s), 3.87 (3 H, s), 7.1 (4 H, m), 7.96 (4 H, m) and 12.29 (1 H, br s); $\nu_{max}(CHCl_3)/cm^{-1}$ 1690, 1640, 1590 and 1570 (Found: M^+, 293.105 14. $C_{18}H_{15}NO_3$ requires M, 293.105 19); *m/z* 292, 278, 252, 171 and 123; and (v) tarry material (65 mg).

Reaction of 4-*Nitrophenyl Azide* **1b** *with* 2-*Methyl*-1,4-*naphthoquionone* **11**.—(a) *In acetonitrile at* 60 °C. Chromatography gave (i) unchanged azide **1b**; (ii) unchanged quinone **11** (0.73 mmol, 73% recovery); (iii) 2-methylindane-1,3-dione **31** (0.11 mmol); (iv) 4-*methyl*-2-(4-*nitrophenyl*)-2H-2-*benzazepine*-1,5-*dione* **21b** (0.032 mmol), m.p. 180–181 °C; δ_H(200 MHz) 2.08 (3 H, d, *J* 1.1 Hz), 6.84 (1 H, q, *J* 1.1 Hz), 7.54 (2 H, d, *J* 9 Hz), 7.68–8.10 (3 H, m) and 8.28–8.42 (3 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 1650 (C=O) and 1620 (C=O) (Found: M^+, 308.079 53. $C_{17}H_{12}N_2O_4$ requires M, 308.079 71); *m/z* 307, 280, 261, 233, 160, 149 and 132; (v) 2-[1-(4-*nitroanilino*)*ethylidene*]*indane*-1,3-*dione* **19b** (0.09 mmol), m.p. 270–272 °C; δ_H(200 MHz) 2.79 (3 H, s), 7.44 (2 H, d, *J* 9 Hz), 7.74 (4 H, m), 8.38 (2 H, d, *J* 9 Hz) and 12.58 (1 H, br s); $\nu_{max}(CHCl_3)/cm^{-1}$ 1690, 1640 and 1620 (Found: M^+, 308.078 92. $C_{17}H_{12}N_2O_4$ requires M, 308.079 71); *m/z* 307, 293, 279 and 261; (vi) 4-nitroaniline (0.035 mmol); (vii) 3-*diazo*-2,3-*dihydro*-2-*methyl*-2-(4-*nitroanilino*)-1,4-*naphthoquinone* **23b** (0.03 mmol), m.p. 140 °C (decomp.); δ_H(200 MHz) 1.88 (3 H, s), 5.18 (1 H, br s), 6.62 (2 H, d, *J* 9 Hz) and 7.74–8.4 (6 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 3410 (NH), 2100 (C=N_2), 1630 (C=O) and 1600 (C=O) (Found: C, 60.6; H, 3.55; N, 16.6. $C_{17}H_{12}N_4O_4$ requires C, 60.7; H, 3.6; N, 16.65%). This compound was converted quantitatively into the enamine **19b** after being heated in boiling toluene (30 min); and (viii) 4-nitroformanilide **32** (0.1 mmol).

(b) *In toluene at* 100 °C. Upon addition of diethyl ether (3 cm^3) the reaction mixture precipitated the enamine **19b** (0.29 mmol). The filtrate was evaporated and the residue was chromatographed to give (i) unchanged azide **1b**; (ii) unchanged quinone **11** (0.33 mmol, 33% recovery); (iii) 2-methylindane-1,3-dione **31** (0.23 mmol); (iv) the benzazepinedione **21b** (0.08 mmol); (v) 4-nitroaniline (0.05 mmol); and (vi) the formanilide **32** (0.25 mmol).

(c) *In HMPA at* 60 °C. Upon addition of diethyl ether (30 cm^3) the reaction mixture precipitated the enamine **19b** (0.18 mmol). Chromatography of the concentrated filtrate afforded (i) unchanged azide **1b**; (ii) unchanged quinone **11** (0.37 mmol, 37% recovery); (iii) the benzazepinedione **21b** (0.042 mmol); (iv) 4-nitroaniline (0.08 mmol); (v) additional enamine **19b** (0.02 mmol); (vi) 3a,8a-*dihydro*-3a-*hydroxy*-8a-*methyl*-3-(4-*nitrophenyl*)-3H-*indeno*[1,2-d][1,2,3]*triazole*-8-*one* **33** (0.21 mmol), m.p. 164–166 °C (decomp.); δ_H(200 MHz) 1.72 (3 H, s), 5.2 (1 H, s, removed upon D_2O shake), 7.52–8.98 (6 H, m) and 8.26 (2 H, d, *J* 9 Hz); $\nu_{max}(CHCl_3)/cm^{-1}$ 3580sh (free OH), 3250br (hydrogen-bonded OH), 1720 (C=O) and 1600 and 1340 (NO_2); *m/z* (30 eV) 324 (M^+), 296, 281, 268, 253, 164, 160, 136, 132 and 104 (Found: C, 59.3; H, 3.7; N, 17.35. $C_{16}H_{12}N_4O_4$ requires C, 59.25; H, 3.75; N, 17.3%); (vii) the diazo dione **23b**; and (viii) 4-nitroformanilide **32** (0.15 mmol).

The same reaction carried out for 24 h, analogous work-up of the reaction mixture, gave (i) unchanged azide **1b**; (ii) unchanged quinone **11** (0.72 mmol, 72% recovery); (iii) the benzazepinedione **21b** (0.01 mmol); (iv) the enamine **19b** (0.12 mmol); (v) the triazoline **33** (0.045 mmol); (vi) the diazo dione **23b** (0.055 mmol); and (vii) the formanilide **32** (0.02 mmol).

Reaction of 4-*Methoxyphenyl Azide* **1a** *with* (E)-1,2-*Dibenzoylethylene in HMPA*.—A solution of the azide **1a** (1 mmol) in HMPA (1 cm^3) containing an equimolar amount of (*E*)-1,2-dibenzoylethylene was heated at 110 °C for 30 min, after which the resulting reaction mixture was chromatographed to give (i) unchanged azide **1a** (0.22 mmol, 22% recovery); (ii) unchanged 1,2-dibenzoylethylene (0.05 mmol, 5% recovery); (iii) an unknown solid compound (10 mg); (iv) (*Z*)-(2-4-methoxyanilino)-1,4-diphenylbut-2-ene-1,4-dione **5**; R = Ph, Ar = C_6H_4OMe-*p* (0.55 mmol, 70% based on consumed azide);[1] and (v) 4-benzoyl-1-(4-methoxyphenyl)-1,2,3-triazole **3**; R = Ph, Ar = C_6H_4OMe-*p* (0.18 mmol, 23% based on consumed azide).[1]

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