Synthesis and Reactivity of 4-Acyl-5-hydroxytriazolines Resulting from Thermal Reaction of Aryl and Tosyl Azides with 2-Substituted Indane-1,3-diones

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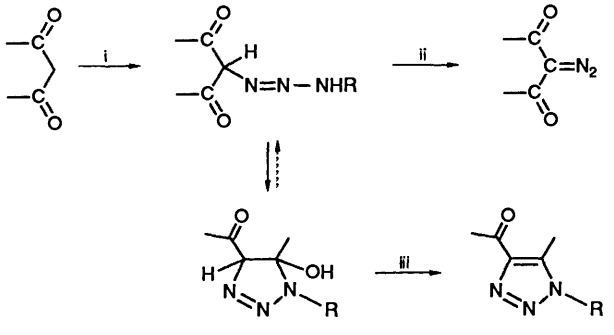
Reaction of aryl azides **1** with 2-methylindane-1,3-dione **3** in HMPA at 55 °C results in the formation of fairly stable tricyclic 4-acyl-5-hydroxytriazolines **6** in yields greatly decreasing with decreasing electrophilic character of the aryl azide reactant. Similar reaction of 4-nitrophenyl azide **1a** with 2-phenylindanedione **4** affords the corresponding 5-hydroxytriazoline **7a** in high isolated yield. Upon photolysis or treatment with trifluoroacetic acid the hydroxytriazolines **6** undergo exclusive decomposition to 2-arylamino-2-methylindanediones **12** through the reactive hydroxyaziridine **19** intermediates. On the other hand, upon thermolysis at 95 °C compounds **6** appear to rearrange preferentially to ring-expanded 2-arylisoquinoline-1,3-diones **13**, which are believed to result eventually from Wolff rearrangement of initially formed diazo keto amides. The strongly electrophilic tosyl azide **2** reacts smoothly with 2-methylindanedione **3** in HMPA, at room temperature, to give a mixture of the 2-tosylisoquinoline-1,3-dione **14** and the isomeric 1,4-dione **17** to a comparable extent. Under similar conditions, the azide **2** reacts with 2-phenylindanedione **4** to give exclusively the isoquinoline-1,3-dione **15** in virtually quantitative yield. The products **14**, **17** and **15** are ascribable to intramolecularly acid-catalysed decomposition of unstable diazocarbonyl compounds resulting from isomerization of reactive 5-hydroxy-1-tosyltriazolines adducts. An X-ray crystal structure analysis of the 4-acyl-5-hydroxytriazoline **6c** has been performed.

It is well known [1,2] that alkane- and arene-sulfonyl azides react with cyclic and acyclic α-methylene β-dicarbonyl compounds in the presence of base to afford a diazo group transfer product (Scheme 1). Related reactions of aryl (and alkyl) azides with

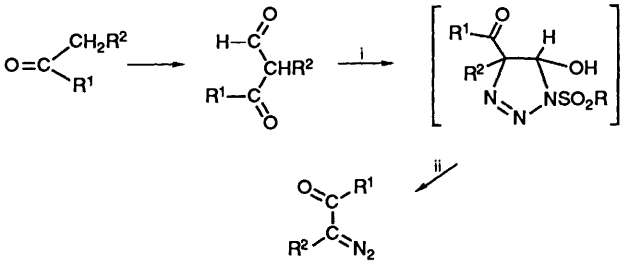


Scheme 1 *Reagents:* i, $+RN_3$ and base; ii, R = sulfonyl, $-RNH_2$; iii, R = aryl or alkyl, $-H_2O$

dicarbonyl compounds are generally reported [3,4] to lead to 1,2,3-triazole products ascribable to aromatization (with elimination of water) of 4-acyl-5-hydroxytriazoline intermediates not capable of surviving the basic reaction conditions (Scheme 1).

With β-dicarbonyl compounds bearing only a single α-hydrogen, sulfonyl azides generally react to give α-diazocarbonyl products with concomitant acyl cleavage.[1,2] Indeed, such a 'deacylating diazo group transfer reaction' finds wide application in the synthesis of α-diazocarbonyl compounds from monocarbonyl compounds whose α-methylene hydrogens are weakly acidic (Scheme 2).

However, no example of such a type of reaction with cyclic β-dicarbonyl compounds appears to have been reported. Moreover, reactions of aryl (or alkyl) azides with β-dicarbonyl compounds monosubstituted at the central carbon are virtually



Scheme 2 *Reagents:* i, $+RSO_2N_3$ and base; ii, $-RSO_2NHCHO$

unexplored.[3,4] In principle, these reactions are of interest in that they might afford still unknown 4-acyl-5-hydroxytriazolines which might be expected to survive the reaction conditions since ready aromatization to triazoles would be prevented in such cases. To our knowledge, the only documented 5-hydroxy substituted triazolines are those resulting from addition of aryl and alkyl azides to the enolate ions of methylene ketones [5] and acetaldehyde.[6] Since a study of the chemical reactivity of these triazolines has been largely confined to their reactions with strong bases, which generally result in dehydration leading to 1,2,3-triazoles, their chemistry remains largely unexplored.

Here we report our results for a study of the thermal reactions of a number of variously substituted aryl azides **1a–h** with 2-methyl-**3** and 2-phenyl-indanedione **4** in hexamethylphosphoric triamide (HMPA). Our primary aim was to uncover a practicable route to the preparation of corresponding tricyclic 4-acyl-5-hydroxy substituted 1-aryltriazolines **6**, **7**, which might open the way to the study of their chemistry. The choice of HMPA as reaction solvent was prompted by our previous observation [7] that 4-nitrophenyl azide **1a** can smoothly react with 2-methylindanedione **3** in such mildly basic and polar solvent to give an isolable hydroxytriazoline **6a**. Additionally, we have subsequently observed [8] that HMPA represents an excellent solvent for diazo transfer reactions between toluene-*p*-sulfonyl (tosyl) azide **2** and methylene 1,3-dicarbonyl com-

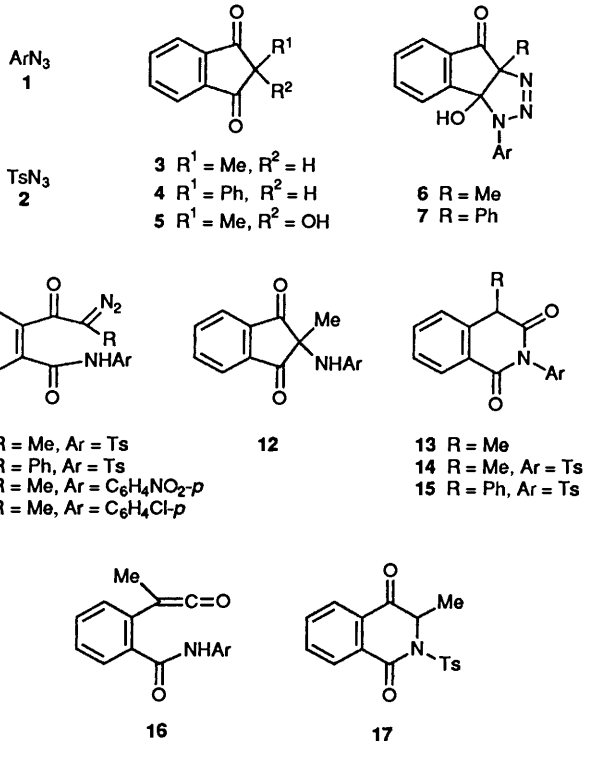
Table 1 Yields (%)[a] of triazoline products **6**, **7** obtained from reaction of the aryl azides **1** with the cyclic diones **3**, **4** in HMPA at 55 °C[b]

Entry	Azide	Dione	Time	Triazoline	Other[a]
1	**1a**[c]	**3**	1.5 h	**6a**, 100	
2	**1b**	**3**	36 h	**6b**, 91	**5**, 9
3	**1c**	**3**	48 h	**6c**, 89	**5**, 11
4	**1d**	**3**	96 h	**6d**, 94	**5**, 6
5	**1e**	**3**	96 h	**6e**, 91	**5**, 9
6	**1f**	**3**	8 days	**6f**, 58	**5**, 42
7	**1g**	**3**	11 days	**6g**, 57	**5**, 42
8	**1h**	**3**	40 days		**5**, 50
9	**1a**	**4**	4 h	**7a**, 95	

[a] Isolated yields based on the appropriate starting dione. [b] Unless stated otherwise, a three-fold azide excess was employed. [c] A two-fold azide excess was employed.

pounds as well as for related reactions of 4-nitrophenyl azide **1a** with same methylene compounds affording diazo and/or 1,2,3-triazole products.

The present study was extended to the corresponding reactions of tosyl azide **2** with the cyclic diones **3** and **4**. It was also of interest to us to ascertain whether such reactions would successfully offer an entry to the synthetically appealing diazo keto amides **8**, **9** which might be expected to be formed as the eventual products of diazo transfer with acyl cleavage.



Results and Discussion

Reaction of 4-nitrophenyl azide **1a** with 0.5 mol equiv. of 2-methylindane-1,3-dione **3** in HMPA at 55 °C for *ca.* 1.5 h (until TLC showed complete disappearance of the dione **3**) led, after column chromatography, to the isolation of the triazoline **6a** [7] in quantitative yield (Table 1, entry 1). Under similar conditions, but at comparatively much longer reaction times, the less

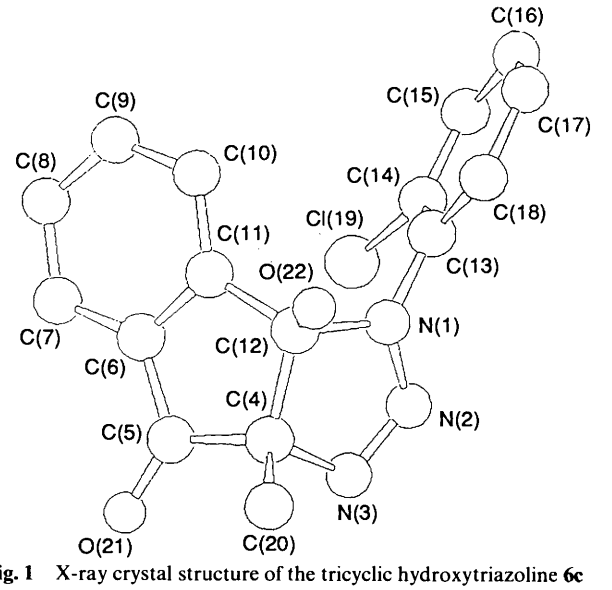


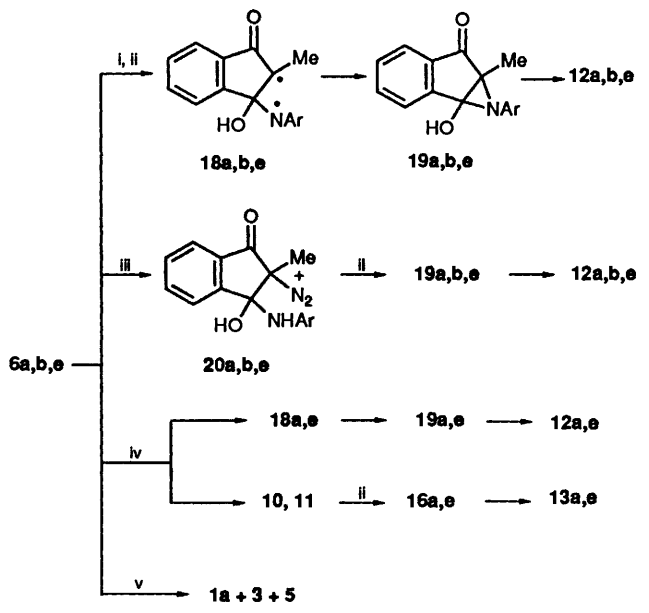
Fig. 1 X-ray crystal structure of the tricyclic hydroxytriazoline **6c**

electrophilic aryl azides **1b–g** also reacted with the dione **3** to give the corresponding triazolines **6b–g** in good to fairly good isolated yields (Table 1, entries 2–7). In such cases, formation of the triazoline products **6b–g** was accompanied by varying amounts of 2-hydroxy-2-methylindane-1,3-dione **5** ascribable to a competing reaction of the dione **3** with oxygen.[9] Indeed, a control experiment revealed that the indanedione **3** could be slowly converted into compound **5** in HMPA solution in the absence of any azide reactant. On the other hand, no reaction was found to occur between the very poorly electrophilic azide **1h** and the dione **3** even over 40 days. After such a time, only formation of the hydroxy dione **5** was observed (Table 1, entry 8).

Similarly to that observed with the indanedione **3**, 4-nitrophenyl azide **1a** was found to react cleanly with 2-phenylindanedione **4** to give the corresponding hydroxytriazoline **7a** in high isolated yield (Table 1, entry 9). The hydroxytriazolines **6a–g** and **7a** were fairly stable, solid compounds, which can be stored indefinitely at room temperature in the dark. Structural elucidation of the new compounds **6b–g** and **7a** was accomplished by IR, ^{1}H NMR and mass spectral analysis (see Experimental section) in addition to elemental analysis. In particular, these triazoline compounds generally exhibited no molecular ion in the mass spectrum, but the corresponding $M^+ - N_2$ fragmentation ion. Moreover, in the IR spectrum they generally exhibited absorption bands at 3600–3540 cm^{-1} (free OH stretching) and 3480–3150 cm^{-1} (hydrogen-bonded OH stretching). In one case, *i.e.* in the case of the *o*-chlorophenyl-substituted triazoline **6c**, structural assignment was fully confirmed by X-ray crystal structure analysis (Fig. 1).

Therefore, our present results would indicate that the reaction of aryl azides with the cyclic diones **3** and **4** in HMPA can offer a convenient synthetic route to 5-hydroxytriazolines **6**, **7**, unless poorly electrophilic azide reactants are employed.

The chemical reactivity of hydroxytriazolines **6** was briefly examined. Irradiation of the compounds **6a**, **b**, **e** in methanol solution, at room temperature, resulted in their ready decomposition with concomitant formation of the 2-arylamino substituted indanediones **12a**, **b**, **e** in virtually quantitative yield (Scheme 3). The same products **12a**, **b**, **e** were also found to result in quantitative yield upon virtually instantaneous reaction of the above compounds **6a**, **b**, **e** with trace amounts of trifluoroacetic acid (Scheme 3). The occurrence of the indanediones **12a**, **b**, **e** from photochemical and acid-catalysed decomposition of the triazolines **6a**, **b**, **e** can be conceivably



Scheme 3 *Reagents and conditions:* i, *hv*, MeOH, 25 °C; ii, $-N_2$; iii, H^+, CH_2Cl_2, 25 °C; iv, **6a**, **e**, benzene, 95 °C; v, **6a**, BuLi, THF, 25 °C

envisioned as eventually resulting from ring-cleavage isomerization of elusive hydroxyaziridine **19a**, **b**, **e** intermediates.

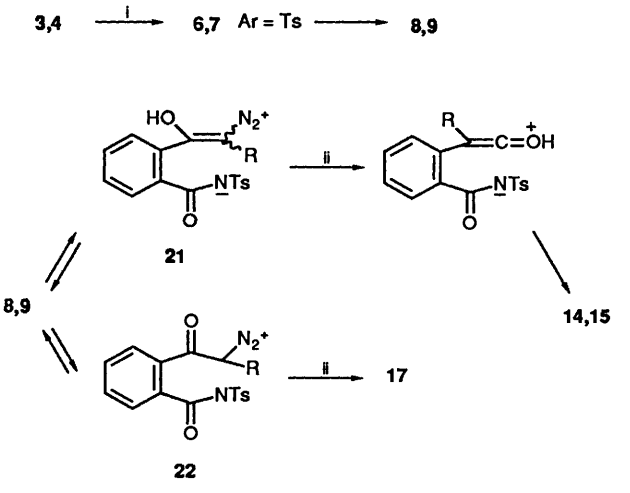
These intermediates **19** would, in turn, result from singlet 1,3-diradicals **18** or from diazonium ion species **20** which would be initially formed upon photochemical or acid-catalysed fragmentation of the triazolines **6**, respectively (Scheme 3). 1,3-Diradicals are commonly accepted as the intermediates in aziridine formation from photolysis (and thermolysis) of 1-aryltriazolines, especially when electron-withdrawing groups are present on the 4-carbon.[10] Moreover, 2-amino substituted diazonium intermediates are commonly believed to occur in acid-induced triazoline decomposition.[10]

Upon thermolysis in benzene at 95 °C for *ca.* 24 h, the hydroxytriazolines **6a**, **e** were shown to afford the corresponding isoquinolinediones **13a**, **e** in *ca.* 40% yield along with minor amounts of the indanediones **12a**, **e** and unidentifiable material (Scheme 3). Structural assignment of the previously unknown isoquinolinediones **13a**, **e** was based on ^1H and ^{13}C NMR, IR and mass spectral data. In particular, the ^1H NMR spectra of the compounds **13a**, **e** showed signals at δ *ca.* 1.8 (3 H, d) and 4.12 (1 H, quartet) whilst their ^{13}C NMR spectra showed two signals at δ *ca.* 165 and 174 which were consistent with their amide C-1 and C-3 carbonyl carbons respectively.

Formation of the ring-expanded products **13a**, **e** would suggest that, under our thermal conditions, the hydroxytriazolines **6a**, **e** should preferentially undergo ring-cleavage fragmentation leading to the corresponding diazo keto amides **10** and **11**. Indeed, thermal Wolff rearrangement of initially formed diazo ketones **10** and **11** and subsequent intramolecular cyclization of the resulting arylketenes **16a**, **e** would conceivably explain the observed isoquinolinedione **13a**, **e** occurrence (Scheme 3). However, our attempts to achieve intermolecular trapping of the presumed arylketene **16a** intermediate by methanol were unsuccessful. In fact, thermolysis of the triazoline adduct **6a**, when carried out in neat methanol, only afforded the azide **1a** and a mixture of 2-methylindanedione **3** and its oxidation product **5** along with minor amounts of the isoquinolinedione **13a** and the indanedione **12a**. Comparable results were obtained when the triazoline **6a** was thermolysed in benzene in the presence of 2 equiv. of methanol, whereas exclusive retro-1,3-dipolar cycloaddition resulted from its thermolysis in acetonitrile in the presence of 2 equiv. of methanol.

Since 1-aryl-5-hydroxytriazolines resulting from addition of aryl azides to the enolate ion of acetaldehyde had previously shown,[6] in the presence of very strong bases, a decomposition mode (leading to diazomethane and formanilide) related to that apparently displayed by our triazolines **6a**, **e** under thermal conditions, we were also led to investigate the decomposition of compound **6a** in the presence of butyllithium. However, upon treatment with 1 mol equiv. of butyllithium in tetrahydrofuran,[6] this triazoline **6a** could provide no evidence for ring-cleavage isomerization to the diazo keto amide **10**, but instead only exhibited formal retro-1,3-dipolar cycloaddition by its alkoxide ion (Scheme 3).

Reaction of 2-methylindanedione **3** with a three-fold excess of the strongly electrophilic tosyl azide **2** in HMPA was found to proceed smoothly at room temperature, going to completion within 2 h. Column chromatography of the resulting reaction mixture afforded, besides an unknown product which was not investigated owing to its very low solubility in common organic solvents, a *ca.* 1:1 mixture of the isomeric 2-tosyl-substituted isoquinolinediones **14** and **17** (Scheme 4). Structural elucidation of the two isomeric compounds **14** and **17** was provided by ^1H and ^{13}C NMR spectroscopic analysis, in addition to IR and mass spectral evidence. In a similar way to the related isoquinoline-1,3-diones **13a**, **e**, isomer **14** showed signals at δ_H 1.71 (d, CH_3) and 4.03 (quartet, CH) and δ_C 163.0 and 172.6 (both CO). Isomer **17**, however, although having a signal at δ 1.71 for the isoquinolinedione methyl doublet exhibited the corresponding methine quartet at δ 5.31; moreover, it exhibited signals at δ_C 161.0 (amide CO) and 193.0 (ketone CO). Analogous reaction of the tosyl azide **2** with 2-phenylindanedione **4** for 4 h led to isolation, virtually quantitatively, of an oily product which slowly solidified. This was found to be a single compound which was assigned the isoquinolinedione structure **15** on the basis of spectral data (see Experimental section) and elemental analysis. Its structure **15** was also fully confirmed by an X-ray crystal struture determination whose details will be reported elsewhere (Scheme 4). In a repeat



Scheme 4 *Reagents and conditions:* i, +**2**, HMPA, 25 °C; ii, $-N_2$

reaction monitored by TLC, we found that the initially formed unstable yellow compound could, by rapid chromatographic separation of the crude reaction mixutre, be isolated pure and shown to be the expected diazo keto amide **9**. Whilst the latter was found to be fairly stable in the solid state, in chloroform or methylene dichloride solution at room temperature (*ca.* 1–2 h) it was totally converted into the quinolinedione **15**.

Thus, the tosyl azide **2** was found to react smoothly with the indanediones **3** and **4** in HMPA solution to give the expected diazo keto amide products **9** and (most likely) **8**, which, presumably, result from facile ring-cleavage isomerization of

Table 2 Fractional co-ordinates of atoms[a] for compound **6c**

Atom	*x*	*y*	*z*
N(1)	0.3708(6)	−0.0041(5)	0.8455(3)
N(2)	0.5909(7)	−0.0035(6)	0.8584(4)
N(3)	0.6645(7)	−0.1336(6)	0.8548(4)
C(4)	0.4796(7)	−0.2466(6)	0.8324(4)
C(5)	0.5092(9)	−0.3287(6)	0.7271(5)
C(6)	0.3332(9)	−0.2847(6)	0.6586(5)
C(7)	0.2953(12)	−0.3280(8)	0.5552(5)
C(8)	0.1169(13)	−0.2713(9)	0.5082(5)
C(9)	−0.0215(11)	−0.1745(9)	0.5620(5)
C(10)	0.0134(8)	−0.1311(7)	0.6636(5)
C(11)	0.1941(8)	−0.1885(6)	0.7123(4)
C(12)	0.2709(7)	−0.1542(6)	0.8225(4)
C(13)	0.2679(6)	0.1274(3)	0.8254(3)
C(14)	0.3263(6)	0.2010(3)	0.7444(3)
C(15)	0.2157(6)	0.3289(3)	0.7249(3)
C(16)	0.0468(6)	0.3832(3)	0.7864(3)
C(17)	−0.0117(6)	0.3096(3)	0.8673(3)
C(18)	0.0989(6)	0.1818(3)	0.8868(3)
Cl(19)	0.5166(3)	0.1300(2)	0.6616(1)
C(20)	0.4825(10)	−0.3500(8)	0.9153(5)
O(21)	0.6519(8)	−0.4168(5)	0.7044(4)
O(22)	0.1147(5)	−0.1800(4)	0.8917(3)

[a] Numbers in parentheses are estimated standard deviations in the least significants digits.

the 5-hydroxy-1-tosyltriazoline adducts **6** (Ar = Ts) and **7** (Ar = Ts) initially formed (Scheme 4). The diazo keto amides **9** and, presumably, **8** proved to be unstable, a result perhaps of the fairly high acidity of their *N*-tosylamido substituent which would bring about acid-catalysed decomposition of the diazo function. In fact, the observed occurrence of the ring-expanded isoquinolinediones **14**, **15** and **17** can be explained in terms of preliminary protonation of the diazo carbonyl oxygen and carbon respectively by *ortho*-amido substituent. In this regard, previous chemical, spectral and theoretical evidence strongly suggests that carbon and, especially, oxygen are the most likely sites for protonation of α-diazo ketones.[11,12] The resulting oxygen protonated intermediates **21** (R = Me, Ph) would lead to the corresponding isoquinolinediones **14**, **15** (see Scheme 4) by initial loss of nitrogen and a (concomitant) 1,2-aryl shift, whereas the carbon protonated intermediate **22** (R = Me) would afford the isoquinoline **17** as a result of nucleophilic displacement of nitrogen by the adjacent nitrogen substituent (Scheme 4). To our knowledge, the acid-promoted decomposition of α-diazo ketones most commonly results in product formation formally ascribable to nucleophilic displacement of nitrogen on the carbon-protonated species.[11,12] Acid-promoted Wolff-type rearrangements of diazo ketones have been previously shown to occur to a significant extent, but only in few instances.[11,12] Therefore, our present results obtained from spontaneous decomposition of the diazo carbonyl compounds **8** and, particularly, **9** are noteworthy and deserve further attention.

In conclusion, we have found that 4-acyl-5-hydroxy-1-aryltriazolines of type **6**, **7** may be usefully prepared by a thermal reaction of the aryl azides **1** with 2-substituted indane-1,3-diones in HMPA, providing that suitable electrophilic azides are employed. The tricyclic hydroxytriazolines **6** have been shown to be of synthetic interest. Upon photochemical or acid-catalysed decomposition, these compounds **6** appear to lead cleanly to 2-arylamino substituted indanediones **12**, thus allowing ready introduction of an arylamino substituent at the indanedione **3** methine position. On the other hand, upon thermolysis, the triazolines **6** appear to rearrange preferentially to the ring-expanded isoquinoline diones **13**, thus providing a new route to 2-aryl isoquinoline-1,3-diones.

Finally, we have also shown that the thermal reaction of the tosyl azide **2** with 2-substituted indanediones in HMPA can offer a convenient method for the preparation of novel 2-tosyl-substituted isoquinoline-1,4-diones and/or -1,3-diones.

Experimental

The aryl azides **1a–h**,[13] tosyl azide **2**[14] and 2-methylindanedione **3**[15] were prepared according to literature methods. 2-Phenylindanedione **4** was commercially available. Known reaction products such as the indanedione **5**[9] and the 4-nitrophenyl-substituted triazolines **6a**[7] were identified on the basis of their physical and spectral data. All m.p.s (Kofler melting point apparatus) are uncorrected. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ (unless otherwise stated) with Me_4Si as internal standard and recorded on 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. Column chromatography was carried out on ICN silica gel 63-200 60A.

Thermal Reactions of Aryl Azides **1a–h** *with the Cyclic Diones* **3**, **4** *in HMPA: General procedure.*—A solution of the appropriate azide **1a–h** (3 mmol) and dione **3**, **4** (1 mmol) in HMPA (1 cm^3) [**Caution:** HMPA is highly toxic and suspected of being a carcinogen] was kept in a sealed tube, in the dark, at 55 °C for the suitable time (generally until TLC showed that the starting dione had essentially disappeared). The crude reaction mixture was then directly separated by column chromatography, using light petroleum (b.p. 40–70 °C) with increasing amounts of diethyl ether (up to 40%) as eluent. Approximate reaction times and isolated product yields are given in Table 1.

The following new hydroxytriazolines **6**, **7** were thus obtained.

(i) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*methyl*-3-(1-*naphthyl*)-3H-*indeno*[1,2-d][1,2,3]*triazol*-8-*one* **6b**, m.p. 131–132 °C (decomp.); δ_H 1.81 (3 H, s), 4.50 (1 H, s) and 6.79–7.92 (11 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 3590sh (free OH), 3300br (hydrogen-bonded OH) and 1730 (C=O); *m*/*z* 301 ($M^+ - N_2$), 283, 273, 258, 230, 202, 168, 158, 132, 127, 115 and 104 (Found: C, 73.15; H, 4.6; N, 12.7. $C_{20}H_{15}N_3O_2$ requires C, 72.95; H, 4.55; N, 12.75%).

(ii) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*methyl*-3-(o-*chlorophenyl*)-3H-*indeno*[1,2-d][1,2,3]*triazol*-8-*one* **6c**, m.p. 157–159 °C (decomp.); $\delta_H(CD_3COCD_3)$ 1.67 (3 H, s), 6.42 (1 H, s), 7.06–7.10 (1 H, m) and 7.39–7.79 (7 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 3560sh (free OH), 3290br (hydrogen bonded OH) and 1730 (C=O); *m*/*z* 285 ($M^+ - N_2$), 270, 250, 242, 222, 214, 204, 194, 160, 152, 139, 132, 127, 111 and 104 (Found: C, 61.2; H, 3.8; Cl, 11.35; N, 13.5. $C_{16}H_{12}ClN_3O_2$ requires C, 61.35; H, 3.85; Cl, 11.3; N, 13.4%).

(iii) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*methyl*-3-(m-*chlorophenyl*)-3H-*indeno*[1,2-d][1,2,3]*triazol*-8-*one* **6d**, m.p. 135–136 °C (decomp.); $\delta_H(CD_3COCD_3)$ 1.70 (3 H, s), 6.67 (1 H, s) and 7.20–7.80 (8 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 3560sh (free OH), 3290br (hydrogen bonded OH) and 1730 (C=O); *m*/*z* 285 ($M^+ - N_2$), 257, 242, 160, 152, 132, 111 and 104 (Found: C, 61.25; H, 3.8; Cl, 11.25; N, 13.35%).

(iv) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*methyl*-3-(p-*chlorophenyl*)-3H-*indeno*[1,2-d][1,2,3]*triazol*-8-*one* **6e**, m.p. 180–181 °C (decomp.); $\delta_H(CD_3COCD_3)$ 1.65 (3 H, s), 6.82 (1 H, s), 7.41 (2 H, d, *J* 8.5), 7.54–7.74 (4 H, m) and 7.76 (2 H, d, *J* 8.5); $\nu_{max}(CHCl_3)/cm^{-1}$ 3580sh (free OH), 3320br (hydrogen bonded OH) and 1730 (C=O); *m*/*z* 285 ($M^+ - N_2$), 257, 242, 213, 160, 152, 132, 111 and 104 (Found: C, 61.4; H, 3.85; Cl, 11.4; N, 13.45%).

(v) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*methyl*-3-*phenyl*-3H-*indeno*-

[1,2-d][1,2,3]*triazol*-8-*one* **6f**, m.p. 139–140 °C (decomp.); δ_H 1.59 (3 H, s), 6.55 (1 H, s) and 7.16–7.79 (9 H, m); ν_{max}(CHCl$_3$)/cm^{-1} 3600sh (free OH), 3380 (hydrogen bonded OH) and 1730 (C=O); *m/z* 251 ($M^+ - N_2$), 236, 223, 222, 208, 194, 180, 160, 132, 118 and 103 (Found: C, 68.9; H, 4.65; N, 15.15. $C_{16}H_{13}N_3O_2$ requires C, 68.8; H, 4.7; N, 15.05%).

(vi) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*methyl*-3-*biphenyl*-2-*yl*-3H-*indeno*[1,2-d][1,2,3]*triazol*-8-*one* **6g**, m.p. 152–153 °C (decomp.); δ_H 1.49 (3 H, s), 3.05 (1 H, s) and 7.04–7.73 (13 H, m); ν_{max}(CHCl$_3$)/cm^{-1} 3540sh (free OH), 3310br (hydrogen bonded OH) and 1730 (C=O); *m/z* 327 ($M^+ - N_2$), 312, 309, 299, 298, 283, 270, 256, 194, 160, 152, 132 and 104 (Found: C, 74.5; H, 4.75; N, 11.75. $C_{22}H_{17}N_3O_2$ requires C, 74.35; H, 4.80; N, 11.85%).

(vii) 3a,8a-*Dihydro*-3a-*hydroxy*-8a-*phenyl*-3-(p-*nitrophenyl*)-3H-*indeno*[1,2-d][1,2,3]*triazol*-8-*one* **7a**, m.p. 180–181 °C (decomp.); δ_H(CD$_3$COCD$_3$) 6.80 (1 H, s), 7.29–7.43 (5 H, m) and 7.63–8.34 (8 H, m); ν_{max}(CHCl$_3$)/cm^{-1} 3540sh (free OH), 3300br (hydrogen bonded OH), 1740, 1720, 1160 and 1340; *m/z* 358 ($M^+ - N_2$), 328, 222, 194, 165, 149, 136, 111 and 104 (Found: C, 65.45; H, 3.6; N, 14.4. $C_{21}H_{14}N_4O_4$ requires C, 65.3; H, 3.65; N, 14.5%).

X-Ray Crystal Structure Analysis of the Tricyclic Hydroxytriazoline **6c**.—*Crystal data.* $C_{16}H_{12}ClN_3O_2$, M = 313.7, triclinic, space group P$\bar{1}$, a = 6.059(3), b = 9.032(3), c = 13.316(4) Å, α = 97.73(3)°, β = 92.58(3)°, γ = 91.15(3)°, V = 721.1 Å^3, Z = 2, D_c = 1.44 g cm^{-3}, Mo-K$_\alpha$ radiation, λ = 0.7107 Å, F(000) = 324.0.

Data collection and processing. Intensity data were collected by a CAD4 diffractometer using $w/2\ \theta$ scan; range 2.5° < θ < 25°. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centred reflections 8° < θ < 14°. Of 2118 independent reflections, 912 having $I < 2.5\ \sigma\ (I)$ were considered unobserved.

Structure solution and refinement. The structure was resolved by direct methods and refined anisotropically by full-matrix least-squares analysis using the SHELX program packages.[16] Phenyl groups were refined as rigid bodies (C–C = 1.395 Å). All the H-atoms, except two, were found in the Fourier difference syntheses, but were not refined. The final agreement index was R = 0.061, S = 2.61. Maximum Δ/σ = 0.035. Final difference Fourier map excursion 0.62 to −0.31 e Å^{-3}. The X-ray molecular structure is shown in Fig. 1. Fractional atomic co-ordinates are given in Table 2. Listings of bond angles and bond lengths have been desposited at the Cambridge Crystallographic Data Centre.*

Photochemical Decomposition of the Hydroxytriazolines **6a**, **b**, **e**: General procedure.—A solution of the appropriate triazoline **6a**, **b**, **e** (0.5 mmol) in methanol (15 cm^3), in a sealed quartz tube, was irradiated at room temperature with a high-pressure Mercury vapour lamp for *ca.* 5–6 h, after which time complete decomposition of the starting triazoline **6** had occurred as judged by TLC. The excess of solvent was evaporated and the resulting residue was eluted through a silica gel column with light petroleum (b.p. 40–70 °C)–diethyl ether (50:50). The following 2-arylamino-2-methylindanediones **12** were obtained in virtually quantitative yield.

(i) 2-*Methyl*-2-(4-*nitrophenylamino*)*indane*-1,3-*dione* **12a**, m.p. 225–226 °C; δ_H 1.65 (3 H, s), 5.0 (1 H, br s), 6.24 (2 H, d, *J* 9), 7.90 (2 H, d, *J* 9) and 7.95–8.10 (4 H, m); ν_{max}(CHCl$_3$)/cm^{-1} 3410 (NH), 1750, 1720 and 1600 (Found: M$^+$, 296.080 13. $C_{16}H_{12}N_2O_4$ requires *M*, 296.079 71); *m/z* 281, 250, 163, 117, 105 and 104.

(ii) 2-*Methyl*-2-(1-*naphthylamino*)*indone*-1,3-dione **12b**, m.p. 214–215 °C; δ_H 1.72 (3 H, s), 5.0 (1 H, br s), 5.9 (1 H, d, *J* 7.1), 6.95 (1 H, t, *J* 7.1), 7.2 (1 H, d, *J* 7.1) and 7.4–8.15 (8 H, m); ν_{max}(CHCl$_3$/cm^{-1} 3420 (NH), 1755 and 1720; *m/z* 301 (M$^+$), 168 and 127 (Found: C, 79.8; H, 5.1; N, 4.6. $C_{20}H_{15}NO_2$ requires C, 79.7; H, 5.0; N, 4.65%).

(iii) 2-*Methyl*-2-(4-*chlorophenylamino*)*indone*-1,3-*dione* **12e**, m.p. 177–178 °C; δ_H 1.56 (3 H, s), 4.39 (1 H, br s), 6.27 (2 H, d, *J* 8), 6.93 (2 H, d, *J* 8) and 7.9–8.1 (4 H, m); ν_{max}(CHCl$_3$)/cm^{-1} 3415 (NH), 1750, 1715 and 1600; *m/z* 285 (M$^+$), 270, 152 and 111 (Found: C, 67.35; H, 4.2; Cl, 12.45; N, 4.95. $C_{16}H_{12}ClNO_2$ requires C, 67.25; H, 4.25; Cl, 12.4; N, 4.9%).

Trifluoroacetic Acid-catalysed Decomposition of the Hydroxytriazolines **6a**, **b**, **e**: *General procedure.*—A solution of the appropriate triazoline **6a**, **b**, **e** (0.5 mmol) in methylene dichloride (15 cm^3) was treated at room temperature with a drop of trifluoroacetic acid. After a few minutes, the excess solvent was evaporated to give the appropriate 2-arylamino-2-methylindanedione **12a**, **b**, **e** in quantitative yield.

Thermal Decomposition of the Hydroxytriazolines **6a** *and* **6e**.—A solution of the 4-nitrophenyl substituted triazoline **6a** (0.5 mmol) in benzene (15 cm^3) was heated in a sealed tube at 95 °C for *ca.* 24 h, after which time TLC showed that the compound **6a** had totally disappeared. After removal of the excess of solvent, the residue was chromatographed. Gradual elution with light petroleum (b.p. 40–70 °C)–diethyl ether (20:80) gave: (i) an unidentified product (15 mg); (ii) 4-*methyl*-2-(4-*nitrophenyl*)*isoquinoline*-1,3(2H,4H)-*dione* **13a** (0.20 mmol, 40%), m.p. 186–188 °C; δ_H 1.79 (3 H, d, *J* 7.5), 4.12 (1 H, q, *J* 7.5), 7.41–7.76 (5 H, m) and 8.24–8.45 (3 H, m); δ_C 22.45 (q), 41.85 (d), 165.0 (s), 174.5 (s), and aromatic C; ν_{max}(CHCl$_3$)/ cm^{-1} 1730, 1680, 1600, 1370 and 1350 (Found: M$^+$, 296.080 10. $C_{16}H_{12}N_2O_4$ requires *M*, 296.079 71); *m/z* 268, 253, 222, 207, 132 and 104; (iii) the indanedione **12a** (0.12 mmol, 24%); and (iv) tarry material (20 mg).

Analogous reaction of the triazoline **6a** (1 mmol) in benzene containing 2 mol equiv. of methanol gave, after column chromatography, the following: (i) 4-nitrophenyl azide **1** (0.17 mmol, 17%); (ii) 2-methylindanedione **3** (0.11 mmol, 11%); (iii) 2-hydroxy-2-methylindanedione **5** (0.12 mmol, 12%); (iv) the isoquinolinedione **13a** (0.45 mmol, 45%); (v) a mixture of unidentified products; and (vi) the indanedione **12a** (0.15 mmol, 15%).

Analogous reaction of the triazoline **6a** (1 mmol) in methanol gave, after column chromatography: (i) 4-nitrophenyl azide **1** (0.38 mmol, 38%); (ii) 2-methylindanedione **3** (0.32 mmol, 32%); (iii) 2-hydroxy-2-methylindanedione **5** (0.32 mmol, 32%); (iv) the isoquinolinedione **13a** (0.14 mmol, 14%); and (v) the indanedione **12a** (0.10 mmol, 10%).

Analogous reaction of the triazoline **6a** (1 mmol) in acetonitrile (8 cm^3) containing 2 mol equiv. of methanol gave, after column chromatography the following: (i) 4-nitrophenyl azide **1** (0.70 mmol, 70%); (ii) 2-methylindanedione **3** (0.40 mmol, 40%); (iii) 2-hydroxy-2-methylindanedione **5** (0.30 mmol, 30%); and (iv) unchanged triazoline **6a** (0.24 mmol, 24% recovery). Analogous reaction of the 4-chlorophenyl substituted triazoline **6e** (0.5 mmol) in benzene gave, after chromatographic separation: (i) a mixture of unidentified products (30 mg); (ii) 4-*methyl*-2-(4-*chlorophenyl*)*isoquinoline*-1,3(2H,4H)-*dione* **13e** (0.19 mmol, 38%), m.p. 142–144 °C; δ_H 1.77 (3 H, d, *J* 7), 4.12 (1 H, q, *J* 7), 7.18 (2 H, d, *J* 9), 7.23–8.17 (5 H, m) and 8.17–8.34 (1 H, m); δ_C 22.55 (q), 41.8 (d), 165.2 (s), 174.75 (s), and aromatic C; ν_{max}(CHCl$_3$)/cm^{-1} 1730 and 1680; *m/z* 285 (M$^+$), 257, 242, 132 and 104 (Found: C, 67.35; H, 4.25; Cl, 12.35; N,

* For details of the scheme, see *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

4.85. $C_{16}H_{12}ClNO_2$ requires C, 67.25; H, 4.25; Cl, 12.4; N, 4.9%); (iii) the indanedione **12e** (0.125 mmol, 25%); and (iv) tarry material (12 mg).

Butyllithium-promoted Decomposition of the Hydroxytriazoline **6a**.—A solution of the hydroxytriazoline **6a** (0.39 mmol) in anhydrous tetrahydrofuran (20 cm^3) was treated at ambient temperature, under a stream of nitrogen, with butyllithium (2.5 mol dm^{-3}) in hexane (0.16 cm^3, 0.39 mmol). After being stirred at room temperature for *ca.* 1 h, the reaction mixture was quenched with aqueous ammonium chloride and then evaporated. The residue was extracted with diethyl ether (100 cm^3), the ether extract was evaporated and the resulting residue was chromatographed. Gradual elution with light petroleum (b.p. 40–70 °C)–diethyl ether (20:80) afforded: (i) 4-nitrophenyl azide **1a** (0.16 mmol, 41%); (ii) 2-methylindanedione **3** (0.30 mmol, 77%); (iii) 4-nitroaniline (0.025 mmol, 6%); and (iv) 2-hydroxy-2-methylindanedione **5** (0.05 mmol, 13%).

Reactions of Tosyl Azide **2** *with the Cyclic Diones* **3**, **4** *in HMPA: General procedure*.—A solution of tosyl azide **2** (3 mmol) and the appropriate dione **3**, **4** (1 mmol) in HMPA (1 cm^3) was allowed to stand at room temperature, until complete reaction of the starting dione **3**, **4** had occurred (TLC). The resulting reaction mixture was then directly separated by silica gel chromatography by gradual elution with diethyl ether–light petroleum (b.p. 40–70 °C) mixtures (up to 100% diethyl ether).

Reaction of Tosyl Azide **2** *with* 2-*Methylindanedione* **3**.—This reaction was carried out for 2 h: Chromatography gave: (i) unchanged azide **2**; (ii) an unresolved mixture (0.55 mmol, 55%) of isomeric 2,3-*dihydro*-3-*methyl*-2-*tosylisoquinoline*-1,4-*dione* **20** and 4-*methyl*-2-*tosylisoquinoline*-1,3-(2H,4H)-*dione* **14** (in *ca.* 1:1 ratio as shown by ^1H NMR analysis) (Found: C, 62.25; H, 4.65; N, 4.25; S, 9.65. $C_{17}H_{15}NO_4S$ requires C, 62.0; H, 4.6; N, 4.25; S, 9.7%). Repeated chromatography of the above mixture allowed partial separation of the two isomeric components. The isoquinolinedione **17** had m.p. 138–139 °C; δ_H 1.71 (3 H, d, *J* 7), 2.43 (3 H, s), 5.31 (1 H, q, *J* 7) and 7.33–8.20 (8 H, m); δ_C 21.9 (q), 23.05 (q), 61.45 (d), 161.0 (s), 193.05 (s), and aromatic C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1760, 1710, 1600, 1370 and 1170; *m*/*z* 329 (M^+), 265, 250, 237, 222, 195 and 174. The isoquinolinedione **14** had m.p. 154–155 °C; δ_H 1.71 (3 H, d, *J* 7.2), 2.44 (3 H, s), 4.03 (1 H, q, *J* 7.2) and 7.30–8.24 (8 H, m); δ_C 19.9 (q), 21.95 (q), 44.85 (d), 163.0 (s), 172.6 (s), and aromatic C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1760, 1710, 1600, 1370 and 1170; *m*/*z* 329 (M^+), 265, 250, 237, 222, 195 and 174; (iii) an unknown product (70 mg); and (iv) tarry material (150 mg).

Reaction of Tosyl Azide **2** *with* 2-*Phenylindanedione* **4**.—This reaction was carried out for 3 h. Chromatography gave: (i) unchanged azide **2** and (ii) 4-*phenyl*-2-*tosylisoquinoline*-1,3-(2H,4H)-*dione* **15** (0.995 mmol, 100%), m.p. 136–138 °C; δ_H 2.42 (3 H, s), 5.18 (1 H, s) and 7.10–8.22 (13 H, m); δ_C 21.8 (q), 56.05 (d), 162.8 (s), 169.6 (s), and aromatic C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1750, 1710, 1600, 1370 and 1170; *m*/*z* 391 (M^+), 327, 280, 237, 236, 219, 208, 194, 165, 149 and 105 (Found: C, 67.7; H, 4.3; N, 3.55; S, 8.25. $C_{22}H_{17}NO_4S$ requires C, 67.5; H, 4.35; N, 3.6; S, 8.2%). In a repeat experiment the crude reaction mixture was rapidly subjected to flash chromatography on silica gel column to give, besides unchanged azide **2** and isoquinolinedione **15**, a pale yellow compound which was shown to be the *diazo keto amide* **9** (0.15 mmol, 15%), m.p. 104–105 °C (decomp.); δ_H 2.33 (3 H, s) and 7.15–7.90 (14 H, m); $\nu_{max}(CHCl_3)/cm^{-1}$ 3380 (NH), 2090 (C=N_2), 1750, 1710, 1600, 1370 and 1170; *m*/*z* 391 ($M^+ - N_2$), 327, 236, 208, 194, 171, 165, 155, 139, 130 and 105. Compound **9** was found to be fairly stable in the solid state, but in solution ($CHCl_3$ or CH_2Cl_2) it suffered total decomposition at room temperature over 1–2 h to give the isoquinolinedione **15** as the sole product (TLC and ^1H NMR).

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