Reactive Intermediates. Part XXII.[1] Formation of 2*H*-Azirines by Oxidation of *N*-Aminophthalimide in the Presence of Alkynes [2]

By **David J. Anderson, Thomas L. Gilchrist, Geoffrey E. Gymer** (in part), and **Charles W. Rees,*** Chemistry Department, The University, Leicester LE1 7RH, and The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

2*H*-Azirines (2) are isolated in low to moderate yields after oxidation of *N*-aminophthalimide by lead tetra-acetate in the presence of the alkynes propyne, but-2-yne, pent-1-yne, and hex-3-yne. A mechanism for the reaction is proposed which involves the transient formation and rearrangement of 1*H*-azirines (1). Some unsuccessful attempts to generate 1*H*-azirines by alternative routes are described. Reports that the products of the reactions of 1,2,3-triazole-4,5-dicarboxylic acid with acetic anhydride and of *p*-benzoquinone with *p*-nitrophenyl azide are 1*H*-azirines are shown to be incorrect.

No 1*H*-azirines (1) have yet been isolated, although many 2*H*-azirines (2) are known.[3] The instability of 1*H*-azirines can be attributed to the antiaromatic character of the planar system. Molecular orbital calculations have confirmed that there is a destabilising interaction between the electrons of the π-bond and the lone pair on nitrogen: the calculations predict a non-planar structure for 1*H*-azirine, with an unusually high barrier to inversion about nitrogen (147 kJ mol^{-1}).[4]

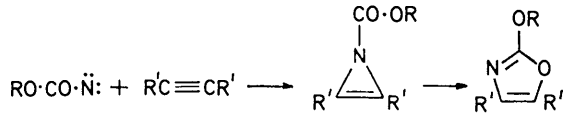
This paper records attempts to prepare 1*H*-azirines by the oxidation of *N*-aminophthalimide in the presence of acetylenes. The corresponding reaction with olefins has been shown to provide a good route to aziridines.[5] Before the present work, a few other attempts had been

[1] Part XXI, C. W. Rees and M. Yelland, *J.C.S. Perkin I*, 1973, 221.
[2] Preliminary communication, D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Comm.*, 1969, 147.
[3] F. W. Fowler, *Adv. Heterocyclic Chem.*, 1972, **13**, 45.
[4] D. T. Clark, *Theor. Chim. Acta*, 1969, **15**, 225.
[5] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc.* (*C*), 1970, 576.

made to prepare 1*H*-azirines by the cycloaddition of nitrenes to acetylenes. Nitrene, :NH, gave vinylideneimine when treated with acetylene in a solid argon matrix at 4° K;[6] and alkoxycarbonylnitrenes gave

(1) (2)

oxazoles with acetylenes.[7] It is possible that the oxazoles are formed by rearrangement of intermediate 1*H*-azirines (Scheme 1) rather than by direct 1,3-dipolar addition of the nitrenes to the acetylenes, because the corresponding cycloaddition of alkoxycarbonylcarbenes to acetylenes gives cyclopropenes which can subsequently rearrange to furans.[8]



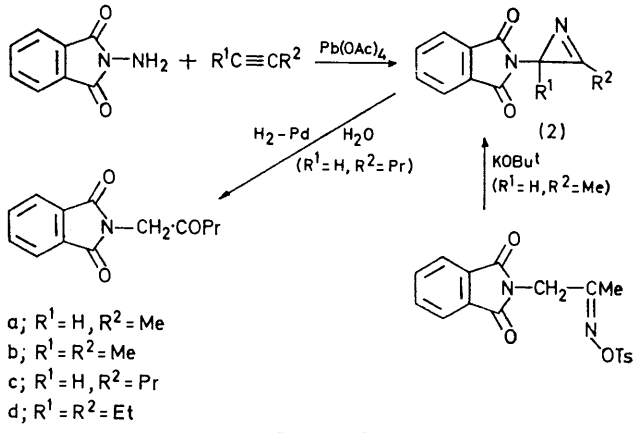
SCHEME 1

A study of the dehydrochlorination of chloroaziridines has also been reported.[9] The aziridines were not easily dehydrochlorinated, and no decisive evidence for the intermediacy of 1*H*-azirines was obtained.

Oxidation of N-*Aminophthalimide in the Presence of Acetylenes.*—Oxidations were carried out by adding lead tetra-acetate to a suspension of *N*-aminophthalimide in dichloromethane containing a five molar excess of the acetylene, at temperatures from −20° to +20°. With the simple alkynes propyne, but-2-yne, pent-1-yne, and hex-3-yne, 1 : 1 adducts were isolated (1—15%), the major product in each reaction being phthalimide. The adducts, which were low-melting crystalline solids, were identified as 2*H*-azirines (2) (Scheme 2). The isomeric 1*H*-azirine structures could be discounted on the basis of the n.m.r. spectra: for example, the adduct (2b) formed from but-2-yne showed two signals at τ 8·23 and 7·24 which were assigned to two non-equivalent methyl groups. The 2*H*-azirine structures were supported by the catalytic reduction of the adduct (2c) in moist ethyl acetate, which gave 1-phthalimidopentan-2-one. This type of reductive cleavage is a known reaction of 2*H*-azirines.[10] Confirmation of the structure of the adduct (2a) was provided by an independent synthesis of the azirine from the oxime toluene-*p*-sulphonate of phthalimidopropan-2-one and potassium t-butoxide, in a modified Neber reaction.

At attempted cycloaddition to di-t-butylacetylene gave only an adduct (3) formed by addition to the double bond of 2,5,5-trimethylhex-1-en-3-yne, an impurity in the acetylene. Even when the enyne concentration was reduced to *ca.* 2% by distillation through a spinning band column the aziridine (3) was the only product of nitrene addition. Reaction at the double bond of the enyne is evidently much more favourable than attack at the triple bond of di-t-butylacetylene.

Several other acetylenes were also used unsuccessfully, phthalimide being the only product isolated. These included phenylacetylene, diphenylacetylene, t-butylacetylene, 1,4-dichlorobut-2-yne, dimethyl acetylene

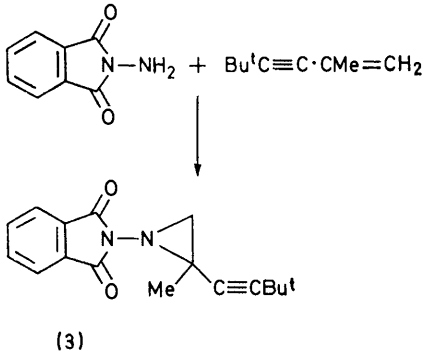


a; $R^1 = H, R^2 = Me$
b; $R^1 = R^2 = Me$
c; $R^1 = H, R^2 = Pr$
d; $R^1 = R^2 = Et$

SCHEME 2

dicarboxylate, and methyl tetrolate. The reaction thus appears to be limited in scope to simple alkynes.

Reaction Mechanism.—The formation of 2*H*-azirines can be rationalised by a reaction sequence involving cycloaddition of phthalimidonitrene to the alkynes to give 1*H*-azirines, followed by rearrangement. It is possible to envisage other ways in which an alkyne



(3)

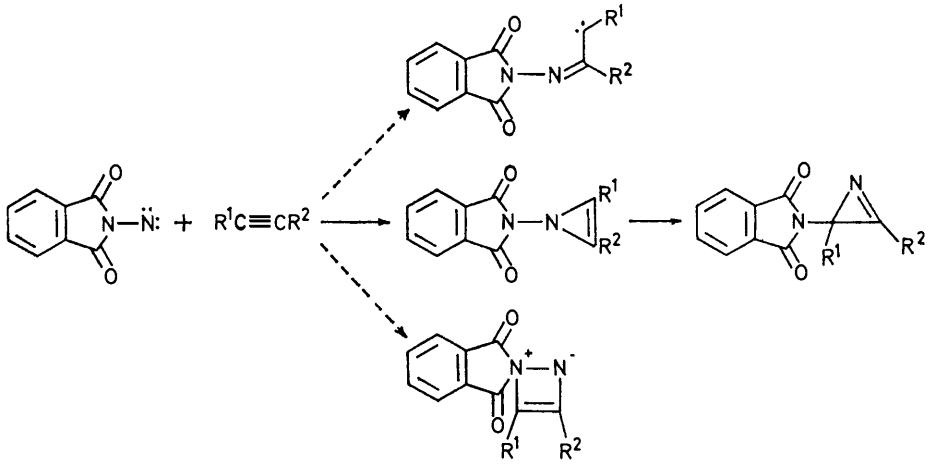
SCHEME 3

might react with phthalimidonitrene (Scheme 4), but the formation of 1*H*-azirines seems the most likely because it has a direct analogy in the reaction of carbenes with alkynes to give cyclopropenes. There is also good evidence from the pyrolysis of triazoles[11] that these 1*H*-azirines can rearrange to the 2*H*-isomers.

With unsymmetrical alkynes, the 1*H*- to 2*H*-azirine

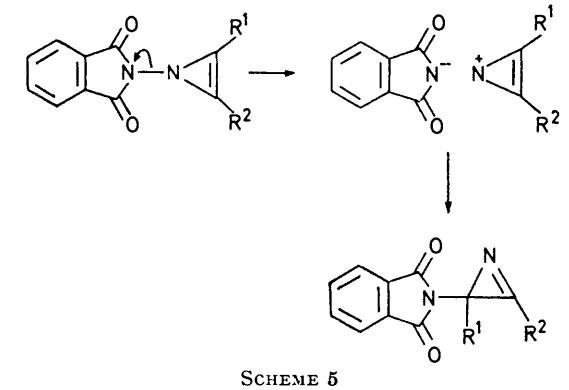
[6] M. E. Jacox and D. E. Milligan, *J. Amer. Chem. Soc.*, 1963, **85**, 278.
[7] R. Huisgen and H. Blaschke, *Chem. Ber.*, 1965, **98**, 2985; J. Meinwald and D. H. Aue, *J. Amer. Chem. Soc.*, 1966, **88**, 2849.
[8] M. I. Komendatov, I. A. D'yakonov, and T. S. Smirnova, *Zhur. org. Khim.*, 1966, **2**, 559; 1967, **3**, 1903.
[9] F. W. Fowler and H. Hassner, *J. Amer. Chem. Soc.*, 1968, **90**, 2875.
[10] D. J. Cram and M. J. Hatch, *J. Amer. Chem. Soc.*, 1953, **75**, 33.
[11] T. L. Gilchrist, G. E. Gymer, and C. W. Rees, following paper.

rearrangement should give two isomeric 2*H*-azirines, whereas only one was isolated in each of the reactions performed. All the unsymmetrical alkynes used were terminal acetylenes, however, and it is known that azirines unsubstituted at the 3-position are unstable and prone to polymerisation.[12]

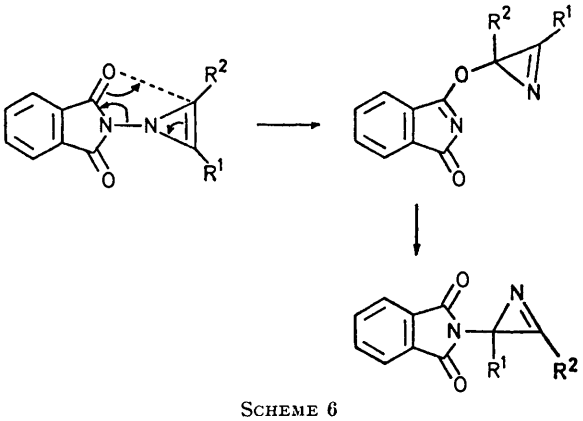


SCHEME 4

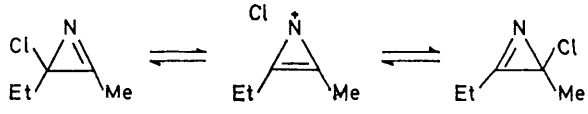
The mechanism of the 1*H*- to 2*H*-azirine rearrangement has not been established. Two possible mechanisms are (*a*) heterolytic cleavage of the N–N bond to give an azirinium cation and the phthalimide anion, followed by recombination at a ring carbon atom (Scheme 5), and (*b*) successive [3,3] sigmatropic shifts, with a second 2*H*-azirine as an intermediate (Scheme 6). The first mechanism is closely related to one proposed for the isomerisation of 3-chloro-2*H*-azirines (Scheme 7); this isomerisation also takes place under very mild conditions.[13]



SCHEME 5

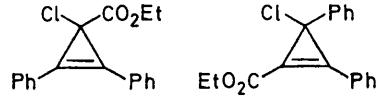


SCHEME 6



SCHEME 7

Addition of chloro(phenyl)carbene to ethyl phenylpropiolate is reported to give the chlorocyclopropene (4) rather than the expected isomer (5).[14] This addition with rearrangement is similar to that observed with *N*-aminophthalimide, and the ion-pair mechanism again provides a rationalisation of the observation.



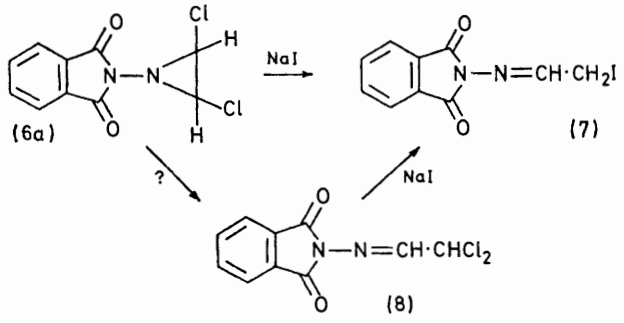
(4) (5)

The second mechanism involves successive rearrangements of the Claisen type. Although it is impossible to estimate accurately the activation energies in this particular system, comparison with related systems (the allylic amidate to amide rearrangements [15]) suggests that there may be insufficient driving force for the second of the two steps to occur rapidly at room temperature. On this basis, mechanism (*a*) (Scheme 5) is preferred.

Attempted Dechlorination of 2,3-Dichloroaziridines.— An alternative synthesis of 1-phthalimido-1*H*-azirines was attempted using 2,3-dichloroaziridines (6) as the precursors. With sodium iodide in acetone, the aziridine (6a) gave the hydrazone (7) as the only isolable product.

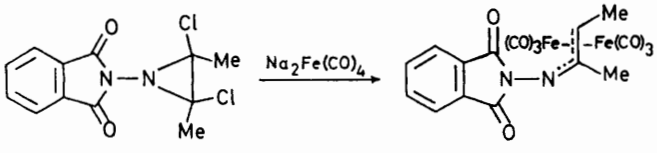
[12] A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 1968, **90**, 2869.
[13] J. Ciabattoni and M. Cabell, *J. Amer. Chem. Soc.*, 1971, **93**, 1482.
[14] C. D. DeBoer, *J.C.S. Chem. Comm.*, 1972, 377.
[15] O. Mumm and F. Möller, *Ber.*, 1937, **70**, 2214; W. M. Lauer and C. S. Benton, *J. Org. Chem.*, 1959, **24**, 804.

The same hydrazone (7) was also formed from the thermal rearrangement product (8) [5] of the aziridine (Scheme 8), and it is possible that rearrangement of the aziridine occurred before reaction with sodium iodide.



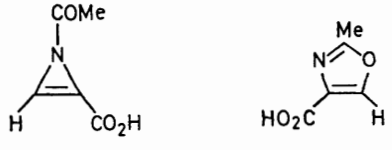
SCHEME 8

In an attempt to carry out the dehalogenation and to intercept the azirine as an iron complex, the reactions of the dichloroaziridines with nonacarbonyldi-iron and with disodium tetracarbonylferrate were investigated. Only in the reaction of the dimethylaziridine (6b) with the latter reagent was a complex isolated. The product, an orange crystalline solid, had properties consistent with the non-cyclic structure (9) shown. Similar complexes have been prepared with sulphur- and selenium-containing ligands by reaction of thiadiazoles and selenadiazoles with nonacarbonyldi-iron.[16]



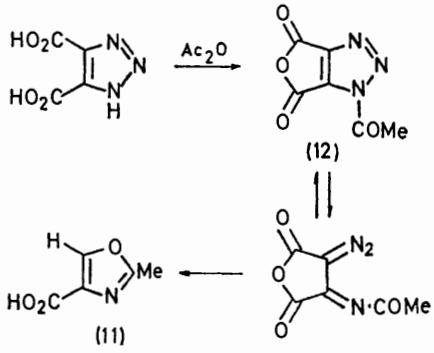
Two reactions which have been claimed to give 1*H*-azirines were reinvestigated. In both cases the 1*H*-azirine structures were incorrect.

Reaction of 1,2,3-*Triazole*-4,5-*dicarboxylic Acid with Acetic Anhydride*.—There is a report [17] that the reaction of 1,2,3-triazole-4,5-dicarboxylic acid with acetic anhydride gives 1-acetyl-1*H*-azirine-2-carboxylic acid (10). A more reasonable product appeared to be 2-methyloxazole-4-carboxylic acid (11), a known compound [18]



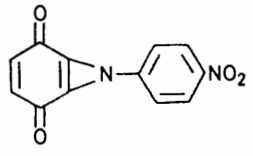
with the same m.p. as that reported for the product of the triazole reaction. Accordingly, the reaction of 1,2,3-triazole-4,5-dicarboxylic acid with acetic anhydride was repeated and a compound with the reported m.p. was isolated. This was compared with an authentic specimen of 2-methyloxazole-4-carboxylic acid, prepared by the literature method; the two were identical.

The cleavage of a monocyclic triazole ring under these conditions is unusual; such triazoles are normally acetylated without opening of the ring. Although the mechanism of the reaction is unknown, it is possible that the anhydride (12) is an intermediate; ring opening of this more strained triazole, followed by hydrolysis and decarboxylation would give 2-methyloxazole-4-carboxylic acid (Scheme 9).



SCHEME 9

Reaction of p-*Benzoquinone with* p-*Nitrophenyl Azide*.—A fused 1*H*-azirine structure (13) has been proposed for the product obtained when benzoquinone is heated in benzene with *p*-nitrophenyl azide.[19] The reaction was repeated and the product was isolated and purified. From the analytical and spectral data the 1*H*-azirine structure (13) can be ruled out. The i.r. spectrum (mull) shows a peak at 3270 cm^{-1}, which can be assigned to an NH stretching absorption, and the mass spectrum has a molecular ion at 244, which is two mass units greater than that required for structure (13). A new structure cannot be assigned with certainty on the basis of the available data.



(13)

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Varian T60 60 MHz spectrometer, and i.r. spectra for KBr discs or Nujol mulls on a Perkin-Elmer 257 spectrometer. Petroleum refers to the fraction b.p. 60—80°.

2-*Phthalimido*-2H-*Azirines*.—*By oxidation of* N-*amino-phthalimide in the presence of alkynes. General procedure.* Lead tetra-acetate (1·1 mol) was added in portions to the *N*-amino-compound (1 mol) and the alkyne (5 mol) in dry dichloromethane. The mixture was stirred for 15 min, lead diacetate was then filtered off and washed with dichloromethane, and the filtrate and washings were

[16] T. L. Gilchrist, P. G. Mente, and C. W. Rees, *J.C.S. Perkin I*, 1972, 2165.

[17] S. Yamada, T. Mizoguchi, and A. Ayata, *J. Pharm. Soc. Japan*, 1957, **77**, 452 (*Chem. Abs.*, 1957, **51**, 14,698b).

[18] J. W. Cornforth and R. H. Cornforth, *J. Chem. Soc.*, 1947, 96.

[19] G. Caronna and S. Palazzo, *Gazzetta*, 1952, **82**, 292.

evaporated. The residue consisted mainly of phthalimide (60—80%) plus the azirine. The azirine was extracted from the mixture with ether and purified by rapid chromatography on deactivated basic alumina. The following azirines were prepared in this manner.

(*a*) Oxidation of *N*-aminophthalimide in the presence of prop-1-yne at −15° gave 3-*methyl*-2-*phthalimido*-2H-*azirine* (2a) (1%), m.p. 131° (from ether–petroleum) (Found: C, 66·0; H, 4·0; N, 14·2. $C_{11}H_8N_2O_2$ requires C, 66·0; H, 4·0; N, 14·0%; *M*, 200); $\nu_{max.}$ (Nujol) 1776, 1730, 1137, 960, 728, 720, and 708 cm^{-1}; τ ($CDCl_3$) 7·24 (3H), 6·16 (1H), and 2·25 (4H, m); *m/e* 200, 185, 161, 147, 132, 104 (base), and 76.

(*b*) Oxidation in the presence of but-2-yne at −15° gave 2,3-*dimethyl*-2-*phthalimido*-2H-*azirine* (2b) (7%), m.p. 78° (from ether–petroleum) (Found: C, 67·0; H, 4·5; N, 12·8. $C_{12}H_{10}N_2O_2$ requires C, 67·3; H, 4·7; N, 13·1%; *M*, 214); $\nu_{max.}$ 1778, 1758, 1712, 1390, 1134, 884, 720, and 716 cm^{-1}; τ ($CDCl_3$) 8·23 (3H), 7·24 (3H), and 2·22 (4H); *m/e* 214, 173, 147, 132, 104, and 76.

(*c*) Oxidation in the presence of pent-1-yne gave 2-*phthalimido*-3-*propyl*-2H-*azirine* (2c) (5%), m.p. 46—47° (from ether–petroleum) (Found: C, 67·7; H, 5·3; N, 12·3. $C_{13}H_{12}N_2O_2$ requires C, 68·4; H, 5·3; N, 12·3%; *M*, 228); $\nu_{max.}$ 1778, 1720, 1138, 733, and 725 cm^{-1}; τ ($CDCl_3$) 8·89 (3H, t, *J* 7 Hz), 8·08 (2H, m), 6·90 (1H, t, *J* 7 Hz), 6·85 (1H, t, *J* 7 Hz), 6·12 (1H), and 2·24 (4H) (irradiation at τ 8·08 caused the signals at τ 6·90 and 6·85 to collapse to singlets separated by 2·5 Hz); *m/e* 228, 200, 185, 160, 147, 122, 104 (base), and 76; *m** (228 ⟶ 200) 175·5.

(*d*) Oxidation in the presence of hex-3-yne gave 2,3-*diethyl*-2-*phthalimido*-2H-*azirine* (1d) as an oil (15%) (Found: C, 68·4; † H, 5·7; N, 11·5. $C_{14}H_{14}N_2O_2$ requires C, 69·4; H, 5·8; N, 11·6%; *M*, 242); $\nu_{max.}$ (film) 1780, 1760, 1720, 1370, 1122, 1080, 879, and 719 cm^{-1}; τ (CCl_4) 9·23 (3H, t, *J* 7 Hz), 8·60 (3H, t, *J* 7 Hz), 7·92 (1H, q, *J* 7 Hz), 7·72 (1H, q, *J* 7 Hz), 6·95 (1H, q, *J* 7 Hz), 6·90 (1H, q, *J* 7 Hz), and 2·27 (4H); *m/e* 242, 224, 211, 209, 187, 158, 132, 104 (base), and 76; *m** (242 ⟶ 187) 144·5, *m** (187 ⟶ 132) 93.

By Neber reaction. 3-*Methyl*-2-*phthalimido*-2H-*azirine* (2a). (*a*) 1-Phthalimidopropan-2-one was converted into its oxime (79%), m.p. 192—197° (from ethanol) (lit.,[20] 172° and 191—192°) (Found: C, 60·5; H, 4·5; N, 12·8. Calc. for $C_{11}H_{10}N_2O_3$: C, 60·5; H, 4·6; N, 12·8%); $\nu_{max.}$ 3250, 1768, 1700, 1112, 1020, 725, and 708 cm^{-1}. (*b*) The oxime (12·5 g, 57 mmol) was dissolved in dry pyridine (50 ml) and stirred at 5°. Toluene-*p*-sulphonyl chloride (11·5 g, 60 mmol) was added and the solution was stirred for 3 h, during which time it became opaque and viscous. It was poured into water and the solid was filtered off.

Crystallisation gave 1-*phthalimidopropan*-2-*one oxime toluene*-p-*sulphonate* (13·5 g, 63%), m.p. 146—147° (from benzene) (Found: C, 58·6; H, 4·4; N, 7·5; S, 8·7. $C_{18}H_{16}N_2O_5S$ requires C, 58·1; H, 4·3; N, 7·5; S, 8·6%); $\nu_{max.}$ 1784, 1727, 1196, 1185, 870, 800, 729, 717, and 675 cm^{-1}. (*c*) Potassium t-butoxide (0·6 g, 5·35 mmol) was added to the toluene-*p*-sulphonate (3·0 g, 8·07 mmol) in dry benzene (180 ml) which was stirred under reflux (N_2 atmosphere). Further portions of potassium t-butoxide (0·6 g) were added after 2 and 4 h; after 10 h a further 1·0 g was added. The reaction was followed by t.l.c. After 10·5 h the mixture was cooled and filtered. The filtrate was evaporated and the residue washed with ether. The ethereal extract gave the crude azirine (0·550 g, 34%) on evaporation. Several recrystallisations gave a pure specimen of 3-methyl-2-phthalimido-2*H*-azirine (2a) (0·150 g, 9%), m.p. 125° (from ether–petroleum), mixed m.p. 123° with a specimen from *N*-aminophthalimide and propyne, and identical (i.r. and n.m.r.) with that specimen.

Reductive Cleavage of 2-*Phthalimido*-3-*n-propyl*-2H-*azirine.*—The azirine (2c) (0·100 g, 0·44 mmol) in ethyl acetate (6 ml) was stirred at room temperature with Pd (10% on charcoal; 0·030 g) under hydrogen, until just more than an equimolar quantity (12 ml at 760 mmHg, 0·53 mmol) had been taken up. The mixture yielded a yellow oil (0·095 g, 95%) which solidified, m.p. 72—82°. Crystallisation gave 1-(*N*-*phthalimido*)*pentan*-2-*one*, m.p. 83—84° (from ether–petroleum) (Found: C, 67·4; H, 5·8; N, 6·1%; *m/e*, 231. $C_{13}H_{13}NO_3$ requires C, 67·5; H, 5·7; N, 6·0%; *M*, 231); $\nu_{max.}$ (KBr) 1774w, 1720, 1420, 940, 725, and 715 cm^{-1}; τ ($CDCl_3$) 9·06 (3H, t, *J* 7 Hz), 8·34 (4H, m), 7·54 (2H, t, *J* 7 Hz), 6·58 (2H), and 2·24 (4H, m). An authentic specimen of 1-(*N*-phthalimido)pentan-2-one was prepared from potassium phthalimide (0·081 mol) and a mixture of 1- and 3-bromopentan-2-one [21] (0·076 mol) in dimethylformamide (60 ml) at room temperature, and had m.p. 83—84°, mixed m.p. 82—83°.

2-(3,3-*Dimethylbut*-1-*ynyl*)-2-*methyl*-1-*phthalimidoaziridine* (3).—Di-t-butylacetylene, prepared [22] by the reaction of 5-chloro-2,2,5-trimethylhex-3-yne with methylmagnesium bromide, had b.p. 113—114° at 763 mmHg (lit.,[22] 111·9° at 746 mmHg). The acetylene prepared by this procedure was not homogeneous: n.m.r. showed the presence of a second component, 2,5,5-trimethylhex-1-en-3-yne (15%). Oxidation of *N*-aminophthalimide (1 mol) by lead tetra-acetate (1 mol) in dichloromethane containing the crude acetylene (6 mol) gave phthalimide (48%) and a yellow solid (35% based on *N*-aminophthalimide), m.p. 70—85°. Crystallisation gave yellow 2-(3,3-*dimethylbut*-1-*ynyl*)-2-*methyl*-1-*phthalimidoaziridine*, m.p. 97—98° (Found: C, 72·3; H, 6·2; N, 10·2%; *m/e*, 282. $C_{17}H_{18}N_2O_2$ requires C, 72·3; H, 6·4; N, 9·9%; *M*, 282); $\nu_{max.}$ 1786w, 1766w, 1723s, and 1707s cm^{-1}; τ ($CDCl_3$) 9·09 (9H), 8·44 (3H), 7·40 (1H, d, *J* 2·5 Hz, H *trans* to ring Me), 6·55 (1H, d, *J* 2·5 Hz, H *cis* to ring Me), and 2·23 (4H).

The aziridine was again the only adduct detected when the proportion of 2,5,5-trimethylhex-1-en-3-yne in the mixture was reduced to <2% by redistillation.

Attempted Dechlorination of 2,3-*Dichloroaziridines.*—trans-2,3-*Dichloro*-1-*phthalimidoaziridine and sodium iodide.* The aziridine (4a) [5] (0·50 g, 1·95 mmol) was dissolved in acetone (10 ml) containing sodium iodide (1·5 g, 10 mmol) and the solution heated under reflux for 1·5 h. Sodium chloride was filtered off and the red filtrate evaporated. The residue was shaken with chloroform and the chloroform solution washed with aqueous sodium thiosulphate (1%; 2 × 75 ml). Evaporation of the chloroform solution left a solid (0·23 g, 38%) which was rapidly recrystallised to give orange crystals of 2-*iodoethylideneaminophthalimide* (7), m.p. 117° (from chloroform–petroleum) (Found: C, 37·8; H, 1·9; N, 9·1%; *m/e*, 314. $C_{10}H_7IN_2O_2$ requires C, 38·2;

† A consistently low carbon analysis was obtained.

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H, 2·2; N, 8·9%; *M*, 314); $\nu_{max.}$ 1783, 1760, and 1730 cm^{-1}; τ ($CDCl_3$) 5·90 (2H, d, *J* 6 Hz), 2·30—1·90 (4H, m), and 1·07 (1H, t, *J* 6 Hz). The same product was isolated from reaction of 2,2-dichloroethylideneaminophthalimide (8) under the same conditions.

trans-2,3-*Dichloro*-2,3-*dimethyl*-1-*phthalimidoaziridine and Disodium Tetracarbonylferrate*.[23]—Sodium borohydride (0·45 g, 8·4 mmol) was suspended in dry 1,2-dimethoxyethane (25 ml) and iron pentacarbonyl (0·9 ml, 6·7 mmol) was added. After 20 min methanol (9 ml) was added to decompose the excess of sodium borohydride. A solution of the aziridine (4b) [24] (0·50 g, 1·75 mmol) in tetrahydrofuran was then added and the mixture stirred for 25 h. A precipitate (0·450 g) was filtered off and the filtrate evaporated. Successive preparative layer chromatography of the residue on alumina (100 × 25 × 0·1 cm) and silica (25 × 25 × 0·1 cm) with benzene–dichloromethane (1 : 1) gave an orange solid (1 mg), m.p. 147° (decomp.); $\nu_{max.}$ (KBr) 2041, 2017, 2003, 1994, 1978, 1950w, 1799w, 1747s, 1706s, 1270, 880w, 718w, and 710 cm^{-1}; *m/e* 494, 466, 438, 410, 382, 354, 326, 285, 259, 147 (base), 104, and 76; *m** (326 ⟶ 285) 249, *m** (285 ⟶ 259) 235 ($C_{18}H_{10}Fe_2N_2O_8$ requires *M*, 494). The low yield is partly due to decomposition of the complex during chromatography: 50 mg of orange solid was applied to the second plate to effect final purification.

1,2,3-*Triazole*-4,5-*dicarboxylic Acid and Acetic Anhydride*.—1,2,3-Triazole-4,5-dicarboxylic acid was prepared from acetylenedicarboxylic acid and hydrazoic acid; m.p. 190—195° (lit.,[17] 200°). The triazole acid (3 g) and acetic anhydride (20 ml) were heated under reflux for 1 h. The acetic anhydride was removed at reduced pressure to leave a brown solid. A portion of the solid was twice sublimed at 120° and 0·1 mmHg to give 2-methyloxazole-4-carboxylic acid, m.p. 183° (lit.,[18] 183—184°), mixed m.p. 182—184° with an authentic specimen prepared by the method of Cornforth and Cornforth; [18] $\nu_{max.}$ 3170w, 3125w, 2550, 1720, 1596, 1300, 1218, 1170, 1113, 995, 931, 777, 761, 750, and 675 cm^{-1}; *m/e* 127 (M^+, base peak), 110, 99, 85, and 83.

p-*Benzoquinone and* p-*Nitrophenyl Azide*.—*p*-Benzoquinone (1·0 g) and *p*-nitrophenyl azide (1·5 g) were heated under reflux in benzene for 48 h (or in toluene for 4 h). A brown solid (0·5 g) was deposited from the red solution. The solid was dissolved in dioxan and the solution treated with charcoal, then evaporated to give an orange amorphous solid. Crystalline material was obtained by subliming the solid at 180° and 0·1 mmHg. The material showed the same physical properties before and after sublimation: m.p. >310° (darkens above 250°) (Found: C, 59·0; H, 3·4; N, 11·2. $C_{12}H_8N_2O_4$ requires C, 59·0; H, 3·3; N, 11·5%); $\nu_{max.}$ (Nujol) 3270, 3100w, 1660, 1500, 1360, 1300, and 850 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 2·83 (2H), 2·45 (2H, d, *J* 10 Hz), 1·59 (2H, d, *J* 10 Hz), and 1·6 (*ca.* 1 H, m); *m/e* 244 (M^+, base peak; $C_{12}H_8N_2O_4$ requires *M*, 244), 228, 227, 216, 215, 214, 197, 189, 170, 169, 143, and 107; *m** (244 ⟶ 227) 211, *m** (244 ⟶ 216) 192, *m** (216 ⟶ 170) 134.

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