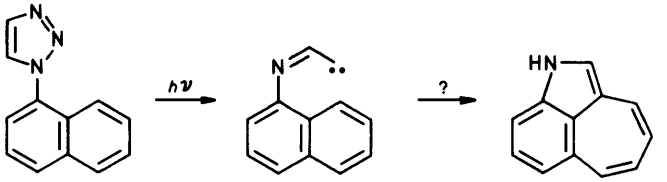
Photolysis of 1-Aryl-1,2,3-triazoles;* Rearrangement via 1*H*-Azirines

Glynn Mitchell and Charles W. Rees
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

The preparation and photolysis of a series of 1-(1-naphthyl)-1,2,3-triazoles, (**2**)—(**5**), and of 1-(2-methyl-1-naphthyl)-1,2,3-triazoles, (**6**)—(**9**), with and without electron-withdrawing groups (CO_2R, $CONH_2$, CN, CHO, COPh) in the triazole ring, are described. In the first series, triazoles (**3**) with two electron-withdrawing groups, and triazoles (**4**) with one such group at C-4, mostly give good yields of the expected benz[*g*]indoles (**10**) and (**11**) respectively. Triazoles (**5**) with the electron-withdrawing group at C-5 also give benz[*g*]indoles but these are now mixtures of the expected (**12**) and rearranged indoles (**11**). Photolysis of the 1-phenyltriazoles (**21**) and (**22**) follows the same pattern, those [(**22**)] with the electron-withdrawing group at C-5 rearranging to give mixtures of indoles (**23**) and (**24**). This is explained by a mechanism (Scheme 3) in which the less stable carbene intermediate (**13**) rearranges to the more stable carbene (**15**) *via* the 1*H*-azirine (**14**), in competition with its direct cyclisation. This provides the first evidence for antiaromatic 1*H*-azirines as intermediates in a photochemical reaction. Photolysis of the 2-methylnaphthyl compounds follows a different path: diester (**7b**) and dinitrile (**7d**) give high yields of the deeply coloured 9-methyl-1*H*-benzo[*de*]quinoline derivatives (**25a**) and (**25b**) respectively, the first stable examples of this ring system to be isolated. Photolysis of the nitrile (**8c**) gives 9b-methyl-9b*H*-benz[*g*]indole-3-carbonitrile (**28**), a rare example of a stable indole with a ring junction substituent. 1,2-Shifts in the carbenes are only observed with the bis(trimethylsilyl)triazoles (**2d**) and (**6f**), in keeping with the known rapid migration of trimethylsilyl groups to carbene centres.

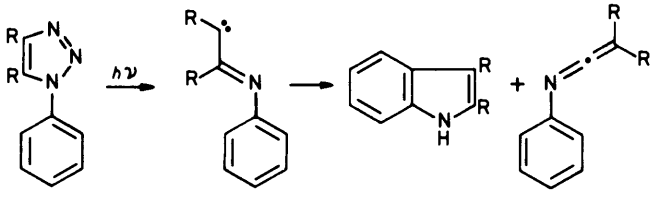
In the preceding paper[1] we described the photolysis of certain 1-(1-naphthyl)benzotriazoles to give cyclo-octa[*def*]carbazoles, by collapse of an intermediate carbene onto the naphthalene ring junction followed by ring expansion. We were intrigued by the possibility that a similar rearrangement (Scheme 1) of the



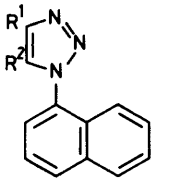
(**1**)

Scheme 1.

related monocyclic 1,2,3-triazoles would result in formation of the cyclohept[*cd*]indole ring system (**1**), a novel heterocyclic analogue of the non-alternant hydrocarbon cyclohepta[*de*]-naphthalene ('pleiadiene').[2] Although the photochemical decomposition of 1-arylbenzotriazoles generally gives high yields of carbazoles,[3,4] 1-aryl-1,2,3-triazoles give variable yields of indoles because of a competing Wolff-type 1,2-rearrangement in the intermediate carbene (Scheme 2).[4,5] We now present our results on the photolyses of an extensive series of monocyclic 1-(1-naphthyl)-, (**2**)—(**5**), and 1-(2-methyl-1-naphthyl)-1,2,3-triazoles, (**6**)—(**9**).[6]*



Scheme 2.

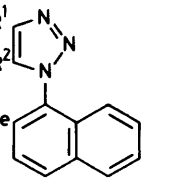


(**2**) **a**; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = C(Me)=CH_2$, $R^2 = H$
d; $R^1 = R^2 = SiMe_3$

(**3**) **a**; $R^1 = R^2 = COPh$
b; $R^1 = R^2 = CO_2Me$
c; $R^1 = R^2 = CONH_2$
d; $R^1 = R^2 = CN$

(**4**) **a**; $R^1 = CO_2Et$, $R^2 = H$
b; $R^1 = CO_2Me$, $R^2 = Me$
c; $R^1 = CN$, $R^2 = H$
d; $R^1 = CN$, $R^2 = Me$
e; $R^1 = CO_2Me$, $R^2 = H$

(**5**) **a**; $R^1 = H$, $R^2 = CO_2Et$
b; $R^1 = Me$, $R^2 = CO_2Me$
c; $R^1 = H$, $R^2 = CN$
d; $R^1 = Me$, $R^2 = CN$



(**6**) **a**; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = H$
d; $R^1 = C(Me) = CH_2$, $R^2 = H$
e; $R^1 = C(Me) = CH_2$, $R^2 = Me$
f; $R^1 = R^2 = SiMe_3$

(**7**) **a**; $R^1 = R^2 = COPh$
b; $R^1 = R^2 = CO_2Me$
c; $R^1 = R^2 = CONH_2$
d; $R^1 = R^2 = CN$

(**8**) **a**; $R^1 = CO_2Me$, $R^2 = H$
b; $R^1 = CO_2Me$, $R^2 = Me$
c; $R^1 = CN$, $R^2 = H$
d; $R^1 = CN$, $R^2 = Me$
e; $R^1 = CHO$, $R^2 = H$

(**9**) **a**; $R^1 = H$, $R^2 = CO_2Me$
b; $R^1 = Me$, $R^2 = CO_2Me$
c; $R^1 = H$, $R^2 = CN$

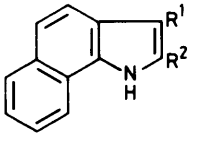
Results and Discussion

Preparation of the Triazoles.—Triazoles (**2**)—(**5**) were prepared from 1-azidonaphthalene by 1,3-dipolar cycloaddition reactions. Thus dibenzoylacetylene (DBA) gave (**3a**), dimethyl acetylenedicarboxylate (DMAD) gave (**3b**), ethyl propiolate (EP) gave (**4a**) and (**5a**) (*ca.* 6:1), methyl tetrolate (MeC≡

* Throughout, 1,2,3-triazoles refers to the 1*H*-tautomers.

CCO_2Me) (MT) gave (**4b**) and (**5b**) (8:1), and bis(trimethylsilyl)acetylene (BTMSA) gave (**2d**). Methyl ester (**4e**) was obtained by transesterification of the homologue (**4a**). Dinitrile (**3d**) was prepared from the diester (**3b**) by treatment with ammonia, to give diamide (**3c**), followed by dehydration with toluene-*p*-sulphonyl chloride and pyridine. The nitriles (**4c,d**) and (**5c,d**) were similarly prepared from the respective monoesters. The isopropenyl derivative (**2c**) was prepared by treatment of ester (**4a**) with an excess of methylmagnesium iodide, followed by dehydration. The triazole (**2a**) was prepared by hydrolysis of the diester (**3b**) and thermal decarboxylation of the diacid, and the triazole (**2b**) was similarly prepared from monoester (**4b**); these decarboxylations proceeded smoothly in boiling toluene. With the exception of aldehyde (**8e**), triazoles (**6**)—(**9**) were all prepared similarly from 1-azido-2-methylnaphthalene, the methyl esters (**8a**) and (**9a**) from methyl propiolate (MP). Aldehyde (**8e**) was prepared from ester (**8a**) by reduction with lithium aluminium hydride followed by oxidation with manganese dioxide.

Photolysis of 1-(1-*Naphthyl*)-1,2,3-*triazoles* (**2**)—(**5**).—Initial results obtained from the photolysis of 1-(1-naphthyl)-1,2,3-triazoles were disappointing. Irradiation of the triazole (**2b**) in acetonitrile at 254 nm gave no isolable products, and irradiation of the triazole (**2a**) gave only a very low yield (5%) of benz[*g*]indole (**10**; $R^1 = R^2 = H$). We therefore photolysed a triazole, (**2c**), with a vinylic group at the 4-position, in the hope that the unsaturated imidoyl carbene formed on extrusion of nitrogen would resemble that formed from the benzotriazoles,[1,7] and cyclise similarly. In the event irradiation of compound (**2c**) gave no identifiable products, and the absence of vinylic proton resonances in the n.m.r. spectrum of the photolysate suggested that extensive polymerisation had occurred.



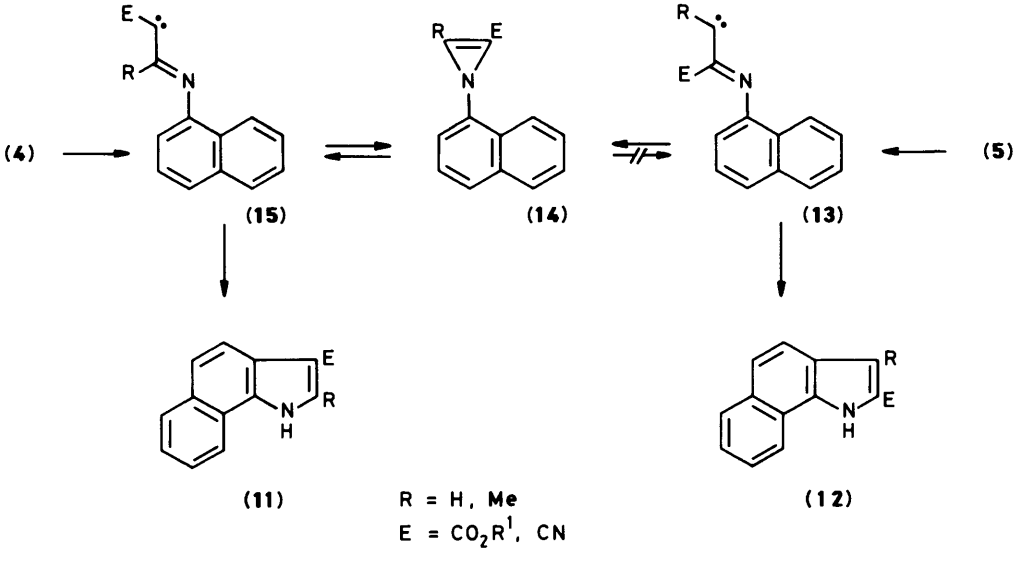
(**10**) **a**; $R^1 = R^2 = COPh$
b; $R^1 = R^2 = CO_2Me$
c; $R^1 = R^2 = CONH_2$
d; $R^1 = R^2 = CN$

(**11**) **a**; $R^1 = CO_2Et$, $R^2 = H$
b; $R^1 = CO_2Me$, $R^2 = Me$
c; $R^1 = CN$, $R^2 = H$
d; $R^1 = CN$, $R^2 = Me$
e; $R^1 = CO_2Me$, $R^2 = H$

(**12**) **a**; $R^1 = H$, $R^2 = CO_2Et$
b; $R^1 = Me$, $R^2 = CO_2Me$
c; $R^1 = H$, $R^2 = CN$
d; $R^1 = Me$, $R^2 = CN$

In contrast, photolysis of triazoles (**3**), which have electron-withdrawing groups on both carbon atoms of the triazole ring, gave much better yields of the appropriately substituted benz[*g*]indoles (**10**), arising from attack of the intermediate carbene at the naphthalene 2-position. Thus triazoles (**3a**—**d**) gave benzindoles (**10a**—**d**) in 18, 100, 81, and 64% yield, respectively, and no other products were detected. The low yield of the dibenzoyl compound (**10a**) is probably associated with photoexcitation of the benzoyl groups competing with nitrogen extrusion, which ultimately leads to extensive decomposition. Photolysis of this triazole (**3a**) was certainly much slower than that of triazoles (**3b**—**d**).

The increase in yields observed on photolysis of triazoles (**3a**—**d**), compared with triazoles (**2a**—**c**), was attributed to dipole stabilisation of the intermediate imidoyl carbene (see Scheme 3) by the adjacent electron-withdrawing group, initially at the triazole 4-position. In agreement with this suggestion, subsequently supported by molecular orbital calculations (see below), photolysis of triazoles (**4a**—**d**) with one electron-withdrawing group at the 4-position gave [with the exception of (**4a**)] good yields of the corresponding indoles (**11a**—**d**) (Table), again isolated as the sole products. However, photolysis of triazoles (**5a**—**d**) with the electron-withdrawing group at the 5-position also gave good yields of products, even though the carbene formed in these reactions cannot be stabilised directly by the electron-withdrawing group. However, the products obtained from these photolyses proved to be mixtures of the expected indoles (**12a**—**d**) together with the isomeric indoles (**11a**—**d**) (Table). The yields in the Table are based on triazole consumed. Starting triazoles were frequently recovered from incomplete photolyses, but in no case was the isomeric triazole detected (t.l.c.), nor could any be isolated, although isomeric pairs of triazoles are well separated on t.l.c. and in column chromatography. Thus reaction mechanisms involving initial interconversion of the triazoles (**4**) and (**5**) were discounted. Although much less likely, it was also shown that the isomeric indole products (**11**) and (**12**) were not interconverted under the photolysis conditions. Thus it seems



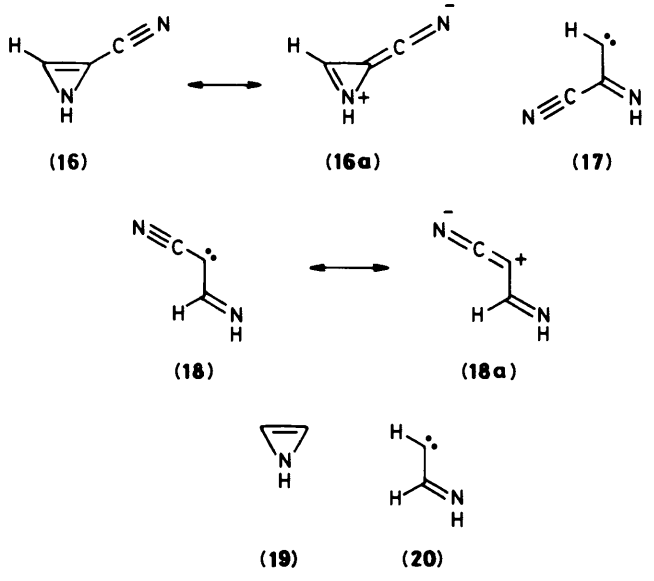
Scheme 3.

Table. Yields of indoles (11) and (12) from the photolysis of triazoles (4) and (5)

Triazole	Indole (11) (%)	Indole (12) (%)
(4a)	0	0
(4b)	47	0
(4c)	76	0
(4d)	48	0
(4e)	38	0
(5a)	19	11
(5b)	36	15
(5c)	39	14
(5d)	37	27

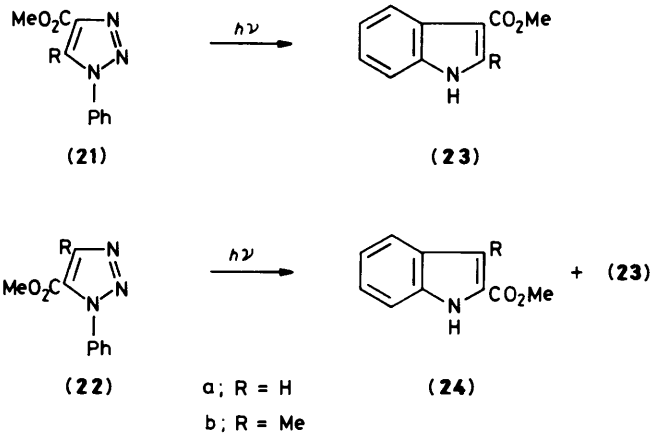
that an intermediate species produced in the photolytic decomposition of triazoles (5) must, at least partially, rearrange to an isomer before the indoles are formed. We suggest the mechanism shown in Scheme 3. The imidoyl carbene (13) undergoes two reactions, direct cyclisation to the naphthalene 2-position to give indole (12), or rearrangement *via* the 1*H*-azirine (14) to the isomeric carbene (15), followed by cyclisation to indole (11). Formation of carbene (15), however, results only in direct cyclisation to indole (11) since no trace of indole (12) is observed on photolysis of triazole (4). This indicates that either cyclisation of carbene (13) to azirine (14), or ring opening of azirine (14) to carbene (15), must be essentially irreversible. Molecular orbital calculations (MNDO) on model compounds indicate that the azirine (16) is more stable than carbenes (17) and (18).[8] However, the difference in energy between azirine (16) and carbene (17) (12.7 kcal mol^{-1})* is calculated to be much greater than between (16) and carbene (18) (1.5 kcal mol^{-1}), and this is attributed to stabilisation of carbene (18) by the dipolar structure (18a). 1*H*-Azirine (19) itself is calculated to be 8.1 kcal mol^{-1} more stable than carbene (20) (*cf. ca.* 20 kcal mol^{-1} given by a less refined earlier method[9]). The larger energy difference between azirine (16) and carbene (17) than between azirine (19) and carbene (20) is attributed partly to a small destabilising effect of the cyano group on carbene (17) but more to stabilisation of the azirine (16) by the non-antiaromatic dipolar structure (16a).

On the basis of these calculations, it appears that a reversible ring closure of the carbene (15) to the azirine (14) is likely, which suggests that cyclisation of carbene (13) to (14) is essentially irreversible, and that once formed azirine (14) opens exclusively to the dipole-stabilised carbene (15). Furthermore, the fact that carbene (13) undergoes preferential rearrangement to (15) prior to cyclisation onto the naphthalene ring provides experimental evidence for a substantial energy difference between these two carbenes.



Although molecular orbital calculations indicate that the formally antiaromatic 1*H*-azirine (19) is stable relative to the isomeric imidoylcarbene (20), little experimental evidence has been obtained for the participation of these azirines in reactions where carbenes of type (20) are generated, and none for such reactions in solution. Thus 1*H*-azirines were generated in the flash vacuum pyrolysis of some substituted 1,2,3-triazoles[10] and 1*H*-benzazirine was generated in a similar decomposition of isatin,[11] but azirines were not detected in the gas-phase thermolysis or solution-phase photolysis of 1-aryl-triazoles and -benzotriazoles.[3,4,12] 1*H*-Azirines have previously been proposed as intermediates in solution in the addition of phthalimidonitrene to alkynes.[13]

In view of the unusual rearrangement which accompanies photolysis of the 1-naphthyltriazoles (5) we investigated the similar decomposition of the 1-phenyltriazoles (21a,b) and their isomers (22a,b) (Scheme 4). In general agreement with the above observations, irradiation of triazoles (21a,b) gave solely the unrearranged indoles (23a,b) in 26 and 55% yield respectively, whilst irradiation of triazoles (22a,b) gave the rearranged products (23a,b) (5 and 42% respectively) together with the unrearranged products (24a,b) (25 and 21% respectively). Thus, although no similar rearrangement was reported in the photolysis of 1,4- and 1,5-diphenyl-1,2,3-triazoles,[3] it is possible that stabilisation of intermediates by electron-withdrawing groups may give rise to a fairly general rearrangement of imidoyl carbenes *via* the formally antiaromatic 1*H*-azirines.



Scheme 4.

The failure of the triazole ethyl ester (4a) to give any detectable amount of the benzindole (11a) is noteworthy; no clean products could be isolated from this photolysis. This result is presumably associated with the presence of the ethyl group, which could for example be lost as ethylene from the intermediate carbene, since the corresponding methyl ester (4e) does give the expected benzindole (11e) on photolysis (Table). The fact that the isomeric triazole ethyl ester (5a) gives some of the benzindole (11a) (as a rearrangement product) suggests that the intermediate carbene formed directly by photolysis is in a

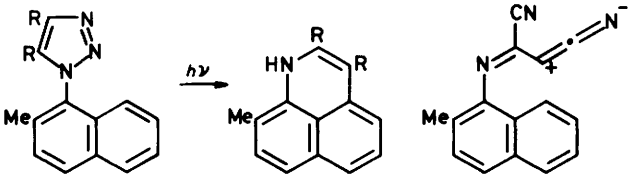
* 1 cal = 4.184 J.

different electronic state (triplet?) to that produced by rearrangement *via* the 1*H*-azirine (singlet?).

Although good yields of indoles were obtained from photolysis of 1-(1-naphthyl)-1,2,3-triazoles when the triazole contained at least one electron-withdrawing group, no traces of products derived from attack of the carbene at the naphthalene ring junction were detected in any of the above reactions. We therefore turned our attention to the photolysis of a series of similar compounds but with a blocking methyl group in the naphthalene 2-position.

Photolysis of 1-(2-*Methyl*-1-*naphthyl*)-1,2,3-*triazoles* (**6**)—(**9**).—As in the photolysis of triazoles (**2a—c**) discussed above, photolysis of 2-methylnaphthyl triazoles (**6a—e**) without an electron-withdrawing group proved unproductive; no products could be obtained from the intractable tars produced. Better results were obtained, however, on photolysis of triazoles with electron-withdrawing groups.

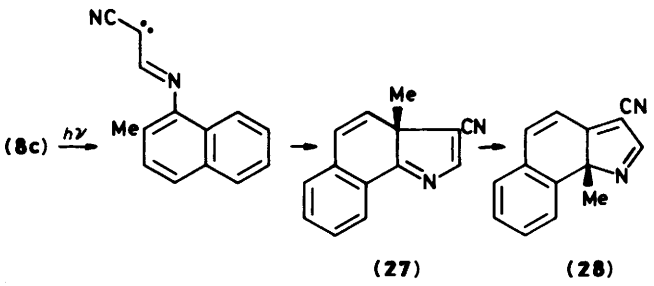
Photolysis of the diester (**7b**) gave a single, red, product (63%) shown to be dimethyl 9-methyl-1*H*-benzo[*de*]quinoline-2,3-dicarboxylate (**25a**) by *X*-ray crystallography.[14] Similarly the dinitrile (**7d**) gave the benzoquinoline (**25b**) (74%) as a deep purple solid. Irradiation of the dibenzoyltriazole (**7a**) and the dicarboxamide (**7c**) gave no identifiable products, however. The heterocyclic compounds (**25a,b**) are isoelectronic with pleiadiene[2] and are the first stable examples of this ring system to be isolated. 1*H*-Benzo[*de*]quinoline itself is unstable though the oxa and thia analogues are not.[15] Presumably compounds (**25a,b**) are stabilised by the electron-withdrawing groups, particularly that on C-3 conjugated with the enamine function. Indeed, attempted reduction of (**25a**) with lithium aluminium hydride led to its decomposition.



(**7**) **b**; R = CO_2Me (**25**) **a**; R = CO_2Me (**26**)
d; R = CN **b**; R = CN

The formation of compounds (**25a,b**) cannot involve an electrocyclisation process like that proposed above for the naphthyltriazoles lacking the blocking methyl group. Instead, the carbene attacks the naphthalene 8-position, either by direct insertion into the C–H bond or by electrophilic aromatic substitution by the very electron-deficient carbene, with contributing forms like (**26**). It is striking that this new reaction pathway is induced merely by the introduction of a methyl group at the naphthalene 2-position.

Photolysis of 1-(2-methyl-1-naphthyl)triazoles (**8a—c**) with one electron-withdrawing group (at the triazole 4-position) was then investigated. Irradiation of the monoester (**8a**) and the aldehyde (**8e**) gave intractable mixtures, but the nitrile (**8c**) gave three products in variable yields. These were 9b-methyl-9b*H*-benz[*g*]indole-3-carbonitrile (**28**) (24—27%), the demethylated compound 1*H*-benzo[*g*]indole-3-carbonitrile (**11c**) (2—17%), and an unidentified, apparently dimeric, product. The demethylated compound (**11c**) was shown to arise by further photolysis of the 9b-methylbenz[*g*]indole (**28**). The stability of the latter compound is unusual for a ring-junction-substituted indole and it is one of the simplest of such structures yet isolated. It is presumably formed by electrocyclic closure of the imidoyl carbene onto the naphthalene 2-position, followed by a (thermal) [1,5]-shift of the methyl group (Scheme 5). This



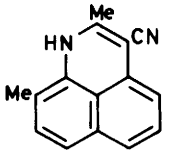
(**27**) (**28**)

Scheme 5.

sigmatropic shift converts the cross-conjugated 3a-methylpyrrole (**27**) into the more stable linearly conjugated 2a-methylpyrrole (**28**); this shift must be quite rapid since none of the products to be expected from further photochemical rearrangement[16] of intermediate (**27**) were observed.

Photolysis of the closely related 5-methyltriazole-4-carbonitrile (**8d**) gave no trace of the methyl-substituted derivative of product (**28**) or of its demethylated product. Instead a very low yield of a single, orange compound was obtained, which slowly decomposed. This is tentatively assigned the 2,9-dimethyl-1*H*-benzo[*de*]quinoline-3-carbonitrile structure (**29**) by comparison of its spectral data with those for compounds (**25a,b**).

In view of the unpredictable nature of these results and of the expectation of further rearrangement of the carbene *via* a 1*H*-azirine, the photolysis of 1-(2-methyl-1-naphthyl)triazoles (**9**) with an electron-withdrawing group at the 5-position only was not extensively studied. Irradiation of the ester (**9a**) gave an

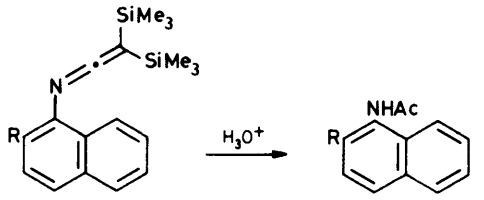


(**29**)

intractable mixture, and the nitrile (**9c**) gave only minor products identified as the 9b-methylbenz[*g*]indole (**28**) (5%), its demethylation product (**11c**) (*ca.* 1%), and the unidentified product also obtained in the photolysis of triazole (**8c**) (*ca.* 2%), all presumably formed by carbene rearrangement *via* the 1*H*-azirine.

The photolysis of 1-(2-methyl-1-naphthyl)triazoles thus proved to be much more complex than that of the related unmethylated compounds, some of the reactions giving no identifiable products at all. Where products were isolated, only those from the triazolecarbonitrile (**8c**) arose from electrocyclic closure of the carbene to the naphthalene 2-position. When this process was apparently suppressed, substitution by the carbene at the 8-position of the naphthalene ring, rather than electrocyclisation to the 8a-position, was observed.

1,2-*Shifts*.—In none of the photolyses described so far in this paper were products observed which arose from a Wolff-type 1,2-shift in the carbene (Scheme 2). However, photolysis of the bis(trimethylsilyl)triazoles (**2d**) and (**6f**) gave such products, the ketenimines (**30**) and (**31**) respectively, in high yield (> 80% by ^1H n.m.r. analysis of the product mixtures). Acidic hydrolysis of the ketenimines gave the corresponding acetamides (**32**) and (**33**). This result parallels the very rapid 1,2-migration of trimethylsilyl groups to other carbenic centres.[17]



(**30**) R = H (**32**) R = H
(**31**) R = Me (**33**) R = Me

Finally, it is interesting to note that in the photolyses of this extensive series of monocyclic 1,2,3-triazoles no evidence was obtained for electrocyclisation of the intermediate carbenes to the naphthalene ring junction (Scheme 1), in striking contrast with the photolyses of the corresponding benzotriazoles.[1]

Experimental

For general points see ref. 16.

4,5-*Dibenzoyl*-1-(1-*naphthyl*)-1,2,3-*triazole* (**3a**).—A solution of 1-azidonaphthalene (170 mg, 1.0 mmol) and DBA (240 mg, 1.0 mmol) in benzene (3 ml) was heated under reflux for 48 h. The mixture was then cooled and evaporated under reduced pressure to leave a red, oily solid. Trituration with ether–hexane (2:1, 5 ml) followed by recrystallisation from ethanol–water gave the *triazole* (**3a**) as crystals (286 mg, 70%), m.p. 143—145 °C (Found: C, 77.2; H, 4.1; N, 10.2. $C_{26}H_{17}N_3O_2$ requires C, 77.4; H, 4.25; N, 10.4%); *m/z* 403 (M^+), 374, 347, 270, 105 (base), and 77.

Similarly prepared was 4,5-*dibenzoyl*-1-(2-*methylnaphthyl*)-1,2,3-*triazole* (**7a**) (75%), m.p. 173–175 °C (Found: C, 77.45; H, 4.6; N, 10.0. $C_{27}H_{19}N_3O_2$ requires C, 77.7; H, 4.6; N, 10.1%); $\nu_{max.}$(Nujol) 1 669, 1 643, 1 599, 1 580, 950, 898, 812, and 699 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.30 (3 H, s), 7.26—7.78 (10 H, m), 7.84—7.98 (3 H, m), 8.06 (1 H, d, *J* 9 Hz), and 8.45—8.51 (2 H, m); *m/z* 417 (M^+), 361, 284, 256, 139, 115, 105 (base), and 77.

Dimethyl 1-(1-*Naphthyl*)-1,2,3-*triazole*-4,5-*dicarboxylate* (**3b**).—A solution of 1-azidonaphthalene (210 mg, 1.2 mmol) and DMAD (170 mg, 1.2 mmol) in benzene (2 ml) was heated under reflux in the dark for 5 h, then cooled and evaporated to leave a solid. Trituration with ether–hexane (1:1, 5 ml) gave the *triazole* (**3b**) (366 mg, 95%), m.p. 128—129 °C (Found: C, 61.6; H, 4.15; N, 13.4. $C_{16}H_{13}N_3O_4$ requires C, 61.7; H, 4.2; N, 13.5%); $\nu_{max.}$(Nujol) 1 735, 1 599, 1 548, 1 511, 1 475, 1 465, 1 397, 1 351, 1 318, 1 072, 970, 810, 780, and 768 cm^{-1}; δ (90 MHz; $CDCl_3$) 3.65 (3 H, s), 4.03 (3 H, s), 7.24 (1 H, m), 7.45—7.63 (4 H, m), and 7.83—8.09 (2 H, m); *m/z* 311 (M^+), 283, 252, 251, 193, 180, 165, 127 (base), and 59.

Similarly prepared was *dimethyl* 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4,5-*dicarboxylate* (**7b**) (94%), m.p. 130.5—132 °C (Found: C, 62.9; H, 4.5; N, 12.8. $C_{17}H_{15}N_3O_4$ requires C, 62.8; H, 4.65; N, 12.9%); $\nu_{max.}$(Nujol) 1 740, 1 560, 1 378, 1 300, 1 258, 1 208, 1 121, 1 076, 968, 941, 840, 820, 800, and 748 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.22 (3 H, s), 3.68 (3 H, s), 4.06 (3 H, s), 6.91 (1 H, m), 7.42—7.54 (3 H, m), 7.89 (1 H, m), and 7.97 (1 H, d, *J* 8 Hz); *m/z* 325 (M^+), 297, 266, 265, 238, 207, 206, 194, 179, 141, 115, 75 (base), and 59.

Cycloaddition of 1-*Azidonaphthalene to Ethyl Propiolate* (*EP*).—A mixture of 1-azidonaphthalene (1.69 g, 10 mmol) and EP (1.5 ml, 15 mmol) was heated to 100 °C (bath temp.) for 8 h, then cooled to room temperature. Excess of EP was removed under reduced pressure to leave a red gum. Chromatography afforded (i) *ethyl* 1-(1-*naphthyl*)-1,2,3-*triazole*-5-*carboxylate* (**5a**) (0.32 g, 12%) as a yellow gum (Found: M^+, 267.1007. $C_{15}H_{13}N_3O_2$ requires *M*, 267.1008); $\nu_{max.}$(neat) 1 732, 1 600, 1 202, 1 079, 805, and 772 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.98 (3 H, t, *J* 8 Hz), 4.08 (2 H, q, *J* 8 Hz), 7.08 (1 H, d, *J* 8 Hz), 7.40—7.61 (4 H, m), 7.93 (1 H, d, *J* 8 Hz), 8.03 (1 H, *d*, *J* 8 Hz), and 8.38 (1 H, s); *m/z* 267 (M^+), 193, 167, 166 (base), 154, and 127; and (ii) *ethyl* 1-(1-*naphthyl*)-1,2,3-*triazole*-4-*carboxylate* (**4a**) (1.90 g, 71%) as a red gum (Found: M^+, 267.1007); $\nu_{max.}$(neat) 1 730, 1 598, 1 375, 1 270, 1 035, 802, and 772 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.39 (3 H, t, *J* 7 Hz), 4.43 (2 H, q, *J* 7 Hz), 7.44—7.58 (5 H, m), 7.89 (1 H, m), 7.98 (1 H, m), and 8.40 (1 H, s); *m/z* 267 (M^+) 194, 180, 167, 166 (base), 154, 143, and 127.

Similarly, cycloaddition of 1-azidonaphthalene to MT gave (i) *methyl* 4-*methyl*-1-(1-*naphthyl*)-1,2,3-*triazole*-5-*carboxylate* (**5b**) as a red gum (9%) (Found: M^+, 267.1008. $C_{15}H_{13}N_3O_2$ requires *M*, 267.1008); $\nu_{max.}$(Nujol) 1 730, 1 597, 1 278, 1 206, 809, 798, and 769 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.72 (3 H, s), 3.62 (3 H, s), 7.13 (1 H, dd, *J* 8, 1 Hz), 7.43—7.63 (4 H, m), 7.96 (1 H, dd, *J* 7, 1 Hz), and 8.04 (1 H, d, *J* 7 Hz); *m/z* 267 (M^+), 239, 224, 207, 196, 180 (base), and 127; and (ii) *methyl* 5-*methyl*-1-(1-*naphthyl*)-1,2,3-*triazole*-4-*carboxylate* (**4b**) (72%), m.p. 178—179.5 °C (Found: C, 67.3; H, 4.8; N, 15.6. $C_{15}H_{13}N_3O_2$ requires C, 67.4; H, 4.9; N, 15.7%); $\nu_{max.}$(Nujol) 1 729, 1 222, 805, 789, and 775 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.38 (3 H, s), 4.01 (3 H, s), 7.11 (1 H, dd, *J* 7, 1 Hz), 7.46—7.64 (4 H, *m*), 7.96 (1 H, dd, *J* 8, 1 Hz), and 8.07, (1 H, d, *J* 8 Hz); *m/z* 267 (M^+), 224, 207, 194, 180 (base), and 127.

Similarly, cycloaddition of 1-azido-2-methylnaphthalene with MP gave (i) *methyl* 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-5-*carboxylate* (**9a**) (11%), m.p. 102.5—103.5 °C (Found: C, 67.1; H, 4.8; N, 15.7%); $\nu_{max.}$(Nujol) 1 742, 1 600, 1 524, 1 510, 1 310, 1 280, 1 262, 1 218, 1 192, 1 173, 1 130, 1 115, 1 079, 980, 962, 942, 938, 910, 870, 861, 820, 803, 780, 770, 750, 703, and 668 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.15 (3 H, s), 3.71 (3 H, s), 6.81 (1 H, dd, *J* 8, 1 Hz), 7.36—7.52 (3 H, m), 7.90 (1 H, dd, *J* 8, 1 Hz), 7.96 (1 H, d, *J* 8 Hz), and 8.44 (1 H, s); *m/z* 267 (M^+), 239, 238, 224, 207, 180 (base), and 115; and (ii) *methyl* 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4-*carboxylate* (**8a**) (66%), m.p. 123.5—124.5 °C (Found: C, 67.5; H, 4.9; N, 15.7%); $\nu_{max.}$(Nujol) 3 120, 1 735, 1 601, 1 210, 1 157, 1 048, 819, 780, and 749 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.22 (3 H, s), 4.04 (3 H, s), 7.00 (1 H, dd, *J* 8, 1 Hz), 7.43—7.55 (3 H, m), 7.91 (1 H, dd, *J* 8, 2 Hz), 7.96 (1 H, d, *J* 9 Hz), and 8.33 (1 H, s); *m/z* 267 (M^+), 239, 237, 224, 207, and 180 (base).

Similarly, cycloaddition of 1-azido-2-methylnaphthalene with MT gave (i) *methyl* 4-*methyl*-1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-5-*carboxylate* (**9b**) as a gum which very slowly solidified (10%) (Found: M^+, 281.1164. $C_{16}H_{15}N_3O_2$ requires *M*, 281.1164); $\nu_{max.}$(Nujol) 1 728, 1 280, 1 200, 1 101, 811, 780, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.12 (3 H, s), 2.71 (3 H, s), 3.62 (3 H, s), 6.83 (1 H, dd, *J* 8, 1 Hz), 7.35—7.49 (3 H, m), 7.87 (1 H, dd, *J* 7, 1 Hz), and 7.92 (1 H, d, *J* 9 Hz); *m/z* 281 (M^+), 238, 221, 194 (base), 141, and 115; and (ii) *methyl* 5-*methyl*-1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4-*carboxylate* (**8b**) as a red gum (54%) (Found: M^+, 281.1173); $\nu_{max.}$(neat) 1 730 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.17 (3 H, s), 2.31 (3 H, s), 4.05 (3 H, s), 6.88 (1 H, dd, *J* 11, 1 Hz), 7.42—7.56 (3 H, m), 7.92 (1 H, dd, *J* 10, 2 Hz), and 7.97 (1 H, d, *J* 11 Hz); *m/z* 281 (M^+), 238, 194 (base), 141, and 115.

Methyl 1-(1-*Naphthyl*)-1,2,3-*triazole*-4-*carboxylate* (**4c**).—A solution of ethyl 1-(1-naphthyl)-1,2,3-triazole-4-carboxylate (**4a**) (60 mg, 0.22 mmol) and sodium hydroxide (80 mg, 2.0 mmol) in methanol (5 ml) was heated under reflux for 1 h, then cooled, and quenched with water (30 ml). The mixture was acidified to pH 1 (2M-hydrochloric acid) and extracted with dichloromethane (3 × 10 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to leave a solid. This was treated with thionyl chloride (0.5 ml) at room temperature for 30 min, then excess of reagent was evaporated

off under reduced pressure, and the residue was treated with methanol (2 ml). Evaporation under reduced pressure left a white foam, which on trituration with ether–pentane (1:2, 2 ml) gave the *methyl ester* (**4e**) (41.3 mg, 74%), m.p. 57—58 °C (Found: C, 66.6; H, 4.4; H, 16.4. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.35; N, 16.6%); $\nu_{max.}$(Nujol) 3 125, 1 731, 1 599, 1 233, 1 045, 800, 781, and 770 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 3.93 (3 H, s), 7.52—7.81 (5 H, m), 8.12 (1 H, dd, *J* 7, 2 Hz), 8.21 (1 H, d, *J* 8 Hz), and 8.97 (1 H, s).

1-(1-*Naphthyl*)-4,5-*bis*(*trimethylsilyl*)-1,2,3-*triazole* (**2d**).—A solution of 1-azidonaphthalene (500 mg, 2.96 mmol) and BTMSA (500 mg, 2.94 mmol) in chloroform (3 ml) was heated under reflux for 96 h; cooling and evaporation under reduced pressure left a black gum, which was chromatographed to give the *title triazole* (**2d**) (370 mg, 37%), m.p. 133—134.5 °C (Found: C, 63.7; H, 7.4; N, 12.3. $C_{18}H_{25}N_3Si_2$ requires C, 63.7; H, 7.4; N, 12.4%); $\nu_{max.}$(Nujol) 1 598, 1 253, 845, 809, and 782 cm^{-1}; δ (250 MHz; $CDCl_3$) −0.11 (9 H, s), 0.48 (9 H, s), 7.03 (1 H, m), 7.41—7.58 (4 H, m), 7.91 (1 H, d, *J* 8 Hz), and 8.01 (1 H, d, *J* 8 Hz); *m/z* 311 (M^+ −28), 296 (base), and 73.

Similarly, cycloaddition of 1-azido-2-methylnaphthalene with BTMSA gave 1-(2-*methyl*-1-*naphthyl*)-4,5-*bis*(*trimethylsilyl*)-1,2,3-*triazole* (**6f**) (75%), m.p. 140—144 °C (Found: C, 64.4; H, 7.8; N, 11.8. $C_{19}H_{27}N_3Si_2$ requires C, 64.5; H, 7.7; N, 11.9%); $\nu_{max.}$(Nujol) 1 411, 1 375, 1 255, 1 249, 1 243, 858, 850, 840, 780, 760, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) −0.17 (9 H, s), 0.50 (9 H, s), 2.09 (3 H, s), 6.75 (1 H, d, *J* 8 Hz), 7.34—7.48 (3 H, m), and 7.81—7.93 (2 H, m); *m/z* 353 (M^+), 325, 310 (base), and 73.

1-(1-*Naphthyl*)-1,2,3-*triazole*-4,5-*dicarboxamide* (**3c**).—A solution of dimethyl 1-(1-naphthyl)-1,2,3-triazole-4,5-dicarboxylate (**3b**) (250 mg, 0.81 mmol) in methanol (8 ml) was treated with saturated aqueous ammonia (6 ml), and the mixture was stirred at room temperature for 24 h, then treated with water (40 ml), and the *diamide* (**3c**) was filtered off and dried (210 mg, 93%), m.p. 245—246 °C (Found: C, 59.6; H, 3.9; N, 24.85. $C_{14}H_{11}N_5O_2$ requires C, 59.8; H, 3.9; N, 24.8%).

Similarly, diester (**7b**) gave 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4,5-*dicarboxamide* (**7c**) (90%), m.p. 233—234 °C (Found: C, 61.1; H, 4.3; N, 23.7%. $C_{15}H_{13}N_5O_2$ requires C, 61.0; H, 4.4; N, 23.7%); $\nu_{max.}$(Nujol) 3 440, 3 230, 3 060, 1 681, 1 670, 1 630, 1 597, 1 535, 1 508, 818, 720, and 671 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.12 (3 H, s), 6.91 (1 H, dd, *J* 8, 2 Hz), 7.08 (1 H, br), 7.40—7.62 (4 H, m), 7.98 (1 H, dd, *J* 8, 2 Hz), 8.03 (1 H, d, *J* 10 Hz), 8.24 (1 H, br), and 10.53 (1 H, br); *m/z* 295 (M^+), 250, 224, 207, 194, 179 (base), and 115.

Ester (**4a**) gave 1-(1-*naphthyl*)-1,2,3-*triazole*-4-*carboxamide* (87%), m.p. 234.5—236 °C (Found: C, 65.25; H, 4.2; N, 23.4. $C_{13}H_{10}N_4O$ requires C, 65.5; H, 4.2; N, 23.5%).

Ester (**4b**) gave 5-*methyl*-1-(1-*naphthyl*)1,2,3-*triazole*-4-*carboxamide* (93%) m.p. 177—179 °C (Found: 66.95; H, 4.55. $C_{14}H_{12}N_4O$ requires C, 66.65; H, 4.8%).

Ester (**5a**) gave 1-(1-*naphthyl*)-1,2,3-*triazole*-5-*carboxamide* (96%), 177—178 °C (Found: C. 65.6; H, 4.15; N, 23.5. $C_{13}H_{10}N_4O$ requires C, 65.5; H, 4.2; N, 23.5%).

Ester (**5b**) gave 4-*methyl*-1-(1-*naphthyl*)-1,2,3-*triazole*-5-*carboxamide* (95%), m.p. 185—187 °C (Found: C, 66.9; H, 4.8; N, 22.1. $C_{14}H_{12}N_4O$ requires C, 66.65; H, 4.8; N, 22.2%).

Ester (**8a**) gave 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4-*carboxamide* (89%), m.p. 269—270 °C (Found: C, 66.8; H, 4.6; N, 22.1%); $\nu_{max.}$(Nujol) 3 380, 3 200, 1 702, 1 620, 1 042, 820, and 781 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.22 (3 H, s), 6.92 (1 H, br), 7.02 (1 H, m), 7.41—7.55 (4 H, m), 8.05 (1 H, m), 8.12 (1 H, d, *J* 9 Hz), and 8.71 (1 H, s); *m/z* 252 (M^+), 207, 185, 180 (base), and 115.

Ester (**8b**) gave 5-*methyl*-1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4-*carboxamide* (92%), m.p. 156—158 °C (Found: C, 67.3; H, 5.2. $C_{15}H_{14}N_4O$ requires C, 67.65; H, 5.3%); $\nu_{max.}$(Nujol) 3 380, 3 200, 1 681, and 1 600 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.17 (3 H, s), 2.29 (3 H, s), 6.78 (1 H, br), 6.92 (1 H, dd, *J* 7, 2 Hz), 7.50 (1 H, br), 7.52—7.62 (2 H, m), 7.64 (1 H, d, *J* 9 Hz), 8.07 (1 H, dd, *J* 7, 2 Hz) and 8.13 (1 H, d, *J* 9 Hz); *m/z* 266 (M^+), 221, 194 (base), 180, 168, and 115.

Ester (**9a**) gave 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-5-*carboxamide* (96%), m.p. 196—198 °C (Found: C, 66.5; H, 4.7; N, 22.0. $C_{14}H_{12}N_4O$ requires C, 66.65; H, 4.8; N, 22.2%); $\nu_{max.}$(Nujol) 3 280, 1 700, 1 231, 988, 855, 815, and 780 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.12 (3 H, s), 6.82 (1 H, dd, *J* 8, 1 Hz), 6.90 (1 H, br s), 7.38—7.49 (3 H, m), 7.62 (1 H, br s), 7.98 (1 H, dd, *J* 7, 1 Hz), 8.03 (1 H, d, *J* 8 Hz), and 8.45 (1 H, s); *m/z* 252 (M^+), 207, 179 (base), 152, and 115.

1-(1-*Naphthyl*)-1,2,3-*triazole*-4,5-*dicarbonitrile* (**3d**).—A solution of 1-(1-naphthyl)-1,2,3-triazole-4,5-dicarboxamide (**3c**) (65 mg, 0.23 mmol) and toluene-*p*-sulphonyl chloride (200 mg, 1.05 mmol) in pyridine (3 ml) was heated under reflux for 18 h, then cooled and diluted with ether (30 ml). This solution was extracted with hydrochloric acid (6M; 6 × 20 ml), water (10 ml), and brine (10 ml), then dried (Na_2SO_4). Evaporation under reduced pressure, and chromatography of the residue, gave the *title dinitrile* (**3d**) (80%), m.p. 147—148 °C (Found: C, 68.4; H, 2.7; N, 28.4. $C_{14}H_7N_5$ requires C, 68.6; H, 2.9; N, 28.6%); $\nu_{max.}$(Nujol) 2 224, 1 599, 1 060, 799, and 772 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.31 (1 H, m), 7.63—7.74 (4 H, m), 8.07 (1 H, m), and 8.22 (1 H, d, *J* 8 Hz); *m/z* 245 (M^+), 217 (base), 190, 165, 140, and 127.

Similarly, diamide (**7c**) afforded 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4,5-*dicarbonitrile* (**7d**) (87%), m.p. 132—133 °C (Found: C, 69.4; H, 3.4; N, 27.2%. $C_{15}H_9N_5$ requires C, 69.5; H, 3.5; N, 27.0%); $\nu_{max.}$(Nujol) 2 254, 1 602, 1 510, 969, 911, 867, 820, 780, and 751 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.27 (3 H, s), 6.86 (1 H, dd, *J* 7, 2 Hz), 7.51—7.65 (3 H, m), 7.99 (1 H, m), and 8.10 (1 H, d, *J* 8 Hz); *m/z* 259 (M^+), 231, 230, 216 (base), 204, 190, 154, 139, 127, 115, and 63.

1-(1-Naphthyl)-1,2,3-triazole-4-carboxamide afforded 1-(1-*naphthyl*)-1,2,3-*triazole*-4-*carbonitrile* (**4c**) (81%), m.p. 134—135 °C (Found: C, 70.9; H, 3.6; N, 25.4. $C_{13}H_8N_4$ requires C, 70.9; H, 3.7; N, 25.4%); $\nu_{max.}$(Nujol) 3 420, 2 224, 1 598, 1 043, 801, and 767 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.46 (1 H, m), 7.54—7.67 (4 H, m), 7.99 (1 H, m), 8.08 (1 H, dd, *J* 7, 2 Hz), and 8.38 (1 H, s); *m/z* 220 (M^+), 192 (base), 165, and 127.

5-Methyl-1-(1-naphthyl)-1,2,3-triazole-4-carboxamide gave 5-*methyl*-1-(1-*naphthyl*)-1,2,3-*triazole*-4-*carbonitrile* (**4d**) (77%), m.p. 91—92 °C (Found: C, 71.8; H, 4.2; N, 24.1. $C_{14}H_{10}N_4$ requires C, 71.8; H, 4.3; N, 23.9%); $\nu_{max.}$(Nujol) 2 221, 1 600, 1 379, 811, and 774 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.30 (3 H, s), 7.10 (1 H, m), 7.47—7.58 (4 H, m), 8.00 (1 H, dd, *J* 8, 2 Hz), and 8.11 (1 H, d, *J* 8 Hz); *m/z* 234 (M^+), 206, 205 (base), 179, 165, and 127.

1-(1-Naphthyl)-1,2,3-triazole-5-carboxamide gave 1-(1-*naphthyl*)-1,2,3-*triazole*-5-*carbonitrile* (**5c**) (89%), m.p. 95—96 °C (Found: C, 70.7; H, 3.6; N, 25.3. $C_{13}H_8N_4$ requires C, 70.9; H, 3.7; N, 25.4%); $\nu_{max.}$(Nujol) 3 250, 2 226, 1 599, 1 520, 1 510, 1 132, 963, 872, 856, 802, and 781 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.34 (1 H, m), 7.56—7.70 (4 H, m), 8.02 (1 H, m), 8.14 (1 H, dd, *J* 8, 2 Hz), and 8.41 (1 H, s); *m/z* 220 (M^-), 192 (base), 165, and 127.

4-Methyl-1-(1-naphthyl)-1,2,3-triazole-5-carboxamide gave 4-*methyl*-1-(1-*naphthyl*)-1,2,3-*triazole*-5-*carbonitrile* (**5d**) (67%), m.p. 101—102 °C (Found: C, 71.6; H, 4.3; N, 23.7. $C_{14}H_{10}N_4$ requires C, 71.8; H, 4.3; N, 23.9%); δ (250 MHz; $CDCl_3$) 2.68 (3 H, s), 7.41 (1 H, m), 7.56—7.68 (4 H, m), 8.01 (1 H, dd, *J* 7, 2 Hz), and 8.12 (1 H, dd, *J* 8, 1 Hz); *m/z* 234 (M^+), 205 (base), 180, 165, 154, and 127.

1-(2-Methyl-1-naphthyl)-1,2,3-triazole-4-carboxamide gave 1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole*-4-*carbonitrile* (**8c**) (92%),

m.p. 131—132 °C (Found: C, 71.7; H, 4.2; N, 23.8%); $\nu_{max.}$(Nujol) 3 140, 2 226, 1 600, 1 045, 819, 780, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.20 (3 H, s), 6.92 (1 H, m), 7.44—7.57 (3 H, m), 7.92 (1 H, dd, *J* 7, 2 Hz), 7.98 (1 H, d, *J* 9 Hz), and 8.23 (1 H, s); *m/z* 234 (M^+), 205 (base), 191, and 115.

5-Methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carboxamide gave *5-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carbonitrile* (**8d**) (92%). m.p. 119—120 °C (Found: C, 72.4; H, 4.8; N, 22.6. $C_{15}H_{12}N_4$ requires C, 72.6; H, 4.9; N, 22.6%); $\nu_{max.}$(Nujol) 2 245, 1 386, 815, 785, and 749 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.17 (3 H, s), 2.21 (3 H, s), 6.85 (1 H, m), 7.47—7.60 (3 H, m), 7.95 (1 H, dd, *J* 6, 2 Hz), and 8.02 (1 H, d, *J* 7 Hz); *m/z* 248 (M^+), 219 (base), 205, 179, and 115.

1-(2-Methyl-1-naphthyl)-1,2,3-triazole-5-carboxamide afforded *1-(2-methyl-1-naphthyl)-1,2,3-triazole-5-carbonitrile* (**9c**) (89%) as a gum (Found: M^+, 234.0905. $C_{14}H_{10}N_4$ requires *M*, 234.0905); $\nu_{max.}$(Nujol) 3 130, 2 221, 1 598, 1 112, 1 099, 964, 866, 816, 780, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.21 (3 H, s), 6.87 (1 H, m), 7.45—7.57 (3 H, m), 7.92 (1 H, dd, *J* 7, 2 Hz), 8.01 (1 H, d, *J* 9 Hz), and 8.43 (1 H, s); *m/z* 234 (M^+), 205 (base), 191, and 115.

4-Isopropenyl-1-(1-naphthyl)-1,2,3-triazole (**2c**).—A solution of ethyl 1-(1-naphthyl)-1,2,3-triazole-4-carboxylate (**4a**) (488 mg) in ether (2 ml) was added dropwise to a solution of methylmagnesium iodide in ether (1M; 10 ml), and the mixture was heated under reflux for 2 h. The cooled reaction mixture was quenched with water (10 ml) and acidified to pH 1 (2M-hydrochloric acid), the ethereal layer was separated, and the aqueous phase was washed with ether (5 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated to leave a pale yellow solid. Recrystallisation from dichloromethane–hexane gave *4-(1-hydroxy-1-methylethyl)-1-(1-naphthyl)-1,2,3-triazole* (410 mg), m.p. 156—157 °C (Found: C, 71.35; H, 6.0; N, 16.7. $C_{15}H_{15}N_3O$ requires C, 71.1; H, 6.0; N, 16.6%); δ (60 MHz; $CDCl_3$) 1.80 (6 H, s), 2.79 (1 H, s), 7.52—7.75 (5 H, m), and 7.90—8.21 (3 H, m).

A solution of this alcohol (282 mg) in toluene (20 ml) containing iodine (3 mg) was heated under reflux for 17 h in a Dean–Stark apparatus. The cooled solution was diluted with ether (20 ml) and extracted with 10% aqueous sodium thiosulphate (2 × 20 ml), washed with water (10 ml), and dried ($MgSO_4$). Evaporation of the solvent and chromatography gave the *alkene* (**2c**) as a gum (181 mg, 69%) (Found: M^+, 235.1113. $C_{15}H_{13}N_3$ requires *M*, 235.1109); $\nu_{max.}$(neat) 3 140, 3 060, 1 690, 1 640, 1 598, 1 575, 1 512, 1 470, 1 430, 1 374, 1 270, 1 232, 1 039, 950, 900, 800, 773, and 670 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.25 (3 H, br s), 5.26 (1 H, m), 5.91 (1 H, m), 7.40—7.70 (5 H, m), and 7.81—8.00 (3 H, m); *m/z* 235 (M^+), 207, 206 (base), 192, 167, 127, 101, and 77.

Similarly, treatment of methyl 1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carboxylate (**8a**) with an excess of methylmagnesium iodide gave *4-(1-hydroxy-1-methylethyl)-1-(2-methyl-1-naphthyl)-1,2,3-triazole* (91%) as a gum (Found: M^+, 267.1378. $C_{16}H_{17}N_3O$ requires *M*, 267.1372); $\nu_{max.}$(neat) 3 400, 1 601, 1 511, 1 038, 819, 780, 745, and 731 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.78 (6 H, s) 2.20 (3 H, s), 2.60 (1 H, br s), 7.02 (1 H, m), 7.39—7.51 (3 H, m), 7.66 (1 H, s), 7.87 (1 H, dd, *J* 7, 2 Hz), and 7.91 (1 H, d, *J* 9 Hz).

Dehydration gave *4-isopropenyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole* (**6d**) (80%) as a gum (Found: M^+, 249.1273. $C_{16}H_{15}N_3$ requires *M*, 249.1267); $\nu_{max.}$(Nujol) 1 681, 1 601, 1 510, 1 040, 815, 780, and 744 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.20 (3 H, s), 2.22 (3 H, s), 5.20 (1 H, m), 5.89 (1 H, m), 7.06 (1 H, m), 7.37—7.51 (3 H, m), 7.71 (1 H, s), and 8.82—8.93 (2 H, m); *m/z* 249 (M^+), 221, 220 (base), 180, and 141.

Similar treatment of methyl 5-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carboxylate (**8b**) with an excess of methylmagnesium iodide gave *4-(1-hydroxy-1-methylethyl)-5-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole* (94%), m.p. 150—152 °C (Found: C, 72.45; H, 6.6; N, 14.9. $C_{17}H_{19}N_3O$ requires 72.6; H, 6.8; N, 14.9%); $\nu_{max.}$(Nujol) 3 390, 1 600, 1 569, 1 255, 1 239, 1 149, 860, 830, and 795 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 1.68 (3 H, s), 1.71 (3 H, s), 2.12 (3 H, s), 2.16 (3 H, s), 2.85 (1 H, s), 6.90 (1 H, m), 7.46—7.63 (3 H, m), 8.03 (1 H, dd, *J* 7, 2 Hz), 8.08 (1 H, d, *J* 9 Hz); *m/z* 281 (M^+), 238, 223, 210, 195 (base), 182, 141, 115, and 98.

Dehydration gave *4-isopropenyl-5-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole* (**6e**) (85%), m.p. 102—104 °C (Found: M^+, 263.1415. $C_{17}H_{17}N_3$ requires *M*, 263.1422); $\nu_{max.}$(Nujol) 1 635, 1 261, 884, 816, 785, 740, and 711 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.11 (3 H, s), 2.16 (3 H, s), 2.37 (3 H, s), 5.27 (1 H, m), 5.37 (1 H, m), 6.93 (1 H, m), 7.39—7.52 (3 H, m), 7.89 (1 H, dd, *J* 7, 2 Hz), and 7.93 (1 H, d, *J* 9 Hz); *m/z* 263 (M^+), 219 (base), and 115.

1-(1-Naphthyl)-1,2,3-triazole (**2a**).—A solution of dimethyl 1-(1-naphthyl)-1,2,3-triazole-4,5-dicarboxylate (**3b**) (620 mg) and potassium hydroxide (1.0 g) in methanol (15 ml) was heated under reflux for 2 h. The cooled mixture was treated with hydrochloric acid (2M; 20 ml) and extracted with ether (3 × 15 ml). The combined extracts were dried ($MgSO_4$) and evaporated. The resulting solid was suspended in toluene (15 ml) and the mixture was heated under reflux for 24 h. Evaporation of the cooled solution and chromatography gave *1-(1-naphthyl)-1,2,3-triazole* (**2a**) as a gum (350 mg, 90%) which solidified after some time, m.p. 57—58 °C (Found: C, 73.6; H, 4.5; N, 21.4. $C_{12}H_9N_3$ requires C, 73.8; H, 4.65; N, 21.5%); $\nu_{max.}$(Nujol) 3 155, 3 138, 1 600, 1 511, 1 231, 1 219, 1 020, 800, and 774 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.48—7.62 (5 H, m) and 7.92—8.07 (4 H, m); *m/z* 195 (M^+), 167, 139, 127 (base), and 101.

Similarly, hydrolysis and decarboxylation of methyl 5-methyl-1-(1-naphthyl)-1,2,3-triazole-4-carboxylate (**4b**) afforded *5-methyl-1-(1-naphthyl)-1,2,3-triazole* (**2b**) (95%), m.p. 125—127 °C (Found: C, 74.8; H, 5.3; N, 20.3. $C_{13}H_{11}N_3$ requires C, 74.6; H, 5.3; N, 20.1%); $\nu_{max.}$(Nujol) 1 598, 1 550, 1 510, 1 368, 1 350, 1 325, 840, 800, and 772 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.10 (3 H, d, *J* 1 Hz), 7.15 (1 H, m), 7.43—7.61 (4 H, m), 7.68 (1 H, d, *J* 1 Hz), 7.93 (1 H, dd, *J* 8, 1 Hz), and 8.02 (1 H, d, *J* 8 Hz); *m/z* 209 (M^+), 180 (base), 153, 127, and 101.

Hydrolysis and decarboxylation of dimethyl 1-(2-methyl-1-naphthyl)-1,2,3-triazole-4,5-dicarboxylate (**7b**) gave *1-(2-methyl-1-naphthyl)-1,2,3-triazole* (**6a**) (93%), m.p. 112—113 °C (Found: C, 74.8; H, 5.3; N, 20.2%); $\nu_{max.}$(Nujol) 3 158, 3 128, 1 599, 1 226, 825, 812, 800, 780, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.20 (3 H, s), 7.00 (1 H, dd, *J* 8, 1 Hz), 7.40—7.53 (3 H, m), 7.81 (1 H, d, *J* 1 Hz), 7.89 (1 H, dd, 8, 2 Hz), 7.94 (1 H, d, *J* 9 Hz), and 8.01 (1 H, d, *J* 1 Hz); *m/z* 209 (M^+), 181, 180 (base), 166, and 115.

Hydrolysis and decarboxylation of methyl 5-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carboxylate (**8b**) gave *5-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole* (**6b**) (76%), m.p. 130.5—131.5 °C (Found: C, 75.0; H, 5.95; N, 18.85. $C_{14}H_{13}N_3$ requires C, 75.3; H, 5.9; N, 18.8%); $\nu_{max.}$(Nujol) 3 135, 1 600, 1 550, 1 510, 1 231, 819, 789, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.04 (3 H, d, *J* 1 Hz), 2.13 (3 H, s), 6.88 (1 H, dd, *J* 8, 1 Hz), 7.38—7.43 (3 H, m), 7.62 (1 H, d, *J* 1 Hz), 7.78 (1 H, dd, *J* 7, 1 Hz) and 7.83 (1 H, d, *J* 9 Hz); *m/z* 223 (M^+), 194 (base), 180, 141, and 115.

Hydrolysis and decarboxylation of methyl 4-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole-5-carboxylate (**9b**) gave *4-methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole* (**6c**) (91%), m.p. 87—88 °C (Found: C, 75.0; H, 5.8; N, 18.9%); $\nu_{max.}$(Nujol) 3 145, 1 597, 1 551, 1 510, 1 225, 830, 820, 785, 759, and 750 cm^{-1}); δ (250 MHz; $CDCl_3$) 2.21 (3 H, s), 2.55 (3 H, s), 7.07 (1 H, m), 7.40—7.53 (4 H, m), and 7.85—7.95 (2 H, m); *m/z* 223 (M^+) 195, 194, 180 (base), 141, and 115.

1-(2-*Methyl*-1-*naphthyl*)-1,2,3-*triazole*-4-*carbaldehyde* (**8e**).—A solution of methyl 1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carboxylate (**8a**) (150 mg) in ether (2 ml) was added dropwise to a slurry of lithium aluminium hydride (150 mg) in ether (4 ml), and the mixture was heated under reflux for 2 h. The cooled mixture was quenched carefully with water (10 ml) and acidified to pH 1 (2M-hydrochloric acid). The ether layer was separated, and the aqueous phase was extracted with ether (3 × 10 ml). The combined ether phases were washed successively with water (2 ml), saturated aqueous sodium hydrogen carbonate (2 × 10 ml), water (10 ml), and brine (10 ml), and dried ($MgSO_4$). Evaporation of the solvent gave 4-(*hydroxymethyl*)-1-(2-*methyl*-1-*naphthyl*)-1,2,3-*triazole* (127 mg, 95%), m.p. 143—144 °C (from CH_2Cl_2–hexane) (Found: C, 70.1; H, 5.6; N, 17.6. $C_{14}H_{13}N_3O$ requires C, 70.3; H, 5.5; N, 17.6%); $\nu_{max.}$(Nujol) 3 320, 1 228, 1 045, 821, 785, 760, and 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.20, (3 H, s), 2.52 (1 H, br) 4.49, (2 H, s), 7.03 (1 H, m), 7.39—7.52 (3 H, m), 7.76 (1 H, m), 7.88 (1 H, dd, *J* 8, 2 Hz), and 7.93 (1 H, d, *J* 9 Hz); *m/z* 239 (M^+), 194 (base), 180, 167, 141, and 115.

A solution of this alcohol (108 mg) in dichloromethane (10 ml) was treated with manganese dioxide (700 mg) for 7.5 h. The mixture was then filtered through Celite and evaporated to leave an oil. Chromatography gave the *title aldehyde* (**8e**) (59 mg, 54%), m.p. 134—136 °C (Found: C, 70.8; H, 4.9; N, 17.6. $C_{14}H_{11}N_3O$ requires C, 70.9; H, 4.7; N, 17.7%); $\nu_{max.}$(Nujol) 3 120, 1 698, 1 531, 1 189, 1 000, 818, 782, 770, and 755 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.21 (3 H, s), 7.00 (1 H, m), 7.45—7.58 (3 H, m), 7.92 (1 H, dd, *J* 8, 2 Hz), 7.99 (1 H, d, *J* 8 Hz), 8.34 (1 H, s), and 10.35 (1 H, s); *m/z* 237 (M^+), 208, 180 (base), and 115.

Photolysis of the Triazoles.—Dilute solutions of the triazoles in acetonitrile were irradiated at 254 nm under a stream of dry nitrogen in quartz vessels (Rayonet photochemical reactor) for the times shown, unless stated otherwise. The solvent was evaporated off and the photolysate was separated by chromatography.

1-(1-Naphthyl)-1,2,3-triazole (**2a**) (180 mg) in acetonitrile (180 ml) (15 h) gave (i) 1*H*-benz[*g*]indole (4 mg, 2%) and (ii) starting triazole (94 mg, 52%).

5-Methyl-1-(1-naphthyl)-1,2,3-triazole (**2b**) (24 mg) in acetonitrile (30 ml) (15 h) gave starting triazole (15 mg, 63%) only.

4-Isopropenyl-1-(1-naphthyl)-1,2,3-triazole (**2c**) (118 mg) in acetonitrile (100 ml) (15 h) gave starting triazole (25 mg, 21%) only.

4,5-Dibenzoyl-1-(1-naphthyl)-1,2,3-triazole (**3a**) (100 mg) in acetonitrile (100 ml) (36 h), then at 300 nm for 24 h, gave (i) starting triazole (11 mg, 11%) and (ii) 2,3-*dibenzoyl*-1H-*benz*[g]*indole* (**10a**) (15 mg, 14%; 16% based on consumed starting triazole), m.p. 265—267 °C (Found: C, 83.2; H, 4.6; N, 3.8. $C_{26}H_{17}NO_2$ requires C, 83.1; H, 4.6; N, 3.7%) $\nu_{max.}$(Nujol) 3 395, 1 648, 1 610, 1 595, 1 501, 1 250, 962, 899, 811, 750, 736, 720, 708, 693. and 687 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.22—7.70 (14 H, m), 8.00 (1 H, d, *J* 9 Hz), 8.87 (1 H, d, *J* 8 Hz), and 13.45 (1 H, s).

Dimethyl 1-(1-naphthyl)-1,2,3-triazole-4,5-dicarboxylate (**3b**) (233 mg) in acetonitrile (170 ml) (10 h) gave *dimethyl* 1H-*benz*[g]*indole*-2,3-*dicarboxylate* (**10b**), m.p. 191—192 °C (from CH_2Cl_2–hexane) (Found: C, 67.7; H, 4.5; N, 4.9. $C_{16}H_{13}NO_4$ requires C, 67.8; H, 4.6; N, 4.9%); $\nu_{max.}$(Nujol) 3 317, 1 720, and 1 690 cm^{-1}; δ (250 MHz; $CDCl_3$) 4.02 (6 H, s), 7.52—7.76 (3 H, m), 7.94 (1 H, dd, *J* 8, 2 Hz), 8.02 (1 H, d, *J* 9 Hz), 8.15 (1 H, dd, *J* 7, 2 Hz), and 10.10 (1 H, br); *m/z* 283 (M^+), 251 (base), 220, 193, 164, 96, 95, and 82.

1-(1-Naphthyl)-1,2,3-triazole-4,5-dicarboxamide (**3c**) (120 mg) in acetonitrile (100 ml) (15 h), followed by filtration of the precipitated product, gave 1H-*benz*[g]*indole* -2,3-*dicarboxamide* (**10c**) (88 mg, 81%) as a pale brown solid, m.p. > 300 °C (Found: C, 66.4; H, 4.4; N, 16.6. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.4; N, 16.6%); δ [250 MHz; $(CD_3)_2SO$] 7.45—7.64 (3 H, m), 7.81 (2 H, s), 7.89—8.00 (2 H, m), 8.33 (1 H, s), 8.63 (1 H, d, *J* 7 Hz), 9.46 (1 H, s), and 12.80 (1 H, s); *m/z* 253 (M^+), 236 (base), 218, 193, and 164.

1-(1-Naphthyl)-1,2,3-triazole-4,5-dicarbonitrile (**3d**) (55 mg) in acetonitrile (50 ml) (12 h) gave 1H-*benz*[g]*indole*-2,3-*dicarbonitrile* (**10d**) (30 mg, 64%), m.p. 288—289 °C (Found: C, 77.1; H, 3.2; N, 19.1. $C_{14}H_7N_3$ requires C, 77.4; H, 3.25; N, 19.3%); $\nu_{max.}$(Nujol) 3 120, 2 218, 1 221, 809, and 741 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 7.64—7.79 (3 H, m), 7.88 (1 H, d, *J* 9 Hz), 8.09 (1 H, m), and 8.43 (1 H, m), NH not observed; *m/z* 217 (M^+, base), 190, and 164.

Ethyl 1-(1-naphthyl)-1,2,3-triazole-4-carboxylate (**4a**) (250 mg) in acetonitrile (180 ml) (15 h) gave starting triazole (124 mg, 50%) only.

Methyl 5-methyl-1-(1-naphthyl)-1,2,3-triazole-4-carboxylate (**4b**) (250 mg) in acetonitrile (180 ml) (15 h) gave *methyl* 2-*methyl*-1H-*benz*[g]*indole*-3-*carboxylate* (**11b**) (73 mg, 33%; 47% based on consumed starting triazole), m.p. 223—225 °C (Found: C, 75.2; H, 5.4; N, 5.75. $C_{15}H_{13}NO_2$ requires C, 75.3; H, 5.5; N, 5.85%); $\nu_{max.}$(Nujol) 3 280, 1 665, 1 599, 1 548, 1 199, 1 112, 820, 750, and 690 cm^{-1}; δ [250 MHz; $(CD_3)_2SO$] 2.75 (3 H, s), 3.82 (3 H, s), 7.42 (1 H, m), 7.52—7.61 (2 H, m), 7.93 (1 H, d, *J* 8 Hz), 8.07 (1 H, d, *J* 9 Hz), 8.33 (1 H, d, *J* 8 Hz), and 12.52 (1 H, s); *m/z* 239 (M^+) 200, 180, 127, 115, and 91 (base).

1-(1-Naphthyl)-1,2,3-triazole-4-carbonitrile (**4c**) (150 mg) in acetonitrile (150 ml) (15 h) gave (i) unchanged starting triazole (5 mg, 3%) amd (ii) 1H-*benz*[g]*indole*-3-*carbonitrile* (**11c**) (96 mg, 74%; 76% based on consumed starting material) as a pale yellow solid, m.p. 169—170.5 °C (from CH_2Cl_2–hexane) (Found: C, 81.1; H, 4.2; N, 14.7. $C_{13}H_8N_2$ requires C, 81.2; H, 4.2; N, 14.6%); $\nu_{max.}$(Nujol) 3 300, 2 220, 1 290, 1 218, 799, and 740 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 7.48—7.79 (4 H, m), 8.03 (1 H, m), 8.13 (1 H, s), 8.38 (1 H, dd, *J* 8, 1 Hz), and 12.12 (1 H, br); *m/z* 192 (M^+, base), 164, 138, and 96.

5-Methyl-1-(1-naphthyl)-1,2,3-triazole-4-carbonitrile (**4d**) (59 mg) in acetonitrile (50 ml) (15 h) gave 2-*methyl*-1H-*benz*[g]*indole*-3-*carbonitrile* (**11d**) (25 mg, 48%), m.p. 251—251.5 °C (Found: C, 81.5; H, 4.85; N, 13.6. $C_{14}H_{10}N_2$ requires C, 81.5; H, 4.9; N, 13.6%); $\nu_{max.}$(Nujol) 3 240, 2 212, 1 221, 801, 739, 690, and 650 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.65 (3 H, s), 7.41—7.70 (4 H, m), 7.98 (1 H, m), 8.27 (1 H, dd, *J* 7, 1 Hz), and 11.80 (1 H, br); *m/z* 206 (M^+, base).

Methyl 1-(1-naphthyl)-1,2,3-triazole-4-carboxylate (**4e**) (55 mg) in acetonitrile (60 ml) (15 h) gave an orange gum (27 mg), shown by n.m.r. spectroscopy to consist of starting triazole (13 mg, 24%) and methyl 1*H*-benz[*g*]indole-3-carboxylate (**11e**) (14 mg, 29%; 38% based on consumed starting triazole).

Ethyl 1-(1-naphthyl)-1,2,3-triazole-5-carboxylate (**5a**) (235 mg) in acetonitrile (180 ml) (15 h) gave (i) ethyl 1*H*-benz[*g*]indole-2-carboxylate (**12a**) (15 mg, 7%; 11% based on consumed starting triazole), m.p. 169—170 °C (lit.,[18] 170 °C), (ii) starting triazole (89 mg, 38%), and (iii) *ethyl* 1H-*benz*[g]*indole*-3-*carboxylate* (**11a**) (24 mg, 13%; 19% based on consumed starting triazole) as a pale yellow solid, m.p. 148—149 °C (Found: C, 75.5; H, 5.2; N, 5.9. $C_{15}H_{13}NO_2$ requires C, 75.6; H, 5.1; N, 5.9%); δ [250 MHz; $(CD_3)_2CO$] 1.39 (3 H, t, *J* 9 Hz), 4.32 (2 H, q, *J* 9 Hz), 7.42—7.68 (3 H, m), 7.93 (1 H, dd, *J* 8, 1 Hz), 8.03 (1 H, d, *J* 3 Hz), 8.25 (1 H, d, *J* 8 Hz), 8.37 (1 H, dd, *J* 8, 1 Hz), and 11.99 (1 H, br); *m/z* 239 (M^+ + 1), 193 (base), 165, and 139.

Methyl 4-methyl-1-(1-naphthyl)-1,2,3-triazole-5-carboxylate (**5b**) (150 mg) in acetonitrile (150 ml) (15 h) gave (i) methyl 3-methyl-1*H*-benz[*g*]indole-2-carboxylate (**12b**) (20 mg, 15%) as an off-white solid, δ [250 MHz; $(CD_3)_2CO$] 2.63 (3 H, s), 3.89 (3 H, s), 7.41—7.60 (3 H, m), 7.70 (1 H, d, *J* 9 Hz), 7.94 (1 H, d, *J* 8 Hz), 8.61 (1 H, d, *J* 8 Hz), and 11.31 (1 H, br); *m/z* 239 (M^+), 207

(base), 179, and 151; transesterification (sodium ethoxide in ethanol) afforded the known ethyl ester, m.p. 174—175 °C (lit.,[18] 176 °C); and (ii) methyl 2-methyl-1*H*-benz[*g*]indole-3-carboxylate (**11b**) (49 mg, 36%).

1-(1-Naphthyl)-1,2,3-triazole-5-carbonitrile (**5c**) (68 mg) in acetonitrile (80 ml) (15 h) gave (i) 1H-*benz*[g]*indole*-2-*carbonitrile* (**12c**) (8 mg, 13%; 14% based on consumed starting triazole), m.p. 164—166 °C (Found: C, 81.4; H, 4.1; N, 14.6. $C_{13}H_8N_2$ requires C, 81.2; H, 4.2; N, 14.6%); $\nu_{max.}$(Nujol) 3 320, 2 218, 823, 820, and 724 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 7.41 (1 H, s), 7.5—7.71 (4 H, m), 7.94 (1 H, dd, *J* 8, 1 Hz), 8.40 (1 H, m), and 12.21 (1 H, br); *m/z* 192 (M^+, base), 165, 140, and 127; (ii) starting triazole (2 mg, 3%); and (iii) 1*H*-benz[*g*]indole-3-carbonitrile (**11c**) (22 mg, 38%; 39% based on consumed starting triazole).

4-Methyl-1-(1-naphthyl)-1,2,3-triazole-5-carbonitrile (**5d**) (70 mg) in acetonitrile (80 ml) (15 h) gave (i) 3-*methyl*-1H-*benz*[g]*indole*-2-*carbonitrile* (**12d**) (16 mg, 26%; 27% based on consumed starting triazole) as a pale yellow solid, m.p. 208—209 °C (Found: C, 81.8; H, 4.9; N, 13.6. $C_{14}H_{10}N_2$ requires C, 81.5; H, 4.9; N, 13.6%); $\nu_{max.}$(Nujol) 3 335, 2 211, 1 398, 1 351, 1 321, 1 235, 811, and 750 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.50 (3 H, s), 7.50—7.70 (4 H, m), 7.95 (1 H, dd, *J* 7, 2 Hz), 8.34 (1 H, dd, *J* 7, 1 Hz), and 10.89 (1 H, br); *m/z* 206 (M^+, base), 178, and 152; (ii) starting triazole (2 mg, 3%); and (iii) 2-methyl-1*H*-benz[*g*]indole-3-carbonitrile (**11d**) (22 mg, 36%; 37% based on consumed starting triazole).

Methyl 1-phenyl-1,2,3-triazole-4-carboxylate (**21a**)[19] (200 mg) in acetonitrile (150 ml) (15 h) gave a pale yellow solid (72 mg), which n.m.r. spectroscopy indicated to consist of starting triazole (46 mg, 23%) and methyl indole-3-carboxylate (**23a**) (26 mg, 20%; 26% based on consumed triazole).

Methyl 5-methyl-1-phenyl-1,2,3-triazole-4-carboxylate (**21b**)[20] (200 mg) in acetonitrile (180 ml) (15 h) gave methyl 2-methylindole-3-carboxylate (**23b**) (96 mg, 55%), m.p. 164—166 °C (lit.,[21] 165 °C).

Methyl 1-phenyl-1,2,3-triazole-5-carboxylate (**22a**)[19] (250 mg) in acetonitrile (180 ml) (15 h) gave (i) methyl indole-2-carboxylate (**24a**) (41 mg, 19%; 25% based on consumed triazole), m.p. 150—152 °C (lit.,[22] 151 °C), (ii) starting triazole (61 mg, 24%), and (iii) methyl indole-3-carboxylate (**23a**) (8 mg, 4%; 5% based on consumed triazole), m.p. 142—144 °C (lit.,[23] 145 °C).

Methyl 4-methyl-1-phenyl-1,2,3-triazole-5-carboxylate (**22b**)[20] (200 mg) in acetonitrile (110 ml) (15 h) gave (i) methyl 3-methylindole-2-carboxylate (**24b**) (37 mg, 21%), m.p. 146—147 °C (lit.,[24] 148 °C), and (ii) methyl 2-methylindole-3-carboxylate (**23b**) (74 mg, 42%), m.p. 162—164 °C (lit.,[21] 165 °C).

Dimethyl 1-(2-methyl-1-naphthyl)-1,2,3-triazole-4,5-dicarboxylate (**7b**) (200 mg) in acetonitrile (170 ml) (10 h) gave *dimethyl* 9-*methyl*-1H-*benzo*[de]*quinoline*-2,3-*dicarboxylate* (**25a**) (64 mg, 35%; 63% based on consumed starting triazole) as a deep red solid, m.p. 139—142 °C (from ether–hexane) (Found: C, 68.4; H, 5.0; N, 4.65. $C_{17}H_{15}NO_4$ requires C, 68.7; H, 5.1; N, 4.7%); $\nu_{max.}$($CHCl_3$) 3 450, 3 419, 1 733, 1 719, 1 635, and 1 575 cm^{-1}; $\nu_{max.}$(Nujol) 3 440, 3 420, 1 735, 1 722, 1 632, and 1 582 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.06 (3 H, s), 3.89 (3 H, s), 3.90 (3 H, s), 6.47 (1 H, dd, *J* 7, 1 Hz), 6.74 (1 H, br), 6.88 (1 H, d, *J* 8 Hz), 7.00 (1 H, d, *J* 8 Hz), 7.03 (1 H, dd, *J* 9, 7 Hz), and 7.17 (1 H, dd, *J* 9, 1 Hz); *m/z* 297 (M^+), 266, 265, 237, and 179 (base).

1-(2-Methyl-1-naphthyl)-1,2,3-triazole-4,5-dicarbonitrile (**7d**) (70 mg) in acetonitrile (80 ml) (12 h) gave (i) an unidentified pale yellow gum (3 mg) and (ii) 9-*methyl*-1H-*benzo*[de]*quinoline*-2,3-*dicarbonitrile* (**25b**) (47 mg, 74%) as a purple solid, m.p. 259—262 °C (decomp.) (Found: C, 77.9; H, 3.9; N, 17.9. $C_{15}H_9N_3$ requires C, 77.9; H, 3.9; N, 18.2%); $\nu_{max.}$(Nujol) 3 300, 2 220, 2 210, 1 635, 1 607, 1 577, 1 490, 1 401, 1 346, 825, 688, and 657 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.10 (3 H, s), 6.69 (1 H, d, *J* 7 Hz), 7.05—7.20 (3 H, m), 7.28 (1 H, d, *J* 8 Hz), and 9.22 (1 H, br); *m/z* 231 (M^+, base), 216, 203, and 176.

1-(2-Methyl-1-naphthyl)-1,2,3-triazole-4-carbonitrile (**8c**) (160 mg) in acetonitrile (180 ml) (15 h) gave (i) unchanged triazole (15 mg, 9%); (ii) 9b-*methyl*-9bH-*benz*[g]*indole*-3-*carbonitrile* (**28**) (35 mg, 25%; 27% based on consumed triazole) as a pale yellow solid, m.p. 148—149.5 °C (from ether–hexane) (Found: C, 81.5; H, 5.1; N, 13.5. $C_{14}H_{10}N_2$ requires C, 81.5; H, 4.9; N, 13.6%); $\nu_{max.}$(Nujol) 2 212, 1 611, 1 600, 1 580, 1 547, 1 511, 1 330, 1 319, 1 015, 995, 950, 930, 911, 896, 840, 815, 753, and 637 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 1.48 (3 H, s), 6.96 (1 H, d, *J* 10 Hz), 7.14 (1 H, d, *J* 10 Hz), 7.27—7.40 (2 H, m), 7.46 (1 H, dd, *J* 7, 2 Hz), 7.78 (1 H, m), and 8.22 (1 H, s); *m/z* 206 (M^+, base), 191, 179, 164, and 151; and (iii) 1*H*-benz[*g*]indole-3-carbonitrile (**11c**) (20 mg, 15%); 17% based on consumed triazole).

In a separate experiment, photolysis of the triazole (**8c**) (75 mg) in acetonitrile (80 ml) (12 h) gave (i) starting triazole (10 mg, 13%); (ii) 9b-methyl-9b*H*-benz[*g*]indole-3-carbonitrile (**28**) (14 mg, 21%; 24% based on consumed triazole); (iii) 1*H*-benz[*g*]indole-3-carbonitrile (**11c**) (1 mg, 2% based on consumed triazole); and (iv) an unidentified yellow solid (17 mg); $\nu_{max.}$(Nujol) 3 300, 2 210, 1 640, 1 618, 1 582, 1 488, 1 403, 1 330, 1 282, 820, and 784 cm^{-1}; δ [250 MHz; $(CD_3)_2CO$] 2.10 (3 H, s), 6.61 (1 H, m), 6.96—7.06 (2 H, m), 7.07—7.15 (2 H, m), and 7.28 (1 H, m); *m/z* 385, 281, 280, 276, 261 (base), 206, 205, 192, 185, 177, 163, 149, 139, and 123.

9b-Methyl-9b*H*-benz[*g*]indole-3-carbonitrile (**28**) (18 mg) in acetonitrile (20 ml) (15 h) gave (i) starting material (5 mg, 28%) and (ii) a mixture (1 mg) shown by n.m.r. spectroscopy to consist predominantly of 1*H*-benz[*g*]indole-3-carbonitrile (**11c**).

5-Methyl-1-(2-methyl-1-naphthyl)-1,2,3-triazole-4-carbonitrile (**8d**) (145 mg) in acetonitrile (150 ml) (15 h) gave (i) starting triazole (44 mg, 30%); (ii) a green gum (6 mg), which n.m.r. spectroscopy indicated to be a complex mixture; and (iii) a pale green gum which solidified on storage at −18 °C (8 mg, 12%; 17% based on consumed triazole), tentatively identified as 2,9-dimethyl-1*H*-benzo[*de*]quinoline-3-carbonitrile (**29**), δ (250 MHz; $CDCl_3$) 2.06 (3 H, s), 2.26 (3 H, s), 6.35 (1 H, br s), 6.77 (1 H, t, *J* 4 Hz), 6.98 (2 H, br s), and 7.13 (2 H, d, *J* 4 Hz).

1-(2-Methyl-1-naphthyl)-1,2,3-triazole-5-carbonitrile (**9c**) (65 mg) in acetonitrile (70 ml) (12 h) gave (i) a mixture (4 mg) which n.m.r. spectroscopy indicated to consist of starting triazole (1 mg) and 9b-methyl-9b*H*-benz[*g*]indole-3-carbonitrile (**28**) (3 mg), and (ii) a mixture (3 mg) which n.m.r. spectroscopy indicated to consist of 1*H*-benz[*g*]indole-3-carbonitrile (**11c**) (1 mg) and an unidentified component (2 mg) identical with that produced on photolysis of triazole (**8c**) described above.

1-(1-Naphthyl)-4,5-bis(trimethylsilyl)-1,2,3-triazole (**2d**) (175 mg) in acetonitrile (180 ml) (10 h), followed by evaporation, left a brown solid; $\nu_{max.}$(Nujol) 1 995 and 1 963 cm^{-1}. A solution of this solid in methanol (3 ml) was treated with dil. hydrochloric acid (0.5M; 3 ml) at room temperature for 16 h. The mixture was then diluted with water (100 ml) and extracted with dichloromethane (6 × 10 ml). The combined extracts were dried ($MgSO_4$) and evaporated to leave a gum, trituration of which with chloroform–ether gave *N*-(1-naphthyl)acetamide (**32**) (52 mg, 54%), m.p. 157.5—159 °C, undepressed on admixture with an authentic sample.

1-(2-Methyl-1-naphthyl)-4,5-bis(trimethylsilyl)-1,2,3-triazole (**6f**) (200 mg) in acetonitrile (180 ml) (10 h), followed by evaporation, left a brown solid; $\nu_{max.}$(Nujol) 1 990 cm^{-1}. Hydrolysis as described above for the product from the triazole (**2d**) gave *N*-(2-methyl-1-naphthyl)acetamide (**33**) (54 mg, 48%), m.p. 185—187 °C, undepressed on admixture with an authentic sample.

Similar irradiation of the following triazoles led only to the

recovery of starting material in the yields shown (**6a**) 75%, (**6b**) 81%, (**6c**) 72%, (**6e**) 16%, (**7a**) 60%, (**7c**) 76%, (**8a**) 43%, (**8b**) 49%, (**8e**) 53%, and (**9a**) 38%. Triazole (**6d**) gave an intractable brown foam.

Acknowledgements

We thank the S.E.R.C. for a fellowship (to G. M.) and Dr. H. S. Rzepa (MNDO Theory) and Dr. D. J. Williams (*X*-ray Crystallography) for their invaluable help.

References

1 G. Mitchell and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, preceding paper.
2 C. R. Watson, R. M. Pagni, J. R. Dodd, and J. E. Bloor, *J. Am. Chem. Soc.*, 1976, **98**, 2551 and references therein.
3 E. M. Burgess, R. Carithers, and L. McCullagh, *J. Am. Chem. Soc.*, 1968, **90**, 1923.
4 K. Tsujimoto, M. Ohashi, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 515.
5 K. Tsujimoto, M. Ohashi, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3605.
6 Preliminary communication, G. Mitchell and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1986, 399.
7 H. Murai, M. Torres, and O. P. Strausz, *J. Am. Chem. Soc.*, 1980, **102**, 1421.
8 H. S. Rzepa, Chemistry Department, Imperial College, unpublished results.
9 M. J. S. Dewar and C. A. Ramsden, *J. Chem. Soc., Chem. Commun.*, 1973, 688.
10 T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1973, 555; 1975, 1.
11 C. Thétaz and C. Wentrup, *J. Am. Chem. Soc.*, 1976, **98**, 1258.
12 C. Wentrup, *Helv. Chim. Acta*, 1972, **55**, 1613.
13 D. J. Anderson, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1973, 550; R. S. Atkinson, J. Fawcett, M. J. Grimshire, and D. J. Russell, *J. Chem. Soc., Chem. Commun.*, 1985, 544.
14 D. J. Williams, Chemistry Department, Imperial College, unpublished results.
15 S. O'Brien and D. C. C. Smith, *J. Chem. Soc.*, 1963, 2907.
16 J. J. Kulagowski, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2725.
17 A. Sekiguchi and W. Ando, *J. Am. Chem. Soc.*, 1984, **106**, 1486 and references therein.
18 G. K. Hughes, F. Lions, J. G. McKean, A. J. Murray, V. Callaman, D. H. Freeman, C. S. Ralph, R. Rassack, J. Dombroski, F. Finch, R. Andrews, R. C. Betty, R. H. Scott, C. W. Vernon, A. Flack, and C. H. Laurence, *Proc. R. Soc. N. S. Wales*, 1938, **71**, 475 (*Chem. Abstr.*, 1939, **33**, 587).
19 R. Huisgen, R. Knorr, L. Möbius, and G. Szeimies, *Chem. Ber.*, 1965, **98**, 4014.
20 P. Battioni, L. Vo-Quang, and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 1978, II, 415.
21 J. Bergman, R. Carlsson, and B. Sjöberg, *J. Heterocycl. Chem.*, 1977, **14**, 1123.
22 I. Baxter and G. A. Swan, *J. Chem. Soc. C*, 1967, 2446.
23 P. E. Peterson, J. P. Wolf, and C. Niemann, *J. Org. Chem.*, 1958, **23**, 303.
24 'Dictionary of Organic Compounds,' 5th. edn., Chapman and Hall, London, Vol. 4, p. 3901.

Received 14*th March* 1986; *Paper* 6/508