Reactive Intermediates. Part XXIII.[1] Pyrolysis of 1-Phthalimido-1,2,3-Triazoles: Formation and Thermal Reactions of 2*H*-Azirines [2]

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Pyrolysis in the vapour phase of 4,5-disubstituted 1-phthalimido-1,2,3-triazoles (1) gives 2*H*-azirines (2) as the primary isolable products. The azirines undergo further thermal reactions under the conditions of the pyrolysis: with a methyl or an ethyl 2-substituent they are cleaved to nitriles and phthalimido-carbenes, but with a phenyl 2-substituent they rearrange to indoles. 4-Methyl-5-phenyl-1-phthalimido-1,2,3-triazole (1c) and 5-methyl-4-phenyl-1-phthalimido-1,2,3-triazole (1d) give identical mixtures of azirines and their pyrolysis products, indicating that the products are formed through a common intermediate, considered to be the antiaromatic 2-methyl-3-phenyl-1-phthalimido-1*H*-azirine.

2*H*-Azirines are the products of oxidation of *N*-aminophthalimide in the presence of alkynes,[1] and the most likely intermediates in the reaction are 1*H*-azirines. In order to investigate the mechanism of the reaction, several alternative routes to 1*H*-azirines have been investigated. The pyrolysis or photolysis of 1-phthalimido-1*H*-1,2,3-triazoles (1) could lead to 1*H*-azirines and hence to 2*H*-azirines by closure of intermediate iminocarbenes formed by loss of nitrogen (Scheme 1). The closure of an iminocarbene to an antiaromatic 1*H*-azirine has recent analogies in the isomerisation of oxocarbenes to oxirens.[3]

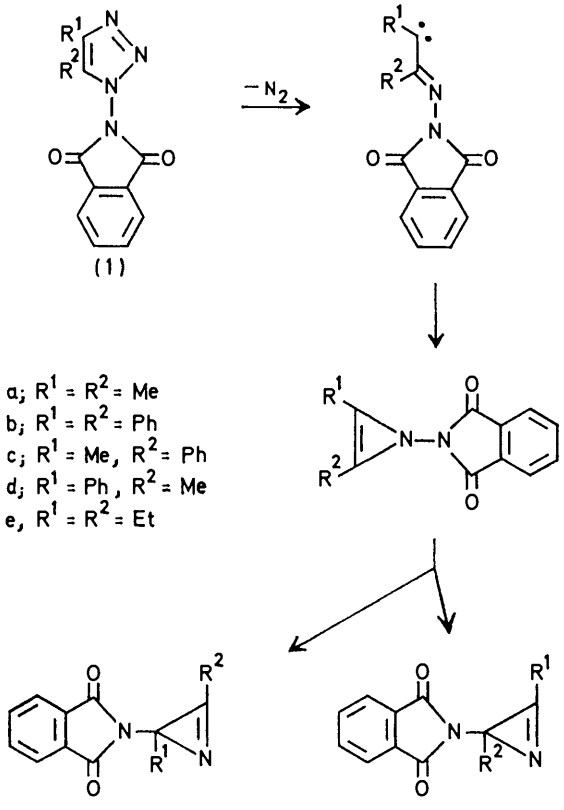
In principle, the method permits the detection of a symmetrical intermediate in the reaction: an isomeric pair of triazoles (1; $R^1 \neq R^2$) should lead to the same 1*H*-azirine and hence to the same mixture of 2*H*-azirines; on the other hand, if the 2*H*-azirines are formed directly from some unsymmetrical intermediate,

[1] Part XXII, D. J. Anderson, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, preceding paper.

[2] Preliminary communications, D. J. Anderson, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *Chem. Comm.*, 1971, 1518; T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *ibid.*, p. 1519.

[3] D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 1768; G. Frater and O. P. Strausz, *ibid.*, p. 6654; J. Ciabattoni, R. A. Campbell, C. A. Renner, and P. W. Concannon, *ibid.*, p. 3826; S. A. Matlin and P. G. Sammes, *J.C.S. Chem. Comm.*, 1972, 11.

the isomeric pair of triazoles would give different products. Accordingly, four triazoles have been synthesised and their pyrolysis investigated: the dimethyltriazole (1a) and the diphenyltriazole (1b), in order to investigate the feasibility of the reaction; and the



SCHEME 1

methylphenyltriazoles (1c) and (1d), in order to determine whether a symmetrical intermediate is involved in the pyrolysis.

Preparation of Triazoles.—1-Phthalimido-1*H*-1,2,3-triazoles have not previously been prepared, but it was found that they can readily be synthesised by condensation of the corresponding 1-aminotriazoles with phthalic anhydride. An improved synthetic procedure for 1-amino-4,5-diphenyl-1,2,3-triazole is reported, involving the cyclisation of benzil bis-(*p*-tolylsulphonylhydrazone) with potassium hydroxide in ethylene glycol. The isomeric 1-amino-4-methyl-5-phenyl-1,2,3-triazole and 1-amino-5-methyl-4-phenyl-1,2,3-triazole were prepared by a similar method, the bis-(*p*-tolylsulphonylhydrazone) of 1-phenylpropane-1,2-dione undergoing cyclisation with potassium hydroxide in ethylene glycol to give a mixture of the two possible 1-*p*-tolylsulphonylamino-1,2,3-triazoles, which were separated by column chromatography and hydrolysed separately. The structures of the isomeric 1-amino-1,2,3-triazoles were assigned on the basis of their n.m.r. spectra: the 5-phenyltriazole shows a singlet for the phenyl protons, presumably because the benzene ring is twisted out of the plane of the triazole ring by steric interaction with the substituents at the 1- and 4-positions, whereas the phenyl protons of the 4-phenyltriazole appear as a multiplet. Similar assignments have been made for other 4- and 5-phenyl-1,2,3-triazoles and have been confirmed by independent synthesis.[4]

Pyrolysis of Triazoles.—Preliminary experiments showed that 4,5-diphenyl-1-phthalimido-1,2,3-triazole was photostable over a range of wavelengths from 230 to 450 nm; this may be because the phthalimido-group acts as the major absorber of energy. No attempts were made to investigate photochemical decomposition of the triazoles further; instead, a pyrolytic method was used, involving vaporisation of the triazoles at low pressure (*ca.* 0·02 mmHg) and passage of the vapour through an empty quartz tube heated to 350—600°. The apparatus is described in Part XX;[5] with it pyrolyses could readily be carried out on a small scale (5—100 mg).

4,5-Dimethyl-1-phthalimido-1,2,3-triazole (1a) was pyrolysed at furnace temperatures between 390 and 550°. At 390°, starting material (80%) was recovered, but in addition, 2,3-dimethyl-2-phthalimido-2*H*-azirine (2a), *N*-vinylphthalimide, and acetonitrile were detected. N.m.r. spectroscopy proved to be a satisfactory method of analysing the crude product mixture; pure specimens of each of the products were then obtained by preparative layer chromatography and compared with authentic specimens. At higher temperatures, the proportion of *N*-vinylphthalimide in the product mixture increased, and phthalimide was also detected: thus, at 470°, the solid pyrolysate consisted of the starting triazole (25%), *N*-vinylphthalimide (55%), 2,3-dimethyl-2-phthalimido-2*H*-azirine (10%), and phthalimide (10%). Above 500° no starting material was recovered, the only products being acetonitrile, *N*-vinylphthalimide, and phthalimide.

It was shown that *N*-vinylphthalimide and acetonitrile can be formed from 2,3-dimethyl-2-phthalimido-2*H*-azirine by pyrolysing an independently prepared specimen of the azirine at 440°: these were the only products detected. Thus a reasonable sequence for the triazole pyrolysis (Scheme 2) is the formation of the azirine (2a) as the primary product, which then undergoes further fragmentation to give acetonitrile and methylphthalimidocarbene, which rearranges to *N*-vinylphthalimide. The phthalimide may be formed by hydrogen transfer from the 5-methyl group of the triazole: a somewhat analogous process has been observed as a thermal reaction of *N*-phthalimidodimethylsulphoximide.[5]

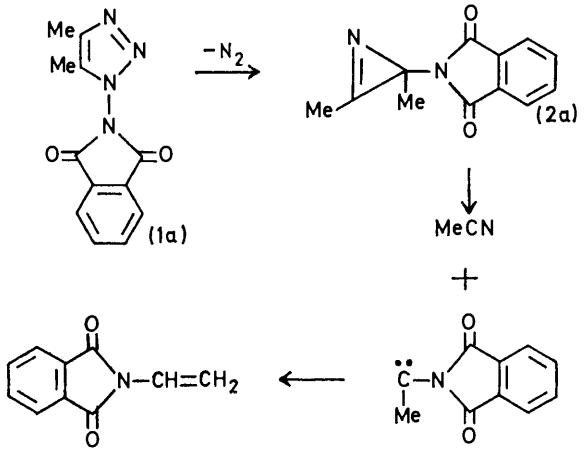
The fragmentation of the dimethylazirine (2a) to give acetonitrile and a carbene has analogies in the useful general method of producing carbenes from diazirines. Carbenes have been tentatively suggested as inter-

[4] G. Garcia-Muñoz, R. Madroñero, M. Rico, and M. C. Saldaña, *J. Heterocyclic Chem.*, 1969, **6**, 921.

[5] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.

mediates in azirine decompositions by other workers,[6] but this is the first indication that the reaction might provide a feasible route to carbenes. Pyrolysis of 2,3-diethyl-2-phthalimido-2*H*-azirine (2e) was found to proceed in the same way, to give propiononitrile and *cis*- and *trans*-*N*-prop-1-enylphthalimide. The fragmentation reaction appears to be limited to azirines which have non-conjugating groups at the 2-position: if either of the 2-substituents is an aryl or an α-carbonyl-containing function, the azirines preferentially undergo ring expansion to indoles or oxazoles on heating.[5,7]

Pyrolysis of 4,5-diphenyl-1-phthalimido-1,2,3-triazole (1b) at temperatures between 350 and 550° gave two products. One was identified as 2,3-diphenyl-2-phthalimido-2*H*-azirine (2b) on the basis of analytical and spectral data; the other as 2-phenyl-3-phthalimidoindole by comparison with an authentic specimen prepared from 3-amino-2-phenylindole and phthalic anhydride. Below 450°, some of the starting triazole was recovered after pyrolysis, and the only product was the azirine (2b). Above 450°, the proportion of indole in the product mixture increased with increasing

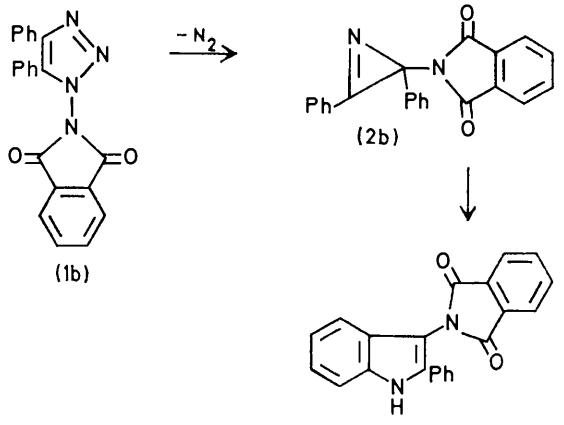


SCHEME 2

temperature, and it was shown by independent pyrolysis of 2,3-diphenyl-2-phthalimido-2*H*-azirine that this rearranged to the indole under these conditions. The course of the reaction can therefore be accounted for by the sequence shown in Scheme 3, where the azirine is the primary isolable product and the indole is derived from it by rearrangement.

Having studied the pyrolysis of the triazoles (1a and b) we were able to anticipate the likely course of decomposition of the unsymmetrically disubstituted triazoles (1c and d), by an appropriate combination of Schemes 2 and 3. These triazoles were investigated next.

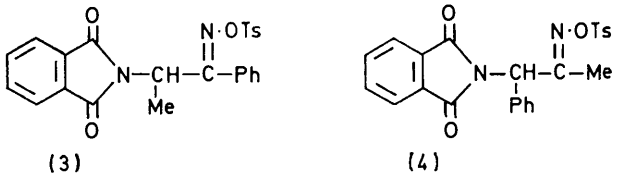
Six products were obtained from the pyrolysis of 4-methyl-5-phenyl-1-phthalimido-1,2,3-triazole (1c) at 400—520°. These were 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine (2c) and 3-methyl-2-phenyl-2-phthalimido-2*H*-azirine (2d), benzonitrile, phthalimide, *N*-vinylphthalimide, and 2-methyl-3-phthalimidoindole. Authentic specimens of the two azirines were prepared



SCHEME 3

by modified Neber reactions in which the oxime toluene-*p*-sulphonates (3) and (4) were heated with potassium t-butoxide in benzene. A specimen of 2-methyl-3-phthalimidoindole was prepared from 3-amino-2-methylindole and phthalic anhydride. As in the pyrolyses described earlier, the proportion of azirines in the product mixture decreased with increasing temperature; at 520°, only benzonitrile, phthalimide, *N*-vinylphthalimide, and 2-methyl-3-phthalimidoindole were detected, the ratio of *N*-vinylphthalimide to the indole being 3 : 2. These products were again shown to be secondary products, derived from the azirines (2c) and (2d), respectively: pyrolysis of 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine (2c) gave benzonitrile and *N*-vinylphthalimide, and 3-methyl-2-phenyl-2-phthalimido-2*H*-azirine (2d) gave 2-methyl-3-phthalimidoindole.

Pyrolysis of 5-methyl-4-phenyl-1-phthalimido-1,2,3-triazole (1d) took a remarkably similar course to that of its isomer. At 520° *N*-vinylphthalimide and 2-methyl-3-phthalimidoindole were formed, the ratio of *N*-vinylphthalimide to indole again being 3 : 2. A common



reaction pathway is clearly implicated. The two triazoles were not interconverted under the conditions of the pyrolyses; in cases where some of the triazole passed through the apparatus unchanged, only the starting isomer could be detected. The azirines are also

[6] W. Bauer and K. Hafner, *Angew. Chem. Internat. Edn.*, 1969, **8**, 772; J. H. Bowie and B. Nussey, *Chem. Comm.*, 1970, 1565.

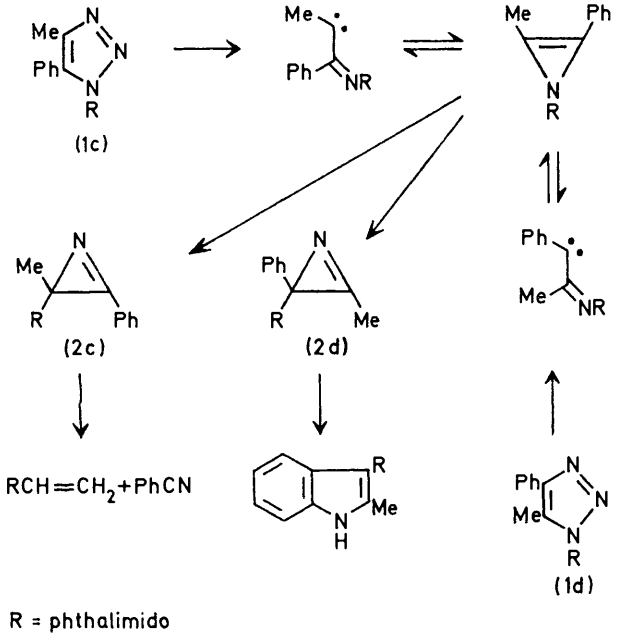
[7] K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Letters*, 1968, 3499; H. Hemetsberger, D. Knittel, and H. Weidmann, *Monatsh.*, 1970, **101**, 161; M. I. Rybinskaya, A. N. Nesmeyanov, and N. K. Kochetkov, *Russ. Chem. Rev.*, 1969, **38**, 433, 449.

apparently not interconverted; they give different products on pyrolysis.

The simplest rationalisation of the observations is that the iminocarbenes generated by expulsion of nitrogen can be interconverted through a 1*H*-azirine intermediate, which can rearrange in two ways to give the azirines (2c) and (2d) and products derived from them (Scheme 4).

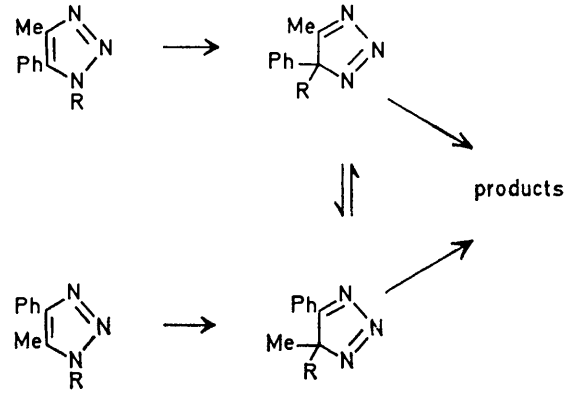
Another mechanism for the formation of common products has been considered, but seems much less likely. This involves a [1,5] sigmatropic shift of the phthalimido-group in the triazoles to give 4*H*-1,2,3-triazoles. If the two possible 4*H*-1,2,3-triazoles were then able to equilibrate before loss of nitrogen, common products would result (Scheme 5). This equilibration does not appear likely, however; the 4*H*-1,2,3-triazoles are no longer aromatic and would lose nitrogen rapidly at high temperatures; they are also valence tautomers of vinyl azides which, although they are known as sources of 2*H*-azirines,[8] do not give mixtures of azirines when they are unsymmetrically substituted.

An unexpected feature of the results is that equilibration appears to be virtually complete, and other potential reactions of iminocarbenes such as 1,2-hydrogen



SCHEME 4

shifts and Wolff rearrangement, are not observed. In contrast, results with oxocarbenes have indicated that only a proportion of the products is formed through oxiren intermediates.[3] Earlier work on the decomposition of triazoles[9] has not provided any evidence that 1*H*-azirines are involved, and this could indicate



SCHEME 5

that the mechanism depends markedly on the nature of the triazole substituents. Such an effect has already been observed in diazo-ketone decompositions:[10] an oxiren intermediate is no longer formed when it would have to be incorporated into a strained cyclic system.

EXPERIMENTAL

Preparation of Triazoles.—*4,5-Dimethyl-1-phthalimido-1,2,3-triazole* (1a). 1-Amino-4,5-dimethyl-1,2,3-triazole[11] (1·14 g) and phthalic anhydride (1·55 g) were dissolved in acetic acid (10 ml) and the solution was heated under reflux for 0·5 h. Evaporation left an oil which solidified on trituration. Crystallisation gave *4,5-dimethyl-1-phthalimido-1,2,3-triazole* (0·95 g, 40%), m.p. 175·5—176·5° (from ethanol) (Found: C, 59·7; H, 4·0; N, 23·2. $C_{12}H_{10}N_4O_2$ requires C, 59·5; H, 4·2; N, 23·2%); $\nu_{max.}$ 1750, 1280, 1255, 880, and 700 cm^{-1}; τ ($CDCl_3$) 7·82 (3H), 7·62 (3H), and 2·02 (4H, m); *m/e* 242 (M^+), 214, 132, 130, 104, 76, and 68; *m** (242 ⟶ 214) 189.

4,5-Diphenyl-1-phthalimido-1,2,3-triazole (1b). (a) *Benzil bis-(p-tolylsulphonylhydrazone).* Benzil (34 g) and toluene-*p*-sulphonohydrazide (62 g) were dissolved in ethanol (1500 ml) containing hydrogen chloride and the solution was heated under reflux for 15 min. The precipitate was filtered off, washed with petroleum, and dried to give benzil bis-(*p*-tolylsulphonylhydrazone) (60 g, 68%), m.p. 175—176° (lit.,[12] 184°). (b) *4,5-Diphenyl-1-p-tolylsulphonylamino-1,2,3-triazole.* Benzil bis-(*p*-tolylsulphonylhydrazone) (74 g) was added rapidly to a stirred solution of potassium hydroxide (9 g) in ethylene glycol (400 ml) at 120°. After 10 min the solution was cooled to 40° and water added slowly, with rapid stirring, until a precipitate began to appear. The mixture was then acidified with 2N-HCl and more water added until the total volume was 1 l. The precipitate was then filtered off, dried, and washed well with petroleum to leave *4,5-diphenyl-1-p-tolylsulphonylamino-1,2,3-triazole* (43 g, 81%), m.p. 232—233° (from

[8] F. W. Fowler, *Adv. Heterocyclic Chem.*, 1972, **13**, 45; G. Smolinsky and C. A. Pryde, in 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, p. 555.

[9] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, 1968, **90**, 1923; R. Huisgen and M. Seidel, *Chem. Ber.*, 1961, **94**, 2509; A. J. Hubert and H. Reimlinger, *ibid.*, 1970, **103**, 3811; R. Selvarajan and J. H. Boyer, *J. Heterocyclic Chem.*, 1972, **9**, 87; H. Meier and I. Menzel, *Annalen*, 1970, **739**, 56; M. Ohashi, K. Tsujimoto, and T. Yonezawa, *Chem. Comm.*, 1970, 1089; C. Wentrup and W. D. Crow, *Tetrahedron*, 1970, **26**, 3965.

[10] Z. Majerski and C. S. Redvanly, *J.C.S. Chem. Comm.*, 1972, 694.

[11] D. Y. Curtin and N. E. Alexandrou, *Tetrahedron*, 1963, **19**, 1697.

[12] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735.

ethanol) (Found: C, 64·5; H, 4·7. $C_{21}H_{18}N_4O_2S$ requires C, 64·6; H, 4·6%). Evaporation of the petroleum washings from the reaction mixture gave diphenylacetylene (5·5 g). (c) 1-*Amino*-4,5-*diphenyl*-1,2,3-*triazole*. 4,5-Diphenyl-1-*p*-tolylsulphonylamino-1,2,3-triazole (23 g) was suspended in water (120 ml) and sulphuric acid (200 ml) was added dropwise to the rapidly stirred suspension. The temperature was then raised to 100° and maintained there until a clear solution was obtained. This was then cooled and poured on ice (600 g), and the precipitate was filtered off, washed with water, and suspended in an excess of aqueous sodium hydroxide. After 10 min the solid was filtered off, washed, and dried to give the crude triazole (14 g, 100%). Crystallisation gave material of m.p. 132—133° (from benzene–petroleum) (lit.,[13] 135°). (d) 1-Amino-4,5-diphenyl-1,2,3-triazole (10·2 g) and phthalic anhydride (10·2 g) in acetic acid (75 ml) were heated under reflux for 0·5 h. On cooling, crystals of 4,5-*diphenyl*-1-*phthalimido*-1,2,3-*triazole* (9·5 g, 60%) were deposited; m.p. 189° (Found: C, 72·15; H, 4·0; N, 14·9. $C_{22}H_{14}N_4O_2$ requires C, 72·1; H, 3·85; N, 15·3%); $\nu_{max.}$ 1810w, 1755s, 1710w, 1275, 1064, 874, 766, 710, and 695 cm^{-1}; *m/e* 366 (M^+), 338, 192 (base), 165, 132, 104, and 79; *m** (192 ⟶ 165) 141·5.

4-*Methyl*-5-*phenyl*-1-*phthalimido*-1,2,3-*triazole* (1c) *and* 5-*methyl*-4-*phenyl*-1-*phthalimido*-1,2,3-*triazole* (1d). (a) 1-*Phenylpropane*-1,2-*dione bis*-(p-*tolylsulphonylhydrazone*). A solution of 1-phenylpropane-1,2-dione (20 g) and toluene-*p*-sulphonohydrazide (50 g) in ethanolic HCl (500 ml) was heated under reflux for 45 min. On cooling, a precipitate appeared which was filtered off, washed, and dried to give the bis-(*p*-tolylsulphonylhydrazone) (44 g, 67%), m.p. 161—162° (lit.,[12] 168°). (b) 4-*Methyl*-5-*phenyl*-1-p-*tolylsulphonylamino*-1,2,3-*triazole and* 5-*methyl*-4-*phenyl*-1-p-*tolylsulphonylamino*-1,2,3-*triazole*. A solution containing 1-phenylpropane-1,2-dione bis-(*p*-tolylsulphonylhydrazone) (40 g) and potassium hydroxide (9 g) in ethylene glycol (400 ml) was heated under reflux for 20 min, cooled, poured into water (1 l), acidified, and extracted with ethyl acetate. The organic extract was dried and evaporated to leave an oil (41 g) which contained ethylene glycol and two products (t.l.c.). The products were separated by column chromatography on silica to give (with ether) substance A (13 g), m.p. 183—184°, and substance B (5 g), m.p. 201—202°. Substance A was identified * as 5-*methyl*-4-*phenyl*-1-p-*tolylsulphonylamino*-1,2,3-*triazole*, m.p. 183—184° (from ethanol) (Found: C, 58·35; H, 4·9; N, 17·2. $C_{16}H_{16}N_4O_2S$ requires C, 58·5; H, 4·9; N, 17·1%); $\nu_{max.}$ 3000br, 1600, 1360, 1260, 1180, 1170, 1090, 810, 770, 700, and 690 cm^{-1}, and substance B as 4-*methyl*-5-*phenyl*-1-p-*tolylsulphonylamino*-1,2,3-*triazole*, m.p. 201—202° (from ethanol) (Found: C, 58·8; H, 5·05; N, 17·2%); $\nu_{max.}$ 3050, 1595, 1370, 1225, 1170, 1080, 1010, 820, 765, 710, and 690 cm^{-1}. (c) 1-*Amino*-4-*methyl*-5-*phenyl*-1,2,3-*triazole*. 4-Methyl-5-phenyl-1-*p*-tolylsulphonylamino-1,2,3-triazole (2·0 g) dissolved in H_2SO_4 (80%; 10 ml) was heated at 80° for 1 h. The solution was cooled, poured on ice, and made basic (KOH). The precipitated potassium sulphate was dissolved by adding water; the aqueous solution was then extracted with ethyl acetate and the extracts dried and evaporated to yield a gum. Trituration gave 1-*amino*-4-*methyl*-5-*phenyl*-1,2,3-*triazole* (0·95 g, 89%), m.p. 69—70° (from benzene) (Found: C, 62·3; H, 5·7; N, 31·9. $C_9H_{10}N_4$ requires C, 62·0; H, 5·8; N, 32·3%); τ ($CDCl_3$) 7·7 (3H), 4·35br (2H, s), and 2·55 (5H, s). (d) 1-*Amino*-5-*methyl*-4-*phenyl*-1,2,3-*triazole*. By a procedure similar to that described in (c), 5-methyl-4-phenyl-1-*p*-tolylsulphonylamino-1,2,3-triazole was converted into 1-*amino*-5-*methyl*-4-*phenyl*-1,2,3-*triazole*, m.p. 143—145° (Found: C, 62·0; H, 5·7; N, 32·4%); τ ($CDCl_3$) 7·5 (3H), 4·9br (2H, s), 2·55 (3H, m), and 2·30 (2H, m). (e) 4-*Methyl*-5-*phenyl*-1-*phthalimido*-1,2,3-*triazole*. 1-Amino-4-methyl-5-phenyl-1,2,3-triazole (0·8 g) and phthalic anhydride (0·8 g) in acetic acid (3 ml) were heated under reflux for 0·5 h. The solution was cooled and gave prisms (1·0 g), m.p. 180—181°. Dilution with water gave a further 0·2 g; total yield 1·2 g (76%). Crystallisation gave 4-*methyl*-5-*phenyl*-1-*phthalimido*-1,2,3-*triazole* (0·60 g), m.p. 180—181° (from ethanol) (Found: C, 66·8; H, 4·15; N, 18·7. $C_{17}H_{12}N_4O_2$ requires C, 67·1; H, 4·0; N, 18·4%); $\nu_{max.}$ 1745, 1380, 1265, 1075, 880, 850, 760, 715, and 695 cm^{-1}; τ (100 MHz; $CDCl_3$) 7·55 (3H), 2·65 (5H), and 2·15 (4H, m); *m/e* 304 (M^+), 277, 276 (base), 275, 261, 247, 160, 135, 132, 131, 130, 129, 104, 103, 77, and 76. (f) 5-*Methyl*-4-*phenyl*-1-*phthalimido*-1,2,3-*triazole*. 1-Amino-5-methyl-4-phenyl-1,2,3-triazole (0·5 g) and phthalic anhydride (0·5 g) were heated in acetic acid (5 ml) under reflux for 20 min. The solution was cooled and two drops of water were added; a dense precipitate appeared. This was washed well with water and dried; yield 0·65 g (75%). Crystallisation gave 5-*methyl*-4-*phenyl*-1-*phthalimido*-1,2,3-*triazole* (0·45 g), m.p. 215—216° (from ethanol) (Found: C, 67·0; H, 4·0; N, 18·3%); $\nu_{max.}$ 1740, 1300, 1280, 1070, 880, 770, 705, and 690 cm^{-1}; τ (100 MHz; $CDCl_3$) 7·60 (3H), 2·60 (3H, m), 2·25 (2H, m), and 2·05 (4H, m); *m/e* 304 (M^+), 277, 276 (base), 179, 147, 135, 132, 131, 130, 129, 105, 104, 103, 77, and 76.

Preparation of Azirines.—2,3-*Dimethyl*-2-*phthalimido*-2H-*azirine* (2a). This was prepared as described earlier [1] by oxidation of *N*-aminophthalimide in the presence of but-2-yne, and had m.p. 78° (lit.,[1] 78°); τ (100 MHz; $CDCl_3$) 8·23 (3H), 7·24 (3H), and 2·22 (4H).

2-*Methyl*-3-*phenyl*-2-*phthalimido*-2H-*azirine* (2c). (i) α-Phthalimidopropiophenone was prepared (74%) from α-bromopropiophenone [14] and *N*-potassiophthalimide in dimethylformamide, and had m.p. 80—83° (from ethanol) (lit.,[15] 87°). (ii) α-Phthalimidopropiophenone was converted into its *oxime* (95%), m.p. 190—195° (from ethanol; further crystallisation did not raise m.p.) (Found: C, 69·3; H, 4·8; N, 9·4. $C_{17}H_{14}N_2O_3$ requires C, 69·4; H, 4·8; N, 9·5%). (iii) The oxime (2·0 g) and toluene-*p*-sulphonyl chloride (1·3 g) were stirred at room temperature in dry dichloromethane (20 ml) containing triethylamine (0·7 g) for 9 h. The solution was washed rapidly with water, dried, and evaporated to leave an oil (3·7 g) which slowly crystallised. Recrystallisation gave α-*phthalimidopropiophenone oxime toluene*-p-*sulphonate* (2·6 g, 85%), m.p. 113—114° (from benzene–petroleum) (Found: C, 64·5; H, 4·4; N, 6·1. $C_{24}H_{20}N_2O_5S$ requires C, 64·3; H, 4·5; N, 6·2%); $\nu_{max.}$ 1785, 1720, 1600, 1380, 1180, 1165, 1080, and 1030 cm^{-1}; τ ($CDCl_3$) 8·4 (3H, d), 7·6 (3H), 4·6 (1H, q), and 2·0—3·05 (13H, m). (iv) The oxime tosylate (5·0 g) was heated under reflux in benzene for 6·5 h, potassium t-butoxide (3·5 g) being added in portions of 0·5 g during this

* Structural assignments were made on the basis of the n.m.r. spectra of the corresponding 1-aminotriazoles formed by hydrolysis.

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[14] A. V. Dombrovskii, M. I. Shebchuk, and V. P. Kravets, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 2246.

[15] H. K. Müller and G. Rieck, *J. prakt. Chem.*, 1959, **9**, 30.

period. The reaction was followed by t.l.c. The n.m.r. spectrum of the product showed it to contain the azirine (40—50%) and starting material. The reaction mixture was filtered through Celite and evaporated to give a gum (2·25 g), which deposited a solid when triturated with ether. This was the oxime tosylate (i.r.). The solid was filtered off and washed with ether. The filtrate was applied to two plates coated with silica (each 100 × 20 × 0·1 cm). Elution with ether–petroleum (2 : 1) gave 2-*methyl*-3-*phenyl*-2-*phthalimido*-2H-*azirine* (0·30 g, 10%), m.p. 139—140° (from ether–petroleum) (Found: C, 73·4; H, 4·4; N, 10·5. $C_{17}H_{12}N_2O_2$ requires C, 73·9; H, 4·4; N, 10·1%); $\nu_{max.}$ 1795, 1725, 1600, 1380, 1340, 1190, 1105, 880, 760, and 710 cm^{-1}; τ ($CDCl_3$; 100 MHz) 8·15 (3H), 2·3 (7H, m), and 1·8 (2H, m); *m/e* 276 (M^+), 173, 132, 104 (base), and 76; *m** (276 ⟶ 173) 168·5.

3-*Methyl*-2-*phenyl*-2-*phthalimido*-2H-*azirine* (2d). (i) 1-*Phenyl*-1-*phthalimidopropan*-2-*one*. 1-Bromo-1-phenylpropan-2-one [16] (38 g) and *N*-potassiophthalimide (38 g) in dimethylformamide (150 ml) were heated and stirred at 100° for 2 h. The mixture was poured into water and extracted with ethyl acetate to give, after drying and evaporation of the solvent, a yellow oil (35 g) which solidified on trituration with ether. Crystallisation gave 1-*phenyl*-1-*phthalimidopropan*-2-*one* (23·5 g, 47%), m.p. 104° (from ether) (Found: C, 73·3; H, 4·7; N, 5·05. $C_{17}H_{13}NO_3$ requires C, 73·1; H, 4·7; N, 5·0%); $\nu_{max.}$ 1755 and 1705 cm^{-1}. (ii) 1-Phenyl-1-phthalimidopropan-2-one (20 g) and hydroxylamine hydrochloride (6 g) in ethanol (75 ml) and pyridine (75 ml) were heated under reflux for 6 h to give the *oxime* (15 g, 70%), m.p. 217—219° (from ethanol) (Found: C, 68·9; H, 4·65; N, 9·4. $C_{17}H_{14}N_2O_3$ requires C, 69·4; H, 4·8; N, 9·5%); $\nu_{max.}$ 3200 and 1710 cm^{-1}. (iii) A solution of the oxime (6·8 g), toluene-*p*-sulphonyl chloride (4·85 g), and triethylamine (2·45 g) in dry dichloromethane (100 ml) was stirred at 20° for 12 h. The pale yellow solution was washed rapidly with water and immediately dried with magnesium sulphate (in contrast to the other oxime tosylates prepared, this derivative appeared to be readily hydrolysed by water). The solution was evaporated to give an oil which crystallised when triturated with petroleum to give a pale cream solid (7·7 g), m.p. 79—82°. Two crystallisations gave needles of the *oxime toluene-p-sulphonate*, m.p. 80—82° (from benzene–petroleum) (Found: C, 67·3; H, 4·9%). N.m.r. spectroscopy showed that these crystals contained 0·75 mol. equiv. of benzene, which was not removed by drying at 60° ($C_{24}H_{20}N_2O_5S$,0·75C_6H_6 requires C, 67·5; H, 4·8%); $\nu_{max.}$ 1760, 1700, 1600, 1380, 1195, 1175, and 1115 cm^{-1}; τ ($CDCl_3$) 8·04 (3H), 7·68 (3H), 4·00 (1H), 2·7 (9H), 3·05—2·35 (4H, m), and 2·28 (4H). A further recrystallisation from cyclohexane gave a low recovery of a benzene-free solid, m.p. 101—103°. (iv) The oxime toluene-*p*-sulphonate (4·0 g) was suspended in dry benzene (100 ml) and the mixture stirred rapidly at 80°. Potassium t-butoxide (1·0 g) was added in one portion. A further portion (0·5 g) was added after the mixture had been heated at 80° for 3 h; heating was continued for a further 1 h. The mixture was cooled and filtered and the filtrate evaporated to give an oil (3·2 g). Preparative layer chromatography (silica; ether–petroleum, 2 : 1) followed by two crystallisations gave needles of 3-*methyl*-2-*phenyl*-2-*phthalimido*-2H-*azirine* (0·075 g), m.p. 119—120° (from ether–petroleum) (Found: C, 73·4; H, 4·5; N, 10·3. $C_{17}H_{12}N_2O$ requires C, 73·9; H, 4·4; N, 10·1%); $\nu_{max.}$ 1785, 1725, 1120, 875, 760, 710, and 700 cm^{-1}; τ ($CDCl_3$) 7·30 (3H), 2·9 (2H, m), 2·8 (3H, m), and 2·2 (4H, m); *m/e* 276 ($C_{17}H_{12}N_2O$ requires *M*, 276), 260, 247, 235, 135, 133, 132, 130, 129, 105, 104, 77, and 76 (base).

Preparation of Indoles.—2-*Methyl*-3-*phthalimidoindole*. (a) 3-*Amino*-2-*methylindole hydrochloride*. A modification of a published procedure [17] was used. To a solution of benzenediazonium chloride [from aniline (0·8 g)] in HCl (4 ml) at 0° was added saturated aqueous sodium acetate (3·5 g) followed by a cooled solution of 2-methylindole (1·0 g) in ethanol (15 ml). The mixture was stirred for 2 min and poured into water (100 ml), and the aqueous mixture was extracted with ether. The ethereal extracts on evaporation gave 2-methyl-3-phenylazoindole (1·7 g), m.p. 115—116° (from petroleum) (lit.,[17] 115—116°). The azo-compound (0·5 g) was dissolved in ethanol (6 ml) and the solution warmed on a water-bath with granulated tin (1·0 g) as conc. HCl was added at such a rate as to maintain brisk effervescence. After 0·5 h, the solution was colourless and gave no precipitate when diluted with water. The residual tin was filtered off and the filtrate evaporated. Tin salts were removed from the residue by washing with dil. HCl; the remaining crystals were dried (0·4 g). The free amine could be liberated as fine colourless needles but these rapidly turned mauve in air. (b) 2-*Methyl*-3-*phthalimidoindole*. The crude amine hydrochloride (0·38 g) and phthalic anhydride (0·45 g) were heated in acetic acid (5 ml) under reflux for 0·5 h. The solution was gradually diluted with water until a yellow precipitate appeared. This was filtered off, dried (0·29 g), and purified by column chromatography (silica; ether–petroleum 1 : 1) which gave 2-*methyl*-3-*phthalimidoindole* (0·12 g, 21%) as yellow prisms, m.p. 225—226° (from ether–ethyl acetate) (Found: C, 74·0; H, 4·4; N, 10·3. $C_{17}H_{12}N_2O_6$ requires C, 73·9; H, 4·4; N, 10·2%); $\nu_{max.}$ 3360, 1770, and 1715 cm^{-1}; τ ($CDCl_3$) 7·80 (3H), 2·8 (3H, m), 2·15 (4H, m), and 1·6br (1H, s).

2-*Phenyl*-3-*phthalimidoindole*. (*a*) By use of a procedure analogous to that described for 3-amino-2-methylindole hydrochloride, 3-phenylazo-2-phenylindole was prepared [m.p. 167—168° (lit.,[18] 166°)] from 2-phenylindole; the azo-compound (0·75 g) was then cleaved to give 3-amino-2-phenylindole hydrochloride (0·64 g) as cream-coloured, air-sensitive needles. (*b*) 3-Amino-2-phenylindole hydrochloride (0·25 g) and phthalic anhydride (0·15 g) were heated in acetic acid (10 ml) under reflux for 40 min. The yellow solution was poured into water and the aqueous mixture extracted with ether. The ethereal extracts gave an oil which was purified by column chromatography (silica). Ether–petroleum 1 : 2 eluted 2-*phenyl*-3-*phthalimidoindole* (0·24 g, 70%), m.p. 209—211° (from ether–ethyl acetate) (Found: C, 77·9; H, 4·2; N, 8·2. $C_{22}H_{14}N_2O_2$ requires C, 78·1; H, 4·2; N, 8·3%); $\nu_{max.}$ 3460, 1790, and 1725 cm^{-1}; τ ($CDCl_3$) 2·7—2·1 (13H, m) and 1·2br (1H, s); *m/e* 339, 338 (M^+, base), 293, 169, 104, 77, and 76; *m** (338 ⟶ 293) 255.

N-*Vinylphthalimide*.— *N*-(2-Acetoxyethyl)phthalimide [19] (0·200 g) was pyrolysed at 800° and 0·02 mmHg to give *N*-vinylphthalimide (0·125 g, 85%), m.p. 85—86° (lit.,[19]

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[17] P. Wagner, *Annalen*, 1887, **242**, 384.
[18] J. Schmitt, M. Langlois, C. Perrin, and G. Callet, *Bull. Soc. chim. France*, 1969, 2004.
[19] A. F. Nikolaev and S. N. Ushakov, *Izvest. Akad. Nauk S.S.S.R., Odtel. khim. Nauk*, 1957, 1235 (*Chem. Abs.*, 1958, **52**, 6283a).

83°); τ ($CDCl_3$) 4·98 (1H, d, *J* 10 Hz), 3·94 (1H, d, *J* 16 Hz), 3·12 (1H, dd, *J* 16 and 10 Hz), and 2·2 (4H, m).

Vapour Phase Pyrolyses.—For a description of the apparatus used, see ref. 5.

4,5-*Dimethyl*-1-*phthalimido*-1,2,3-*triazole* (1a). Pyrolysis of the triazole (100 mg) was carried out on several batches at temperatures between 390 and 550° at 0·02 mmHg, giving a colourless solid (80—90 mg) on the water-cooled condenser. Acetonitrile was isolated from a trap cooled in liquid nitrogen and estimated by i.r. spectroscopy (in $CHCl_3$). ^1H N.m.r. spectra (100 MHz) of the solid pyrolysate showed signals at τ 8·28 and 7·32 (azirine ring methyls), 7·83 and 7·63 (triazole ring methyls), 5·00, 3·96, and 3·15 (vinylic H of *N*-vinylphthalimide), and 2·0—2·2 (aromatic H). Product ratios were determined from the integrals of these signals. The crude product mixture was triturated with petroleum (b.p. 60—80°) to give a colourless solid. For pyrolyses conducted at or below 450°, the solid was identified as starting triazole (5% at 450°; 80% at 390°). Above 500°, it was phthalimide (i.r., t.l.c.). The petroleum-soluble fraction was then applied to a chromatography plate (silica; 20 × 20 × 0·1 cm). Ether–petroleum (2 : 1) eluted two bands. The material at R_F 0·85 was identified as *N*-vinylphthalimide, m.p. 86° (from petroleum), mixed m.p. with an authentic specimen 85—86° (i.r., n.m.r.). A band at R_F 0·45 was 2,3-dimethyl-2*H*-azirine, m.p. 78° (i.r., n.m.r., and mass spectra).

4,5-*Diphenyl*-1-*phthalimido*-1,2,3-*triazole* (1b). The triazole (50—100 mg batches) was sublimed at 200° and 0·02 mmHg, and the vapour passed through a tube at 350—550°. Below 450°, one major product was observed, and was purified directly by crystallisation to give 2,3-*diphenyl*-2-*phthalimido*-2H-*azirine* (1b) (80%), m.p. 180° (from ethanol) (Found: C, 77·9; H, 4·3; N, 8·4. $C_{22}H_{14}N_2O_2$ requires C, 78·1; H, 4·2; N, 8·3%); $\nu_{max.}$ 1790w, 1720s, 1145, 1110, 885, 776, 769, 710, and 697 cm^{-1}; *m/e* 338 (M^+), 322, 235, 192, 190, 165, 132, 104, and 76. Above 450°, a second major product was formed, and this was the only product at 550°. Crystallisation gave 2-phenyl-3-phthalimidoindole, m.p. 208—211° (from ether), mixed m.p. 208—211° (i.r., n.m.r.).

4-*Methyl*-5-*phenyl*-1-*phthalimido*-1,2,3-*triazole* (1c). The triazole (30—100 mg) was pyrolysed at furace temperatures between 400 and 520°, and at 0·02 mmHg. At 400°, the triazole was unchanged. At 450° the pyrolysate contained the triazole (50%) together with 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine (30%) and 3-methyl-2-phenyl-2-phthalimido-2*H*-azirine (20%) (n.m.r.). At 510° the product mixture contained 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine, *N*-vinylphthalimide, and 2-methyl-3-phthalimidoindole in the ratio 6 : 5 : 9, as well as phthalimide and benzonitrile. At 520°, *N*-vinylphthalimide and 2-methyl-3-phthalimidoindole (3 : 2) were detected, together with phthalimide and benzonitrile. Preparative layer chromatography (silica; ether–petroleum, 3 : 2) of the pyrolysates gave specimens of 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine, *N*-vinylphthalimide, and 2-methyl-3-phthalimidoindole, identical (i.r., m.p. and mixed m.p.) with authentic specimens. A specimen of 3-methyl-2-phenyl-2-phthalimido-2*H*-azirine was obtained as an oil, contaminated (i.r., t.l.c.) with the 2-methyl-3-phenyl isomer, from which it could not be separated.

5-*Methyl*-4-*phenyl*-1-*phthalimido*-1,2,3-*triazole* (1d). The triazole (50 mg) was pyrolysed at a furnace temperature of 400° and at 0·02 mmHg to give 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine (35%), 3-methyl-2-phenyl-2-phthalimido-2*H*-azirine (15%), *N*-vinylphthalimide (20%), and 2-methyl-3-phthalimidoindole (30%) (n.m.r.). At 520° the products were *N*-vinylphthalimide (60%) and 2-methyl-3-phthalimidoindole (40%); benzonitrile was detected in the cold trap. Preparative layer chromatography gave specimens of the azirine (2c), *N*-vinylphthalimide, and 2-methyl-3-phthalimidoindole, identical (i.r., m.p. and mixed m.p.) with authentic specimens.

2,3-*Dimethyl*-2-*phthalimido*-2H-*azirine* (2a). The azirine was pyrolysed at 440° (furnace) and 0·02 mmHg to give *N*-vinylphthalimide, m.p. and mixed m.p. 84—86°.

2,3-*Diphenyl*-2-*phthalimido*-2H-*azirine* (2b). At 600° (furnace) and 0·03 mmHg the azirine gave 2-phenyl-3-phthalimidoindole (i.r., t.l.c.).

2-*Methyl*-3-*phenyl*-2-*phthalimido*-2H-*azirine* (2c). By use of a water-cooled condenser and a liquid nitrogen-cooled trap, the azirine was pyrolysed at 500° (furnace) and 0·05 mmHg. Some decomposition occurred when the azirine was heated, and not all of the specimen sublimed through the furnace. The pyrolysate on the water-cooled condenser consisted of colourless prisms of *N*-vinylphthalimide, m.p. 83—85°, mixed m.p. 84—86°. Benzonitrile was detected (i.r., t.l.c.) in the cold trap.

3-*Methyl*-2-*phenyl*-2-*phthalimido*-2H-*azirine* (2d). The azirine was heated at 110° and 0·01 mmHg, and the vapour passed through the furnace at 460°. Extensive decomposition of the azirine was observed, and this gave involatile products. The portion which vaporised gave a pyrolysate consisting of 2-methyl-3-phthalimidoindole (i.r., t.l.c.); no *N*-vinylphthalimide was detected.

2,3-*Diethyl*-2-*phthalimido*-2H-*azirine* (2e). The azirine (200 mg) was pyrolysed at 480° (furnace) and 0·02 mmHg. The pyrolysate (135 mg) contained two components. Preparative layer chromatography (silica; ether–petroleum 3 : 7) gave *trans*-*N*-propenylphthalimide (65 mg), m.p. 152—153° (from ether–petroleum) (lit.,[20] 151°) (Found: C, 70·4; H, 4·9; N, 7·5%; *m/e* 187. Calc. for $C_{11}H_9NO_2$: C, 70·6; H, 4·9; N, 7·5%; *M*, 187); τ (100 MHz; $CDCl_3$) 8·09 (3H, d, *J* 5 Hz), 3·4—3·5 (2H, m), and 2·1—2·4 (4H, m). The second component was *cis*-*N*-propenylphthalimide (6 mg), m.p. 84—86° (from ether–petroleum), *m/e* 187 (mass spectrum identical with that of the *trans*-isomer); τ (100 MHz; $CDCl_3$) 8·30 (3H, dd, *J* 8 and 1 Hz), 4·12 (1H, dq, *J* 7 and 8 Hz), 3·90 (1H, dq, *J* 7 and 1 Hz), and 2·1—2·4 (4H, m).

We thank the S.R.C. for a Research Studentship (to G. E. G.), and Dr. D. J. Anderson for preliminary experiments on the preparation and pyrolysis of 4,5-diphenyl-1-phthalimido-1,2,3-triazole.

[2/2167 *Received*, 18*th September*, 1972]

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