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Organic and Bio-organic Chemistry

Reactive Intermediates. Part XXIV.[1] 1*H*-Azirine Intermediates in the Pyrolysis of 1*H*-1,2,3-Triazoles [2]

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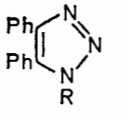
Nitrogen has been extruded from several 1,2,3-triazoles by flash vacuum pyrolysis and the fate of the resulting iminocarbenes has been determined. 1-Alkyl-4,5-diphenyl-1,2,3-triazoles (1) gave nitriles (Scheme 1) and isoquinolines and hydroxyisoquinolines (Scheme 2), the former by Wolff rearrangement and the latter by 1,4-hydrogen transfer in the iminocarbene. 1,4-Dimethyl-5-phenyl-1,2,3-triazole (3) and 1,5-dimethyl-4-phenyl-1,2,3-triazole (4) both gave 3-methylisoquinoline; a mechanism involving a common, 1*H*-azirine intermediate is proposed (Scheme 4). From both 4- and 5-phenyl-1-(1-phenylvinyl)-1,2,3-triazole [(5a) and (6a)] mixtures of 2,4- and 2,5-diphenylpyrrole were isolated; similarly the corresponding 1-phenyltriazoles gave mixtures of 2- and 3-phenylindole (Scheme 5). 4,5-Diphenyl-*v*-triazole also gave 2-phenylindole. The formation of these products is rationalised in terms of 1*H*-azirine intermediates in the pyrolyses.

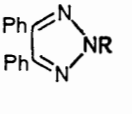
THE status of the unsaturated three-membered heterocyclic systems oxiren, thiiren, and 1*H*-azirine as viable reaction intermediates has recently been the subject of considerable experimental and theoretical work. These compounds can formally be classed as antiaromatic, since they contain four π-electrons in a cyclic system. No derivative of these heterocyclic systems has so far been isolated or detected directly, although there is now considerable evidence that oxirens are intermediates in both photochemical and thermal decompositions of diazo-ketones.[3]

In an earlier paper we produced evidence for the intermediacy of 1*H*-azirines in the thermal decomposition of 1-phthalimido-1,2,3-triazoles.[1] We now describe the results of a much more general study of the vacuum pyrolysis of 1,2,3-triazoles, which was principally designed to discover whether 1*H*-azirines are involved as intermediates in all cases, or whether the mechanism is a special feature of the chemistry of 1-phthalimidotriazoles and related compounds. One problem which arose at the outset was that, unlike diazo-ketones, very little work has been done on the thermal or photochemical decomposition of 1,2,3-triazoles. In many cases it was necessary to make a preliminary study of the products formed from model systems in order to discern the major reaction pathways. 1-Alkyl-1,2,3-triazoles have been investigated most thoroughly, and representative 1-vinyl- and 1-phenyl-1,2,3-triazoles have also been prepared and pyrolysed.

1-Alkyl-1,2,3-triazoles.—No compounds of this type have previously been pyrolysed or photolysed. A series of 1-alkyl-4,5-diphenyl-1,2,3-triazoles (1) was prepared, either by alkylation of 4,5-diphenyl-*v*-triazole [compounds (1a—c)] or by cycloaddition of the alkyl azide to diphenylacetylene [compounds (1a and d)]. Although alkylation gave mixtures of the 1- and the 2-alkyltriazoles (2), it was possible to obtain the 1-alkyl derivatives in



(1) a; R = Me
b; R = Et
c; R = Pr^i
d; R = CH_2Ph



(2) a; R = Me
b; R = Et
c; R = Pr^i

fair yields by the reaction of the silver or thallium salt of 4,5-diphenyltriazole with the appropriate iodoalkane. The 1-alkyltriazoles all show an ion ($M^+ - 28$) in the mass spectrum corresponding to the loss of nitrogen from

[1] Part XXIII, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1973, 555.

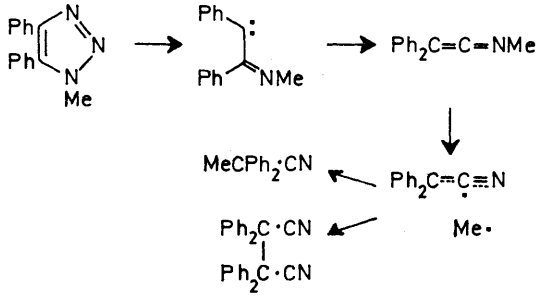
[2] Preliminary communication, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Chem. Comm.*, 1973, 835.

[3] J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1973, **95**, 124; P. W. Concannon and J. Ciabattoni, *ibid.*, p. 3284; S. A. Matlin and P. G. Sammes, *J.C.S. Perkin I*, 1972, 2623; Y. Ogata, Y. Sawaki, and H. Inoue, *J. Org. Chem.*, 1973, **38**, 1044.

the parent ion, but this is absent from the spectra of the 2-alkyltriazoles.

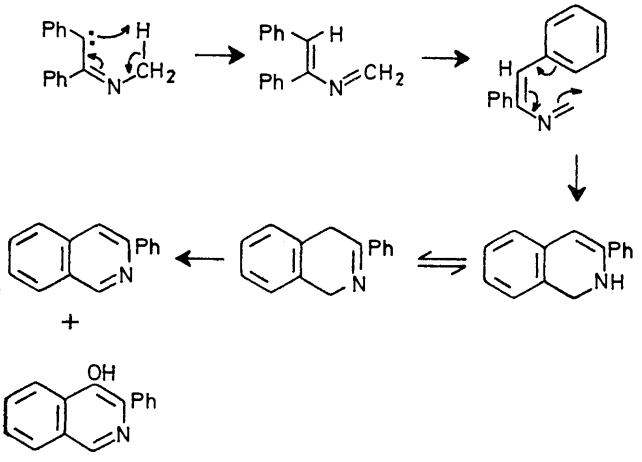
Four products were isolated, in good overall yield, from the pyrolysis of 1-methyl-4,5-diphenyltriazole. The major product (50—60% based on the triazole) was identified as 2,2-diphenylpropiononitrile by comparison with an authentic specimen. Two minor products were identified as 3-phenylisoquinoline (19%) and 4-hydroxy-3-phenylisoquinoline (12%); in each case the material isolated was compared with a specimen prepared by a standard route. Tetraphenylsuccinonitrile (5%) was detected as a fourth product.

The formation of 2,2-diphenylpropiononitrile can be explained by the sequence shown in Scheme 1. A singlet iminocarbene, generated by thermal extrusion of nitrogen from the triazole, may undergo Wolff rearrangement to *N*-methyldiphenylvinylideneamine; this in turn can give diphenylpropiononitrile by methyl migration. It was found that an independently prepared [4] specimen of *N*-methyldiphenylvinylideneamine, when pyrolysed under the same conditions, gave 2,2-diphenylpropiononitrile as the major product. The other product detected in the pyrolysis of the vinylideneamine was tetraphenylsuccinonitrile, which is the dimer of the stabilised cyano(diphenyl)methyl radical; this is strong evidence that the rearrangement of the vinylideneamine involves a radical mechanism. Similar rearrangements of vinylideneamines have been described previously.[5]



SCHEME 1

Wolff rearrangement is also the major reaction of the corresponding singlet oxocarbene, so products formed by this route were to be expected. On the other hand, the formation of isoquinolines involves participation of the *N*-methyl group, the methyl carbon atom being incorporated into the isoquinoline skeleton. The products are most simply explained by invoking a 1,4-hydrogen transfer from the methyl group of the intermediate iminocarbene, followed by *cis–trans* isomerisation and electrocyclic ring closure to give a dihydroisoquinoline (Scheme 2). Such a compound could readily aromatise to 3-phenylisoquinoline. The formation of 4-hydroxy-3-phenylisoquinoline may result from autoxidation of the dihydroisoquinoline at the 4-position, followed by dehydration; a similar hydroxylation of a dihydropyridine derivative has been observed.[6] Attempts to prevent the formation of 4-hydroxy-3-phenylisoquinoline by excluding oxygen during work-up were unsuccessful, and it seems that the autoxidation must occur extremely readily.



SCHEME 2

The key feature of the mechanism outlined in Scheme 2 is the 1,4-hydrogen transfer. Such reactions of carbenes are rare. Hydrogen transfers which are formally analogous have been observed in reactions of vinylcarbenes; [7] mechanisms involving intramolecular abstraction by the triplet carbene (or 1,3-diradical) are usually preferred. Similar hydrogen transfers have been proposed to account for products of photolysis of 1-aminobenzotriazole [8a] and of 1-benzylbenzotriazole,[8b] radical mechanisms again being assumed. Such hydrogen transfers could also be envisaged in singlet carbene or 1,3-dipolar structures.

The proposed 1,4-hydrogen transfer was investigated by studying the deuterium distribution in 3-phenylisoquinoline isolated from the pyrolysis of 1-[$^2H_3$]methyl-4,5-diphenyl-1,2,3-triazole. If the mechanism depicted in Scheme 2 is operative, deuterium should be found at C-1 and -4. C-1 should be fully deuteriated but C-4 may not be since it is likely that this deuterium would be scrambled by interconversion of the dihydroisoquinolines shown in the Scheme. This was borne out by experiment; the 3-phenylisoquinoline obtained from this pyrolysis was fully deuteriated at C-1, according to the n.m.r. spectrum, but the mass spectrum indicated that only about one third of the molecules in the specimen contained two deuterium atoms.

Support for the mechanisms proposed in Schemes 1

[4] C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, 1954, **76**, 4398.

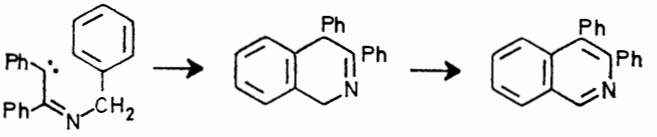
[5] G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *J. Amer. Chem. Soc.*, 1959, **81**, 4878; H. D. Waits and G. S. Hammond, *ibid.*, 1964, **86**, 1911; L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1964, 1887; L. deVries, *J. Org. Chem.*, 1973, **38**, 4357.

[6] J. J. Artus, J.-J. Bonet, and A. E. Pena, *J.C.S. Chem. Comm.*, 1973, 579.

[7] G. L. Closs, L. E. Closs, and W. A. Böll, *J. Amer. Chem. Soc.*, 1963, **85**, 3796; R. Srinivasan, *ibid.*, 1969, **91**, 6250; J. A. Pinock, R. Morchat, and D. R. Arnold, *ibid.*, 1973, **95**, 7536; L. A. Wendling and R. G. Bergman, *ibid.*, 1974, **96**, 308; R. D. Streeper and P. D. Gardner, *Tetrahedron Letters*, 1973, 767.

[8] (*a*) E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, 1968, **90**, 1923; (*b*) M. P. Serve and H. M. Rosenberg, Abstracts 164th National Meeting Amer. Chem. Soc., 1972, Orgn. 5.

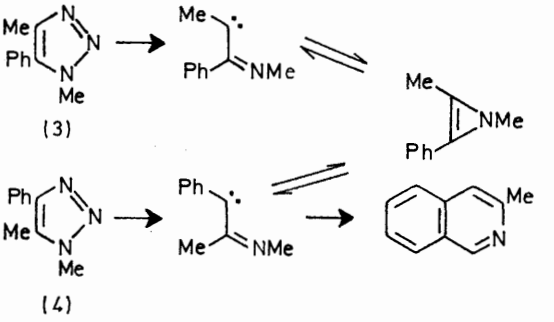
and 2 came from the pyrolysis of the triazoles (1b—d). 1-Ethyl-4,5-diphenyl-1,2,3-triazole (1b) gave the products expected on this basis, namely 2,2-diphenylbutyronitrile and tetraphenylsuccinonitrile (*cf.* Scheme 1) and 1-methyl-3-phenylisoquinoline and 4-hydroxy-1-methyl-3-phenylisoquinoline (*cf.* Scheme 2). From 1-isopropyl-4,5-diphenyl-1,2,3-triazole (1c) deoxybenzoin was isolated; in this case, the intermediate formed by the type of hydrogen transfer shown in Scheme 2 cannot so readily cyclise and aromatise, and may survive, to be hydrolysed to deoxybenzoin during the isolation procedure. Deoxybenzoin was also isolated from the pyrolysis of 1-benzyl-4,5-diphenyl-1,2,3-triazole (1d); in this pyrolysis the major products were bibenzyl and tetraphenylsuccinonitrile, probably formed by radical cleavage of *N*-benzyldiphenylvinylideneamine (*cf.* Scheme 1). Two isoquinolines were also isolated in low yield. One, which could not be fully characterised, had a molecular weight and spectra as expected for 4-hydroxy-1,3-diphenylisoquinoline, which is a product to be predicted by analogy with the mechanism of Scheme 2. The other was 3,4-diphenylisoquinoline; this is probably formed by a variant of the mechanism of Scheme 2, in which the intermediate iminocarbene undergoes direct cyclisation rather than hydrogen transfer. This is depicted in Scheme 3. A similar type of reaction has been observed in the photolysis of 1-benzylbenzotriazole.[8b]



SCHEME 3

The two major reactions of 1-alkyl-4,5-diphenyltriazoles thus involve Wolff rearrangement and cyclisation to isoquinolines. The second of these was used as the basis of a test for the intermediacy of 1*H*-azirines in the reactions. From the isomeric 1,4-dimethyl-5-phenyl- (3) and 1,5-dimethyl-4-phenyl-1,2,3-triazole (4), common products might be expected if the intermediate carbenes can undergo interconversion through a 1*H*-azirine (Scheme 4); in particular, 3-methylisoquinoline might be expected from the pyrolysis of both triazoles although it can be formed directly from only one of the two carbenes.

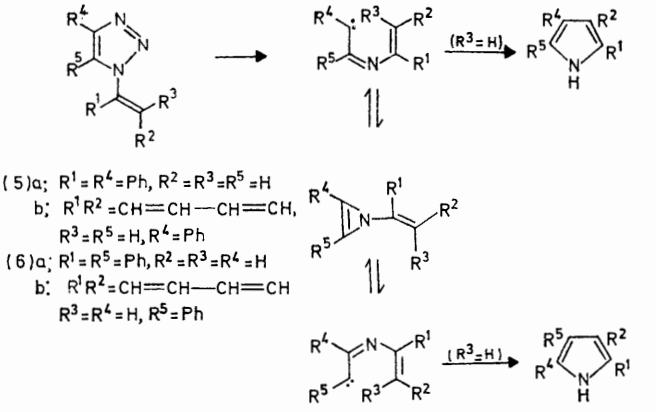
The triazoles were prepared by the methylation of the silver salt of 4-methyl-5-phenyl-*v*-triazole with iodomethane; the structures were assigned unambiguously by a second synthesis of the triazole (4) from azidomethane, phenylpropanone, and potassium t-butoxide. Two products were isolated from the pyrolysis of 1,4-dimethyl-5-phenyltriazole (3). One was 3-methylisoquinoline, obtained in 8% yield and identified by comparison with an authentic specimen. The other was tentatively identified as 2-methyl-2-phenylpropionitrile, the product expected from Wolff rearrangement. From the pyrolysis of 1,5-dimethyl-4-phenyl-1,2,3-triazole (4), 3-methylisoquinoline, and 4-hydroxy-3-methylisoquinoline were isolated and identified through their



SCHEME 4

picrates. There was no evidence for the interconversion of the triazoles (3) and (4) under the pyrolysis conditions. The isolation of 3-methylisoquinoline from the pyrolysis of the triazole (3) is thus consistent with the mechanism shown in Scheme 4.

1-(1-*Phenylvinyl*)- *and* 1-*Phenyl*-1,2,3-*triazoles*.—1*H*-1,2,3-Triazoles with an unsaturated substituent at the 1-position have a predictable reaction pathway open to them for thermal or photochemical decomposition. This involves cyclisation of the intermediate carbene or 1,3-diradical, leading to products containing a new five-membered ring. Similar reactions of benzotriazoles have long been known as the basis of the Graebe–Ullmann synthesis of carbazoles.[9] Reactions of this type have also been observed in monocyclic 1*H*-triazoles, involving cyclisation onto a 1-phenyl,[8a] 1-benzoyl,[10a] or 1-pyrimidin-2-yl [10b] substituent. If 1*H*-azirines are involved in the decomposition of such triazoles, their intermediacy requires the formation of isomeric cyclisation products (Scheme 5) from unsymmetrically substituted triazoles.



(5)a; $R^1 = R^4 = Ph$, $R^2 = R^3 = R^5 = H$
b; $R^1R^2 = CH{=}CH{-}CH{=}CH$, $R^3 = R^5 = H$, $R^4 = Ph$
(6)a; $R^1 = R^5 = Ph$, $R^2 = R^3 = R^4 = H$
b; $R^1R^2 = CH{=}CH{-}CH{=}CH$ $R^3 = R^4 = H$, $R^5 = Ph$

SCHEME 5

The isomeric 4- and 5-phenyl-1-(1-phenylvinyl)-1,2,3-triazoles (5a) and (6a) were prepared from α-azidostyrene with phenylacetaldehyde and ethyl benzoylacetate, respectively; the 5-phenyl isomer (6a) has been prepared previously.[11] The triazole (5a) was pyrolysed

[9] C. Graebe and F. Ullmann, *Annalen*, 1896, **291**, 16; W. Freudenberg, in 'Heterocyclic Compounds,' vol. 3, ed. R. D. Elderfield, Wiley, New York, 1952, p. 298.

[10] (*a*) R. Huisgen and M. Seidel, *Chem. Ber.*, 1961, **94**, 2509; (*b*) A. J. Hubert and H. Reimlinger, *ibid.*, 1970, **103**, 3811.

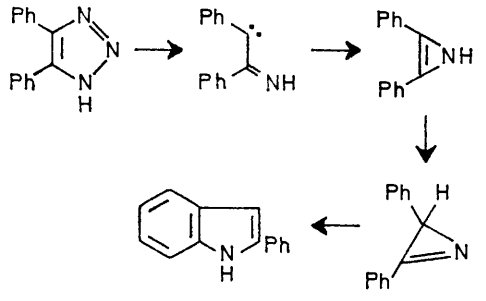
[11] G. L'abbé and A. Hassner, *J. Heterocyclic Chem.*, 1970, **7**, 361.

at 570° and 0·01 mmHg, and gave a mixture containing 2,4-diphenylpyrrole, the product to be expected from direct cyclisation of the intermediate carbene, as the major product. 2,5-Diphenylpyrrole was also found as a significant product, this being isolated in 14% yield after chromatography. A third, minor product, 2,3-diphenylbut-3-enonitrile, can be accounted for by Wolff rearrangement of the intermediate carbene, followed by a 1,3-shift of the 1-phenylvinyl group. The isomeric triazole (6a) also gave a mixture of 2,4- and 2,5-diphenylpyrrole on pyrolysis, with the 2,5-diphenyl isomer predominating in this case. There was no evidence for interconversion of the triazoles (5a) and (6a) before decomposition.

The isomeric 1,4- and 1,5-diphenyltriazoles [12] (5b) and (6b) gave an analogous pattern of products. The triazole (5b), when pyrolysed at 650°, gave a mixture of 2- and 3-phenylindole, with the latter as the major component. The triazole (6b) at 550° gave the same products but with 2-phenylindole as the major isomer.

These results are apparently in accord with Scheme 5, the initially formed iminocarbene either cyclising directly or isomerising *via* the 1*H*-azirine. An alternative interpretation had to be considered when it was found that 2- and 3-phenylindole could be interconverted by pyrolysis, though at a higher temperature, *i.e.* 800° and 0·02 mmHg. It thus seemed possible that the triazoles (5) and (6) could all decompose initially to give cyclisation products without rearrangement, and that these products then rearranged to the isomeric pyrroles or indoles in the pyrolysis tube. Further evidence bearing on this problem was obtained by a detailed study of the pyrolysis of the diphenyltriazoles (5b) and (6b) using ^{13}C-labelled compounds; this is reported in the following paper.[13]

4,5-*Diphenyl*-v-*triazole*.—Pyrolysis of the triazole at 650° gave a mixture containing diphenylacetonitrile (the product to be expected from Wolff rearrangement) and



SCHEME 6

2-phenylindole. Mechanisms for the formation of 2-phenylindole are speculative; one possibility, involving 2,3-diphenyl-1*H*-azirine and its isomerisation to 2,3-diphenyl-2*H*-azirine, is shown in Scheme 6. The thermal rearrangement of 2,3-diphenyl-2*H*-azirine to 2-phenylindole is known to occur readily.[14]

[12] L. Horner and W. Kirmse, *Annalen*, 1958, **614**, 1.
[13] T. L. Gilchrist, C. W. Rees, and C. Thomas, following paper.
[14] (*a*) T. L. Gilchrist, C. W. Rees, and E. Stanton, *J. Chem. Soc.* (*C*), 1971, 3036; (*b*) R. Selvarajan and J. H. Boyer, *J. Heterocyclic Chem.*, 1972, **9**, 87.

In summary, all the 1,2,3-triazoles investigated gave products which were consistent with intermediacy of 1*H*-azirines, and mechanisms involving 1*H*-azirines provide a common rationalisation for the diversity of products found. Dewar and Ramsden have predicted [15] that 1*H*-azirines should be capable of existence as long-lived reaction intermediates, in accord with this rationalisation.

EXPERIMENTAL

Preparative layer chromatography was performed using silica gel PF 254 (Merck). Vapour phase pyrolyses were carried out using the apparatus previously described,[16] and a condenser cooled to −78°. Pyrolysis temperatures quoted were obtained by means of a pyrometer with the thermocouple inserted into the centre of the oven before application of the vacuum.

Preparation of Triazoles.—(a) 4,5-*Diphenyl*-v-*triazole*. 1-Amino-4,5-diphenyl-1,2,3-triazole [1] dissolved in acetic acid (10 ml) was stirred rapidly at 0°, sufficient water being added to prevent the mixture freezing. Sodium nitrite (0·60 g) in water (2 ml) was added dropwise; the mixture was then diluted with water (100 ml) and the precipitate filtered off and dried (1·7 g, 91%). Crystallisation gave needles of 4,5-diphenyl-*v*-triazole, m.p. 135—137° (from benzene–hexane) (lit.,[17] 138°).

(b) 1-*Methyl*-4,5-*diphenyl*-1,2,3-*triazole* (1a). 4,5-Diphenyl-*v*-triazole (1·50 g, 6·8 mmol) in ethanol (25 ml) was stirred rapidly, and silver nitrate (2·0 g) in water (3 ml) was added dropwise. After 10 min the suspension was neutralised with ammonia, and the precipitated silver salt was filtered off, washed, and dried. It was then stirred with iodomethane (5 g) in chloroform (25 ml) for 12 h. Silver iodide was filtered off and the filtrate was evaporated to leave a pale cream crystalline solid (1·1 g). Trituration with ether left a solid (0·7 g, 44%) which was a single substance (t.l.c.). Two crystallisations gave 1-*methyl*-4,5-*diphenyl*-1,2,3-*triazole* (1a), m.p. 129—130° (from ethyl acetate–petroleum) (Found: C, 76·4; H, 5·6; N, 18·0. $C_{15}H_{13}N_3$ requires C, 76·6; H, 5·6; N, 17·9%); τ ($CDCl_3$) 6·10 (3H) and 2·30—2·90 (10H, m); *m/e* 235 (M^+), 221, 207, 192 (base), and 165; *m** (235 → 207) 182·5, (207 → 192) 178, and (192 → 165) 142. The ether solution obtained after trituration of the solid contained two components (t.l.c.): the triazole (1a) and 2-methyl-4,5-diphenyl-1,2,3-triazole (2a), which is prepared in better yield by the procedure described in the following section.

1-[$^2H_3$]Methyl-4,5-diphenyl-1,2,3-triazole (126 mg, 60%) was prepared in an analogous manner from the silver salt of 4,5-diphenyl-*v*-triazole (291 mg) and iodo[$^2H_3$]methane (99·5% $^2H_3$).

(c) 2-*Methyl*-4,5-*diphenyl*-1,2,3-*triazole* (2a). 4,5-Diphenyl-triazole (0·60 g, 2·7 mmol) in ether (25 ml) was added to ethereal diazomethane [generated from *N*-nitrosomethylurea (2·0 g)]. The yellow solution was stirred for 16 h and evaporated to leave an oil (0·63 g). Chromatography (silica; ether–petroleum, 4 : 1) gave an oil (0·45 g, 70%) which crystallised. Recrystallisation gave needles of 2-methyl-4,5-diphenyl-1,2,3-triazole (2a), m.p. 60—61° (from

[15] M. J. S. Dewar and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1973, 688.
[16] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.
[17] R. Stollé, W. Münch, and W. Kind, *J. prakt. Chem.*, 1904, **70**, 433.

petroleum) (lit.,[18] 61·5—63°); τ ($CDCl_3$) 5·75 (3H) and 2·30—2·90 (10H, m). Further elution gave 1-methyl-4,5-diphenyl-1,2,3-triazole (0·15 g, 23%).

(d) 1- *and* 2-*Ethyl*-4,5-*diphenyl*-1,2,3-*triazole* [(1b) *and* (2b)]. 4,5-Diphenyl-*v*-triazole (5·0 g, 22·6 mmol) was converted into its silver salt, as described in (a). The salt, suspended in chloroform, was heated under reflux with iodoethane (15 g) for 24 h. The mixture was filtered, the filtrate was evaporated, and the residue, an oil (4·0 g), was separated into its two components by chromatography [silica (150 g)]. (i) Ether–petroleum (1 : 10) eluted 2-*ethyl*-4,5-*diphenyl*-1,2,3-*triazole* (2b) (2·0 g, 35%) as a viscous oil (Found: M^+ 249·127. $C_{16}H_{15}N_3$ requires M^+ 249·128); τ ($CDCl_3$) 8·50 (3H, t, *J* 7 Hz), 5·62 (2H, q, *J* 7 Hz), 2·75—2·90 (6H, m), and 2·35—2·75 (4H, m); *m/e* 249 (M^+,base), 234, and 220. (ii) Ether–petroleum (1 : 5) eluted 1-*ethyl*-4,5-*diphenyl*-1,2,3-*triazole* (1b) (1·4 g, 25%), m.p. 110—111° (from ether–petroleum) (Found: C, 77·1; H, 5·9; N, 16·9. $C_{16}H_{15}N_3$ requires C, 77·1; H, 6·1; N, 16·9%); τ ($CDCl_3$) 8·65 (3H, t, *J* 7 Hz), 5·80 (2H, q, *J* 7 Hz), and 2·40—2·90 (10H, m); *m/e* 249 (M^+), 221, 193, 192 (base), and 165; *m** (249 ⟶ 221) 196, (221 ⟶ 192) 167, and (192 ⟶ 165) 142.

(e) 1- *and* 2-*Isopropyl*-4,5-*diphenyl*-1,2,3-*triazole* [(1c) *and* (2c)]. 4,5-Diphenyl-*v*-triazole silver salt (3·0 g, 9·1 mmol) and 2-iodopropane (10 g) were heated in chloroform (50 ml) under reflux for 24 h. The precipitate was filtered off and the filtrate evaporated to leave an oil (1·2 g). Chromatography (silica) gave (i) (with ether–petroleum, 1 : 20) an oil (1·09 g, 42%) which slowly crystallised. Recrystallisation gave 2-*isopropyl*-4,5-*diphenyl*-1,2,3-*triazole* (2c), m.p. 64—65° (from ethanol) (Found: C, 77·4; H, 6·7; N, 16·1. $C_{17}H_{17}N_3$ requires C, 77·5; H, 6·5; N, 15·9%); τ ($CDCl_3$) 8·40 (6H, d, *J* 7 Hz), 5·18 (1H, septet, *J* 7 Hz), 2·60—2·90 (6H, m), and 2·30—2·60 (4H, m); *m/e* 263 (M^+), 249, 248, and 221. (ii) Elution with ether–petroleum (1 : 5) gave a solid (0·2 g, 8%). Crystallisation gave 1-*isopropyl*-4,5-*diphenyl*-1,2,3-*triazole* (1c), m.p. 126—128° (from benzene–hexane) (Found: C, 77·6; H, 6·5; N, 15·7%); τ ($CDCl_3$) 8·55 (6H, d, *J* 7 Hz), 5·70 (1H, septet, *J* 7 Hz), and 2·70 (10H, m); *m/e* 263 (M^+), 221, and 178 (base).

(f) 1-*Isopropyl*-4,5-*diphenyl*-1,2,3-*triazole from* 2-*azidopropane and diphenylacetylene*. 2-Iodopropane (10 g) and sodium azide (10 g) were heated in dimethylformamide (30 ml) and water (20 ml) at 100° for 12 h; the solution was then distilled and the distillate collected until the temperature of the distillation flask reached 140°. The distillate was shaken with toluene (5 ml) and the organic solution was separated and dried. The solution, which contained 2-azidopropane (2·4 g; estimated by n.m.r.), was heated with diphenylacetylene (3·0 g, 17 mmol) at 135° (sealed tube) for 15 h. The toluene was distilled off and the residue triturated with ether to give 1-isopropyl-4,5-diphenyl-1,2,3-triazole (1·3 g), m.p. 126—128°. Chromatography of the ethereal solution gave diphenylacetylene (1·8 g) and a second crop of the triazole (1c) (0·5 g) (total 1·8 g; 100% based on diphenylacetylene consumed).

(g) 1-*Benzyl*-4,5-*diphenyl*-1,2,3-*triazole* (1d). Diphenylacetylene and benzyl azide were heated together according to a published procedure [19] to give 1-benzyl-4,5-diphenyl-1,2,3-triazole (93%), m.p. 112—112·5° (from ethanol) (lit.,[19] 110—112°); τ ($CDCl_3$) 4·65 (2H) and 2·40—3·10 (15H, m).

(h) 4-*Methyl*-5-*phenyl*-v-*triazole*. (i) The available [1] mixture of 1-amino-4-methyl-5-phenyl-1,2,3-triazole and 1-amino-5-methyl-4-phenyl-1,2,3-triazole (0·38 g) in acetic acid (3 ml) was cooled and stirred while aqueous sodium nitrite (0·19 g in 1 ml) was added dropwise. Water was added occasionally to prevent the mixture solidifying. After 1 h water was added to make the volume 25 ml. The fine white precipitate was filtered off, washed, dried, and crystallised to give 4-methyl-5-phenyl-*v*-triazole (0·32 g, 92%), m.p. 160—162° (from aqueous ethanol) (lit.,[20] 162°). (ii) The available [1] mixture of 4-methyl-5-phenyl- and 5-methyl-4-phenyl-1-*p*-tolylsulphonylamino-1,2,3-triazole (4·0 g), treated with sodium (1 g) in liquid ammonia (40 ml), gave 4-methyl-5-phenyl-*v*-triazole (1·65 g, 85%), m.p. 160—162°.

(j) 1,4-*Dimethyl*-5-*phenyl*-1,2,3-*triazole* (3), 1,5-*dimethyl*-4-*phenyl*-1,2,3-*triazole* (4), *and* 2,4-*dimethyl*-5-*phenyl*-1,2,3-*triazole*. 4-Methyl-5-phenyl-*v*-triazole (1·65 g, 10·4 mmol) was converted into its silver salt. The dry salt was suspended in chloroform (75 ml) and stirred with iodomethane (16 g) at room temperature for 16 h. The precipitate was filtered off and the filtrate was evaporated to leave an oil (1·62 g). Chromatography [silica (80 g)] gave (i) (with ether–petroleum, 1 : 10) an oil (0·10 g), tentatively identified as 2,4-*dimethyl*-5-*phenyl*-1,2,3-*triazole*; τ ($CDCl_3$) 7·53 (3H), and 2·20—2·80 (5H, m); *m/e* 173 (M^+, base), 144, 132, 131, and 130. (ii) Elution with ether–petroleum (3 : 10) gave back 4-methyl-5-phenyl-*v*-triazole (0·21 g). (iii) Ether–petroleum (1 : 1) eluted 1,4-*dimethyl*-5-*phenyl*-1,2,3-*triazole* (3) (0·785 g, 50%), m.p. 103—105° (from petroleum) (Found: C, 69·2; H, 6·3; N, 24·5. $C_{10}H_{11}N_3$ requires C, 69·3; H, 6·4; N, 24·3%); $\nu_{max.}$ 1615w, 1580w, and 1500 cm^{-1}; τ ($CDCl_3$) 7·70 (3H), 6·09 (3H), and 2·40—2·80 (5H, m); *m/e* 173 (M^+), 145, 130, and 103 (base). (iv) Further elution with ether–petroleum (1 : 1) gave 1,5-*dimethyl*-4-*phenyl*-1,2,3-*triazole* (4) (0·43 g, 27%), m.p. 98—100° (from petroleum) (Found: C, 69·6; H, 6·4; N, 24·3%); $\nu_{max.}$ 1610w and 1370 cm^{-1}; τ ($CDCl_3$) 7·55 (3H), 6·00 (3H), and 2·10—2·80 (5H, m); *m/e* 173 (M^+), 145, 144, and 130 (base).

(k) 1,5-*Dimethyl*-4-*phenyl*-1,2,3-*triazole from azidomethane and* 1-*phenylpropan*-2-*one*. A dry solution of azidomethane (1 g; estimated by n.m.r.) in benzene (6 ml) was prepared by a published procedure.[21] 1-Phenylpropan-2-one (2·35 g, 17·5 mmol) and dry tetrahydrofuran (25 ml) were added and the solution stirred at 0°. Potassium t-butoxide (2·0 g) was added in portions during 0·5 h, and the solution was stirred for a further 6 h. The solvent was distilled off and the residue washed with ether. The ethereal solution was evaporated to leave a crystalline solid (1·4 g, 46%). Recrystallisation gave 1,5-dimethyl-4-phenyl-1,2,3-triazole (4), m.p. 98—100°, identical (mixed m.p., i.r. spectrum, t.l.c.) with the specimen prepared by methylation of 4-methyl-5-phenyl-*v*-triazole.

(l) 4-*Phenyl*-1-(1-*phenylvinyl*)-1,2,3-*triazole* (5a). Phenylacetaldehyde (0·60 g, 5 mmol), α-azidostyrene (0·75 g, 5·2 mmol), and potassium t-butoxide (0·7 g) were stirred in dry tetrahydrofuran (20 ml) for 12 h. The solvent was distilled off and the residue washed with ether. The ethereal solution was evaporated to leave a gum (0·8 g) which was heated with petroleum. The mixture was filtered and the filtrate evaporated to leave an oil which slowly crystallised. Recrystallisation gave 4-*phenyl*-1-(1-*phenylvinyl*)-1,2,3-*triazole* (5a) (0·725 g, 60%), m.p. 67·5—68·5° (from petroleum) (Found: C, 77·5; H, 5·3; N, 16·9. $C_{16}H_{13}N_3$ requires C, 77·7; H, 5·3; N, 17·0%); τ ($CDCl_3$) 4·57 (1H, d, *J* 1 Hz),

[18] R. R. Fraser, Gurudata, and K. E. Haque, *J. Org. Chem.*, 1969, **34**, 4118.

[19] R. Huisgen and M. Seidel, *Chem. Ber.*, 1961, **94**, 2509.

[20] R. Meier, *Chem. Ber.*, 1953, **86**, 1483.

[21] F. O. Rice and C. J. Grelecki, *J. Phys. Chem.*, 1957, **61**, 830.

4·29 (1H, d, J 1 Hz), 2·60—2·90 (8H, m), and 2·10—2·40 (3H, m); *m/e* 247 (M^+), 219, 218, and 77 (base).

(m) 5-*Phenyl*-1-(1-*phenylvinyl*)-1,2,3-*triazole* (6a). Ethyl benzoylacetate (0·70 g, 3·6 mmol) and α-azidostyrene (0·60 g, 4·1 mmol) in tetrahydrofuran (5 ml) were added dropwise to potassium t-butoxide (0·5 g) in tetrahydrofuran (5 ml). The mixture was stirred at room temperature for 20 h, heated under reflux for 6 h, cooled, and poured into water. The precipitate was filtered off, washed with ether, and digested with aqueous sodium hydroxide (5N; 10 ml). Acidification gave a precipitate of 5-phenyl-1-(1-phenylvinyl)-1,2,3-triazole-4-carboxylic acid (0·20 g, 19%), m.p. 155—157° (decomp.) (from chloroform–carbon tetrachloride) [lit.,[12] 156—157° (decomp.)]. The carboxylic acid (0·20 g) was heated at 200° for 2 min. The orange, viscous residue of 5-phenyl-1-(α-styryl)-1,2,3-triazole (6a) [11] was sufficiently pure (t.l.c.) for use in the pyrolysis experiments. In subsequent pyrolysis experiments the carboxylic acid was decarboxylated *in situ*.

(n) 1,4- *and* 1,5-*Diphenyl*-1,2,3-*triazole* [(5b) *and* (6b)]. These triazoles were prepared by heating azidobenzene with phenylacetylene according to a published procedure.[12]

Preparation of Isoquinolines.—(a) 3-*Phenylisoquinoline*. This was prepared by a published procedure [22] involving reduction of 1-chloro-3-phenylisoquinoline, and had m.p. 102—104° (from ethanol) (lit.,[22] 103—105°); τ ($CDCl_3$) 1·90—2·80 (10H, m) and 0·80 (1H); *m/e* 205 (M^+) (100% and 204 (50%).

(b) 3-*Phenylisoquinolin*-4-*ol*. 3-Phenylisoquinoline (0·18 g) and aqueous hydrogen peroxide (30%; 0·3 ml) were heated in acetic acid (3 ml) at 70° for 40 h. More aqueous hydrogen peroxide (0·2 ml) was added after 12 h. After 40 h, t.l.c. (silica; ether) showed that some 3-phenylisoquinoline still remained. The solution was evaporated to dryness at 70° and 20 mmHg, water (3 ml) was added, and the mixture was again evaporated to dryness. Chloroform was added to the residue and the solution dried and evaporated, leaving an oil (0·156 g) which solidified on trituration with ether, giving a buff solid (0·097 g, 49%). Two recrystallisations gave 3-*phenylisoquinoline* N-*oxide*, m.p. 158—160° (from ether), $\nu_{max.}$ 3400br and 1570 cm^{-1}. The *N*-oxide (68 g) was heated with acetic anhydride (1·5 ml) under reflux for 0·5 h. The acetic anhydride was distilled off and the residue was triturated with ether. An insoluble solid (9 mg) was filtered off; $\nu_{max.}$ 1670 and 1630 cm^{-1}, as expected for 2-acetyl-3-phenylisoquinolin-1(2*H*)-one. The ethereal solution was evaporated to a gum (90 mg) which was heated under reflux with hydrochloric acid (2N; 5 ml) for 40 min. The pale yellow solution was made basic (aqueous sodium hydrogen carbonate), and the yellow precipitate was filtered off and dissolved in ether. The solution was evaporated to a yellow gum (22 mg, 32%) which crystallised when triturated with ether–pentane. Recrystallisation gave 3-*phenylisoquinolin*-4-*ol*, m.p. 159—161° (yellow prisms from benzene) (Found: M^+ 221·082. $C_{15}H_{11}NO$ requires M^+ 221·084); $\nu_{max.}$ ($CHCl_3$) 3550 (OH), 1635, and 1590 cm^{-1}; $\lambda_{max.}$ (EtOH) 255 (ε 26,500), 313 (7500), 335 (5500), and 402 nm (700); τ ($CDCl_3$) 4·25br (1H, OH), 1·70—2·80 (9H, m), and 1·22 (1H); *m/e* 221 (M^+), 220, 205, 192, 165, and 85 (base); picrate, m.p. 226—227° (from ethanol).

(c) 3-*Methylisoquinolin*-4-*ol*.[23] 3-Methylisoquinoline (7·0 g) and aqueous hydrogen peroxide (30%; 8 ml) were heated in acetic acid (15 ml) at 70° for 18 h. The product was isolated as in (b) and gave 3-methylisoquinoline *N*-oxide (7·0 g, 90%), m.p. 138—139° (from benzene–cyclohexane) (lit.,[23] 136—139°). The *N*-oxide (3 g) was heated under reflux in acetic anhydride (30 ml) for 1 h. The acetic anhydride was distilled off and the residue was washed with water, then triturated with ether. This gave a solid tentatively identified as 2-acetyl-3-methylisoquinolin-1(2*H*)-one (1·1 g), m.p. 215—216° (from ethanol); $\nu_{max.}$ 1670, 1648, and 1610 cm^{-1}. The ethereal solution was added to ethanolic picric acid. The yellow precipitate (1·4 g) was filtered off, aqueous sodium carbonate was added, and the mixture was extracted with ether. Chromatography (silica) gave an oil (0·65 g) which slowly crystallised; $\nu_{max.}$ 1766 cm^{-1}, as expected for 4-acetoxy-3-methylisoquinoline. This solid (0·20 g) was heated with hydrochloric acid (5%; 20 ml) under reflux for 40 min. An excess of aqueous sodium carbonate was added and the product was extracted with ether. This gave a solid which was recrystallised to give 3-methylisoquinolin-4-ol (134 mg), m.p. 178—180° (from benzene) (lit.,[23] 180°); $\nu_{max.}$ 2700br, 1633, and 1584 cm^{-1}: τ ($CDCl_3$) 7·36 (3H), 3·75br (1H, OH), 1·70—2·70 (4H, m), and 1·35 (1H); *m/e* 159 (M^+, base) and 158; picrate, m.p. 202—203°.

Pyrolysis of Triazoles.—(a) 1-*Methyl*-4,5-*diphenyl*-1,2,3-*triazole* (1a). The triazole (100—200 mg portions) was pyrolysed at 600° and 0·01 mmHg. At lower temperatures, some of the triazole was unchanged, and at higher temperatures, a more complex mixture of products was detected. The mixture of pyrolysis products (86 mg from 100 mg) gave, by preparative layer chromatography (silica; ether–petroleum, 1 : 1): (i) at R_F 0·9, 2,2-diphenylpropiononitrile (45 mg, 51%), identical (i.r., n.m.r., and mass spectra) with an authentic specimen; (ii) at R_F 0·5, 3-phenylisoquinoline (17 mg, 19%), m.p. and mixed m.p. 102—104°, identical (i.r. and n.m.r. spectra) with an authentic specimen; and (iii) at R_F 0·4, 3-phenylisoquinolin-4-ol (11 mg, 12%), m.p. and mixed m.p. 160·5—161·5°, identical (i.r., u.v., and n.m.r. spectra) with an authentic specimen. If the crude pyrolysis mixture was triturated with ether, tetraphenylsuccinonitrile (4 mg, 5%), m.p. 204—206° (from ethanol) (lit.,[24] 215°), remained.

To test for the intermediacy of *N*-methyldiphenylvinylideneamine, the imine [4] (150 mg) was pyrolysed at 600° and 0·01 mmHg and gave an amber oil (130 mg). Trituration with ether gave tetraphenylsuccinonitrile (30 mg, 21%), m.p. 204—206°, and 2,2-diphenylpropiononitrile (95 mg, 63%).

(b) 1-*Ethyl*-4,5-*diphenyl*-1,2,3-*triazole* (1b). The triazole (100 mg) was pyrolysed at 600—620° and 0·01 mmHg, and a yellow gummy solid (85 mg) collected in the condenser. Preparative layer chromatography (silica; ether–petroleum, 1 : 1) gave three products which were not fully characterised; structural assignments were made on the basis of their spectra, and by analogy with the products from the triazole (1a). They were: (i) at R_F 0·7, an oil (44 mg, 50%), identified as 2,2-diphenylbutyronitrile; $\nu_{max.}$ (film) 2250 (CN) and 1605w cm^{-1}; τ ($CDCl_3$) 8·98 (3H, t, J 7 Hz), 7·62 (2H, q, J 7 Hz), and 2·70 (10H, m); (ii) at R_F 0·55, 1-methyl-3-phenylisoquinoline (5 mg, 6%), m.p. 47—49° after resublimation (lit.,[25] 48—49°); and (iii) at R_F 0·48, 1-*methyl*-3-*phenylisoquinolin*-4-*ol* (12 mg, 13%), m.p. 105—106° (from

[22] S. Gabriel, *Ber.*, 1885, **18**, 3473.
[23] M. M. Robison and B. L. Robison, *J. Org. Chem.*, 1956, **21**, 1337.
[24] E. P. Kohler and N. L. Drake, *J. Amer. Chem. Soc.*, 1923, **45**, 1281.
[25] S. Goszczynski, *Roczniki Chem.*, 1964, **38**, 893.

benzene); $\nu_{max.}$ 3000br (OH), 1620w, and 1598w cm^{-1}; $\lambda_{max.}$ (EtOH) 257, 314, and 338 nm; τ ($CDCl_3$) 7·15 (3H) and 1·70—2·80 (9H, m); *m/e* 235 (M^+, base), 234, and 206; *m** (234 → 206) 182.

(c) 1-*Isopropyl*-4,5-*diphenyl*-1,2,3-*triazole* (1c). The triazole (50 mg) was pyrolysed at 650° and 0·01 mmHg and gave a yellow gum (43 mg). The gum was warmed with dilute hydrochloric acid and the mixture shaken with ether. The ethereal solution was dried and evaporated. The residue gave, with 2,4-dinitrophenylhydrazine, the 2,4-dinitrophenylhydrazone of deoxybenzoin, m.p. and mixed m.p. 196—198°. No other products were investigated.

(d) 1-*Benzyl*-4,5-*diphenyl*-1,2,3-*triazole* (1d). This was pyrolysed in batches (total 1500 mg) at 600° and 0·01 mmHg and gave a complex mixture of products (1250 mg). Trituration with ether gave tetraphenylsuccinonitrile (300 mg, 32%), m.p. 204—206° (from ethanol) (lit.,[24] 215°) (Found: C, 87·5; H, 5·2; N, 7·1. Calc. for $C_{28}H_{20}N_2$: C, 87·5; H, 5·3; N, 7·3%), $\nu_{max.}$ ($CHCl_3$) 2250w (CN) cm^{-1}; *m/e* 193 (base). The ether solution was evaporated to an oil (950 mg). Chromatography (silica; ether–petroleum, 1 : 20) gave (i) a yellow oil (330 mg) from which crystals of bibenzyl (190 mg, 43%) separated. The residual oil had $\nu_{max.}$ 2250 cm^{-1}, consistent with the presence of 2,2,3-triphenylpropiononitrile, but this was not purified further. (ii) Deoxybenzoin (225 mg, 27%) was identified by conversion into its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 194—196° (from ethanol); *m/e* 376 (M^+, base). (iii) A yellow gum (80 mg) was not fully characterised; the spectral data are consistent with a diphenylisoquinolinol; $\nu_{max.}$ ($CHCl_3$) 3540 and 1590 cm^{-1}; $\lambda_{max.}$ (EtOH) 255, 316, and 342 nm; *m/e* 297 (base) 296, and 190. (iv) 3,4-Diphenylisoquinoline (140 mg, 10%) had m.p. 159—159·5° (lit.,[26] 155—156°); $\nu_{max.}$ 1625w, 1580w, and 1565w cm^{-1}; τ ($CDCl_3$) 1·80—3·00 (14H, m) and 0·6 (1H); *m/e* 281 (M^+) and 280 (base).

(e) 1,4-*Dimethyl*-5-*phenyl*-1,2,3-*triazole* (3). The triazole (100 mg) was pyrolysed at 750° and 0·01 mmHg, and gave a red oil (78 mg). This was triturated with ether, and the ethereal solution was evaporated to give an oil (60 mg); the ether-insoluble residue appeared to be polymeric. Preparative layer chromatography of the oil (silica; ether–petroleum, 3 : 1) gave two products: (i) at R_F 0·45, 3-methylisoquinoline [27] (7 mg, 8%), m.p. and mixed m.p. 60—61°; (ii) at R_F 0·8, an oil (16 mg, 19%), tentatively identified as 2-methyl-2-phenylpropiononitrile; $\nu_{max.}$ ($CHCl_3$) 2240 cm^{-1} (CN); *m/e* 145 (M^+) and 129 (base).

(f) 1,5-*Dimethyl*-4-*phenyl*-1,2,3-*triazole* (4). The triazole (100 mg) was pyrolysed at 750° and 0·01 mmHg and gave a gum (80 mg). The product mixture was triturated with ether to remove a polymeric solid (10 mg); the ether-soluble fraction contained two major components (t.l.c.); τ ($CDCl_3$) 7·38 and 7·35 (methyl protons), and 1·37 and 1·01 (1-H of isoquinolines). Ethanolic picric acid was added and gave a precipitate (55 mg). Fractional crystallisation from ethanol gave two pure picrates, identical (m.p., mixed m.p., and i.r. spectra) with authentic specimens of 3-methylisoquinoline picrate and 3-methylisoquinoline-4-ol picrate. The free bases were liberated from the picrates with aqueous potassium hydroxide. They were extracted by addition of ether and identified (m.p., i.r.) by comparison with authentic specimens.

(g) 4-*Phenyl*-1-(1-*phenylvinyl*)-1,2,3-*triazole* (5a). The triazole (200 mg) was pyrolysed at 570° and 0·01 mmHg and gave a mixture (152 mg) containing three major components, which were isolated by preparative layer chromatography (silica; ether–petroleum, 2 : 3): (i) at R_F 0·4, 2,4-diphenylpyrrole (48 mg, 27%), m.p. and mixed m.p. 178—180° (from petroleum) (lit.,[28] 180°), identified by comparison (i.r.) with an authentic specimen (this pyrrole gives an indigo colour with Ehrlich's reagent); (ii) at R_F 0·6, 2,5-diphenylpyrrole (24 mg, 14%), m.p. and mixed m.p. 142—144° (from benzene) (lit.,[29] 143°), identified by comparison (i.r.) with an authentic specimen (the pyrrole gives a mauve colour with Ehrlich's reagent); (iii) at R_F 0·7, a viscous oil (53 mg) which was not homogeneous. Two further purifications by layer chromatography gave an oil, identified as 2,3-*diphenylbut*-3-*enonitrile* (9 mg, 5%); $\nu_{max.}$ 2250w cm^{-1}; τ ($CDCl_3$) 5·01 (1H, dd, *J* 1 and 0·75 Hz), 4·41 (1H, d, *J* 1 Hz), 4·37 (1H, d, *J* 0·75 Hz), and 2·70—2·90 (10H, m); *m/e* 219 (M^+), 192, and 103 (base). The assignment of structure was supported by the following reaction. The nitrile (9 mg) was heated in dioxan (2 ml) under reflux with triethylamine (10 mg) for 1 h. This gave an oil (8 mg) which was purified by layer chromatography (silica; ether–petroleum, 1 : 3). One major component was isolated; it was 2,3-diphenylcrotononitrile (3 mg), m.p. 79—81° (lit.,[30] 81°), identified by comparison (i.r., t.l.c., n.m.r.) with a specimen prepared by the method of ref. 30; $\nu_{max.}$ 2215 cm^{-1}; τ ($CDCl_3$) 7·43 (3H) and 2·50—3·00 (10H, m); *m/e* 219 (M^+) and 204 (base).

(h) 5-*Phenyl*-1-(1-*phenylvinyl*)-1,2,3-*triazole* (6a). 5-Phenyl-1-(1-phenylvinyl)-1,2,3-triazole-4-carboxylic acid (80 mg) was decarboxylated *in situ* by heating briefly at 200°. The residue was pyrolysed at 575° and 0·1 mmHg and gave a mixture (52 mg) containing two major components. These were separated by layer chromatography (silica; ether–petroleum 2 : 1); they were (i) at R_F 0·5, 2,4-diphenylpyrrole (10 mg, 17%), m.p. and mixed m.p. 177—180°, and (ii) at R_F 0·75, 2,5-diphenylpyrrole (27 mg, 45%), m.p. and mixed m.p. 142—144°.

(j) 1,4-*Diphenyl*-1,2,3-*triazole* (5b). The triazole (50 mg) was pyrolysed at 650° and 0·02 mmHg. The product, a yellow gum (38 mg), consisted of 2- and 3-phenylindole as the major products, the 3-phenyl isomer predominating (t.l.c.). No isolation or quantitative analysis was attempted.

(k) 1,5-*Diphenyl*-1,2,3-*triazole* (6b) (with C. Thomas). The triazole (33 mg) was pyrolysed at 550° and 0·02 mmHg. This gave a yellow gum (27 mg) which consisted of 2- and 3-phenylindole, with the 2-phenyl isomer predominating, together with a little starting triazole (t.l.c.). No quantitative analysis was performed.

In control experiments, both 2- and 3-phenylindole were unchanged after pyrolysis at 600° and 0·02 mmHg. In experiments performed at 800° and using a tube packed with silicon carbide chips to increase the contact times, the indoles were observed to undergo interconversion. 2-Phenylindole (30 mg) gave 3-phenylindole (9·3 mg, 31%) (isolated by preparative layer chromatography) and 2-phenylindole (15·5 mg, 52%). 3-Phenylindole gave 2-phenylindole (18·7 mg, 62%) and 3-phenylindole (4·5 mg, 15%).

(l) 4,5-*Diphenyl*-v-*triazole*. The triazole (100 mg) was pyrolysed at 650° and 0·02 mmHg, and gave a yellow gum

[26] G. Berti and P. Corti, *Gazzetta*, 1958, **88**, 704.
[27] W. H. Mills and J. L. B. Smith, *J. Chem. Soc.*, 1922, **121**, 2732.
[28] L. W. Dady, *Tetrahedron*, 1967, **23**, 3505.
[29] L. F. H. Allen, D. M. Young, and M. R. Gilbert, *J. Org. Chem.*, 1937, **2**, 227.
[30] T. Kumamoto, K. Hosoi, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 1968, **41**, 2742.

(77 mg). This was crystallised and gave diphenylacetonitrile (57 mg, 85%), m.p. 70—71° (from ether–hexane) (lit.,[15] 71—72°); $\nu_{max.}$ 2250 cm^{-1} (CN); τ ($CDCl_3$) 4·90 (1H) and 2·70 (10H, m). Preparative layer chromatography of the mother liquors gave diphenylacetonitrile and 2-phenylindole (5 mg), m.p. 187—189° (from ethanol), identical (i.r., mixed m.p.) with an authentic specimen.

(m) 1-[$^2H_3$]*Methyl*-4,5-*diphenyl*-1,2,3-*triazole* (with C. Thomas). The triazole (60 mg) was pyrolysed at 630° and 0·005 mmHg. 3-Phenylisoquinoline (4·8 mg) was isolated from the products by preparative layer chromatography; τ ($CDCl_3$) 1·90—2·80 (m), the signal at τ 0·80 observed in undeuteriated specimens being absent; *m/e* 207 (53%), 206 (100%), 205 (50%), and 204 (10%).

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