Studies on Heterocyclic Chemistry. Part IX.[1] Reaction of 2-(Carbonyl)-2*H*-azirines with Hydrazine. A Novel and Unequivocal Synthesis of 1,2,4-Triazin-6-ones

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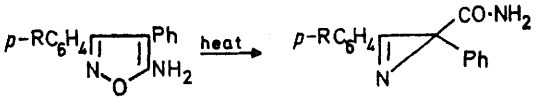
The reaction of 2*H*-azirines containing a carbamoyl or alkoxycarbonyl group at C-2 with hydrazine and phenylhydrazine has been studied. 2-Aryl-2*H*-azirine-2-carboxamides produce tetrahydro-1,2,4-triazin-6-ones in moderate yield and aziridines, which are 1 : 1 adducts of the reactants, in small yield. Alkyl 2*H*-azirine-2-carboxylates and 2*H*-azirine-2-carboxamides which have no additional substituent at C-2 afford highly coloured 2-pyrazolin-5-one derivatives.

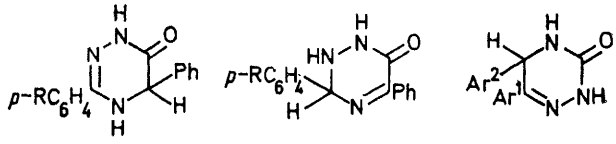
CARBONYL-SUBSTITUTED 2*H*-azirines have recently been prepared by the thermal [2] or photochemical [3] rearrangement of isoxazoles and by the reaction of nitrile oxides with a phosphorus ylide,[4] but their chemical reactions have been little studied. Prompted by our observation that the reaction of 3-aryl-2*H*-azirine-2-carboxamides and 2-methyl-3-phenyl-2*H*-azirine-2-carboxamide with arylamines takes place at the carbonyl function rather than at the C=N bond,[1] we have studied their behaviour towards hydrazine.[5] The reaction of 2-benzoyl-3-phenyl-2*H*-azirine with hydrazine has previously been briefly described.[3]

2,3-Diaryl-2*H*-azirine-2-carboxamides (2; R = H, Cl, or Me) were prepared from the 5-amino-3,4-diarylisoxazoles (1; R = H, Cl, or Me) in high-boiling solvent under reflux. The experimental conditions had to be carefully chosen to avoid decomposition of the azirines during heating: for example, compound (1; R = H) could isomerise into (2; R = H) in up to 70% yield in tetralin, whereas (1; R = Me) gave (2; R = Me) in negligible yield in this solvent, but in 52% yield in decalin. Photochemical isomerisation [2c,3] of (1; R = H) into (2; R = H) was also studied, but the yield was too low for preparative purposes.



(1) (2)

The reaction of these 2,3-diaryl-2*H*-azirine-2-carboxamides with hydrazine was rapid: mixing of the reactants at room temperature was exothermic and within minutes the u.v. spectrum showed absorption at *ca.* 305 nm. Chromatography of the products from the azirine (2; R = H) afforded a crystalline material $C_{15}H_{13}N_3O$ in 38% yield. Its i.r. spectrum lacked the ν(C=N) band of 2*H*-azirines,[2b] indicating that reaction might have taken place at the C=N bond, and suggested the presence of a six-membered lactam having an additional NH group [$\nu_{max.}$ (Nujol) 1670 (C=O) and 3340 and 3150 (NH) cm^{-1}]. Its n.m.r. spectrum accounted for all the protons. The presence of two doublets, at τ 4·98 (1H, *J* 2 Hz) and 1·94 (1H, *J* 2 Hz), and the fact that the former changed into a singlet and the latter disappeared on deuteriation showed the presence of a CH–NH group. There were two phenyl groups in different chemical environments [τ 2·63 (5H, s) and 2·08—2·55 (5H, m)]. An exchangeable one-proton signal at —0·70 suggested the presence of a lactam proton. The reaction of other azirines (2; R = Cl and Me) with hydrazine proceeded analogously and gave crystalline materials ($C_{15}H_{12}ClN_3O$ and $C_{16}H_{15}N_3O$, respectively) in comparable yield, the n.m.r. spectra of which were similar to that of the compound just described. The u.v. spectra of these three compounds resembled each other and indicated a common structure. On the basis of these observations, tetrahydro-1,2,4-triazinone structures (3)—(5) can be formulated. Structure (5) can be eliminated since the compound (5; $Ar^1 = Ar^2 = Ph$) has m.p. 278°.[6] The product from (2; R = H) has m.p. 203°, and its u.v. and i.r. spectra are different from those reported.[6]



(3) (4) (5)

The structures (3; R = H, Cl, or Me) were assigned to these products in the light of their mass spectra. The spectrum of compound (3; R = H) [M^+, 251 90%)] exhibited ions at *m/e* 146 (100%) and 105 (26%); the spectrum of the product (3; R = Cl) [M^+, *m/e* 285 and 287 (82 and 28%)] had corresponding ions at 180 and 182 (100 and 33%) and 105 (31%). Structure (3) satisfactorily explains the origin of these ions: scission at the dotted line produces ions at *m/e* (145 + R) (*a*) and 105 (*b*). As the ion (*b*) is an odd-electron species, it can decompose into a stable protonated nitrile ion, *m/e* 104 [43% for (3; R = H) and 33% for (3; R = Cl)].

[1] Part VIII, T. Nishiwaki, T. Saito, S. Onomura, and K. Kondo, *J. Chem. Soc.* (*C*), preceding paper.

[2] (*a*) T. Nishiwaki, *Tetrahedron Letters*, 1969, 2049; (*b*) T. Nishiwaki, T. Kitamura, and A. Nakano, *Tetrahedron*, 1970, **26**, 453; (*c*) T. Nishiwaki, A. Nakano, and H. Matsuoka, *J. Chem. Soc.* (*C*), 1970, 1825.

[3] B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, 1967, **89**, 6911.

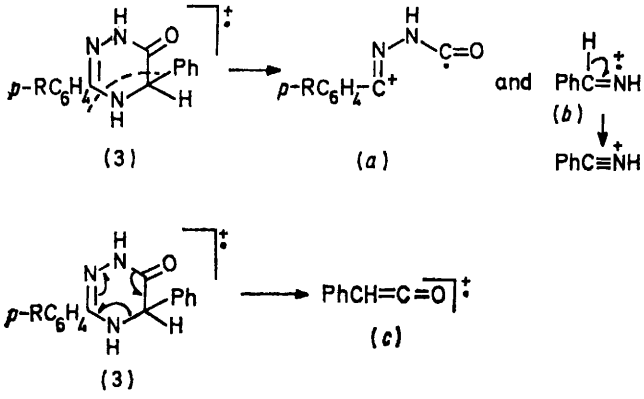
[4] H. J. Bestman and R. Kunstmann, *Chem. Ber.*, 1969, **102**, 1816.

[5] Preliminary account, T. Nishiwaki and T. Saito, *Chem. Comm.*, 1970, 1479.

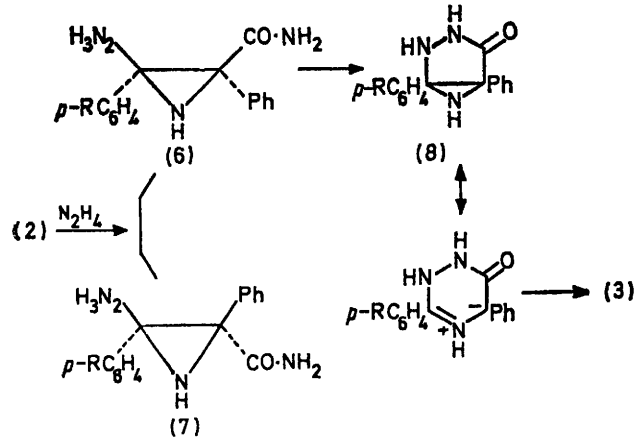
[6] T. Sasaki and K. Minamoto, *J. Org. Chem.*, 1966, **31**, 3914.

Additional support for structure (3) was given by the presence of the ion *m/e* 118 (10% in both spectra), generated by a retro-Diels–Alder fragmentation, as has been observed for 1,3,4-trimethyluracil,[7] which can be depicted as a phenylketen radical ion (*c*). An appreciable ion current at (*M* − 29) also supported the presence of an N_2H structural unit.

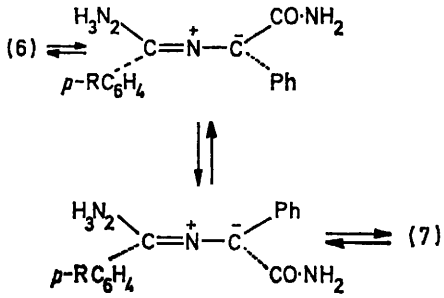
T.l.c. of the crude product from the azirine and hydrazine indicated the presence of a second compound, with a lower R_F value; the products from (2; R = H) and (2; R = Me) were examined in detail. A crystalline material with analytical figures corresponding to a 1 : 1 adduct of (2) and hydrazine was isolated in <10% yield. As its i.r. spectrum lacked the ν(C=N) band of 2*H*-azirines and showed absorptions at *ca.* 3000 ascribable to ν(NH_2 and NH) and at 1678 cm^{-1} (C=O), it must be the 3-hydrazinoaziridine-2-carboxamide (6)



or (7). This compound could be recrystallised with no loss of ammonia from boiling solvent; thus the structure (7) in which the hydrazino-group is *trans* to the carboxamide group is assigned to it.



The aziridine (6) must also be produced if the approach of the hydrazine to the C=N bond of 2,3-diaryl-2*H*-azirine-2-carboxamides is less stereospecific. But the stereochemistry of the substituents of (6) would make the loss of ammonia easy and the resulting bicyclic aziridine (8) would undergo ring opening to give structure (3), probably *via* the azomethine ylide.[8] The driving force behind the conversion (8) ⟶ (3) will be the relief of the ring strain in (8). This reaction resembles the recently reported thermal (conrotatory) ring opening of an indeno[1,2-*b*]azirine,[9] although the reaction reported herein proceeds at room temperature. We consider it unlikely that hydrazine approaches the C=N bond from one side only, relative to the carboxamide group, and that the aziridine produced equilibrates thermally [10] with its tautomer *via* an azomethine ylide, since the reaction proceeded rapidly at room temperature and (7) was unchanged on heating. It is known that reaction of 2*H*-azirines with nucleophiles

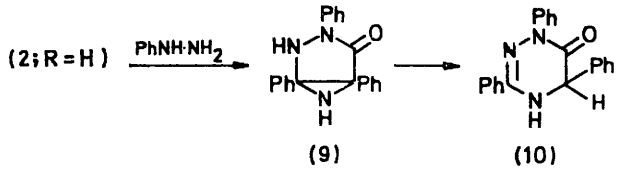


such as lithium aluminium hydride,[11a] Grignard reagents,[11b] sulphinic acids,[11c] and trialkyl phosphites [11d] yields aziridines, and the addition is such as to give the product derived from attack on the least hindered side of the azirine.[11a,b] In view of this, the isolation of (3) and (7) from the reaction of (2) with hydrazine is interesting.

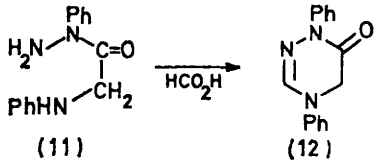
The foregoing reactions also proceed with substituted hydrazines. The reaction of the azirine (2; R = H) with phenylhydrazine took place in methanol under reflux but more slowly. A crystalline product $C_{21}H_{17}N_3O$ was isolated in 7% yield; its composition indicated the loss of ammonia from the 1 : 1 adduct of the reactants. Its i.r. spectrum suggested the presence of a lactam, and its n.m.r. spectrum displayed coupled doublets (*J* 3 Hz) at τ 4·73 (1H) and 1·45 (1H). On deuteriation the former changed into a singlet and the latter disappeared, thus indicating the presence of a CH–NH group. Complex signals at τ 2·00—2·72 were ascribed to the three phenyl groups. Therefore, the product has structure (10), which must be produced *via* a bicyclic intermediate (9). The yield of (10) was, however, poor; this suggests the operation of other reactions, but the remaining materials could not be identified.

In 1893, Widman proposed the tetrahydro-1,2,4-triazin-6-one structure (12) for the product from *N*-phenyl-*N*-(*N*-phenylglycyl)hydrazine (11) and formic acid

[7] T. Nishiwaki, *Tetrahedron*, 1966, **22**, 3117.
[8] R. Huisgen, W. Scheer, and H. Hubert, *J. Amer. Chem. Soc.*, 1967, **89**, 1753.
[9] J. W. Lown and K. Matsumoto, *Chem. Comm.*, 1970, 692.
[10] J. A. Deyrup, *J. Org. Chem.*, 1969, **34**, 2724.
[11] (*a*) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 1968, **90**, 2869; (*b*) R. M. Carlson and Sin Yen Lee, *Tetrahedron Letters*, 1969, 4001; (*c*) J. S. Meek and J. S. Fowler, *J. Org. Chem.*, 1968, **33**, 3418; (*d*) T. Nishiwaki, unpublished results.

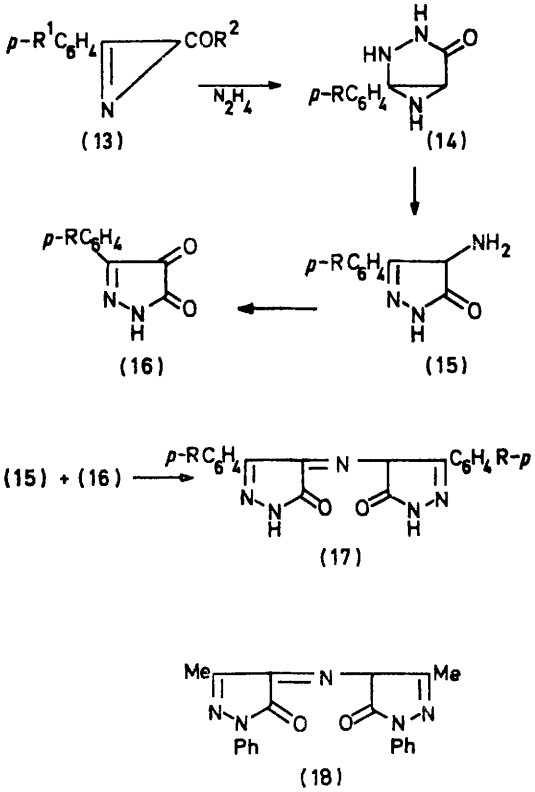


on the basis of analysis and chemical properties: it did not dissolve in dilute alkali, was soluble in concentrated hydrochloric acid, and did not react with Fehling's solution.[12] Since then, there have been no reports of



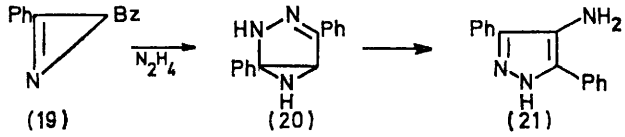
this ring system.[13] Our synthesis is simple and unequivocal. In addition, it attests to the usefulness of isoxazole derivatives[14] in the syntheses of heterocyclic compounds; the azirines can be conveniently prepared from isoxazoles.

However, the reaction of alkyl 2*H*-azirine-2-carboxylates and 2*H*-azirine-2-carboxamides having no additional substituent at C-2 proceeded differently. When methyl 3-*p*-chlorophenyl-2*H*-azirine-2-carboxylate (13;



R^1 = Cl, R^2 = OMe)[2b] was mixed with hydrazine, a reddish violet colour developed immediately with the evolution of heat, and a yellow-purple compound ($\nu_{max.}$ 260 nm) was obtained. The colour of the compound deepened gradually in air and rapidly in an alcoholic solvent, from which red crystals were isolated. Addition of sodium dithionite to the alcoholic solution resulted in loss of colour; in air, the red colour slowly returned. The colour changed to purple on adding dilute sodium hydroxide to the alcoholic solution (see Experimental section) and reverted to red on acidification. These properties resemble those reported for rubazonic acid (18),[15] and analysis suggests, though not completely satisfactorily, the presence of compound (17; R = Cl), an analogue of (18).

Ullman *et al.* obtained 4-amino-3,5-diphenylpyrazole (21) by the reaction of 3-phenyl-2*H*-azirin-2-yl phenyl ketone (19) with hydrazine.[3] They did not discuss the mechanism, but the reaction probably proceeds *via* structure (20). 4-Amino-3-methyl-1-phenyl-2-pyrazolin-5-one is a labile compound[15] and easily changes into 3-methyl-1-phenyl-2-pyrazoline-4,5-dione in air. Condensation of these two compounds affords rubazonic



acid (18). Thus, the initial product from (13; R = Cl, R^2 = OMe) must be (15; R = Cl), formed *via* the bicyclic aziridine (14; R = Cl), and if so, the observed value of $\lambda_{max.}$ (260 nm) and labile nature can be explained as being due to (15; R = Cl). Therefore, we regard the final coloured product as (17; R = Cl). As the reactions of (13; R^1 = H, R^2 = OMe) and (13; R^1 = H, R^2 = NH_2) proceeded similarly, only the product from the ester was chemically examined, and structure (17; R = H) was assigned.

The ring cleavage of the intermediate bicyclic aziridines (8) and (9) takes place at a C–C bond, whereas the scission of (14) and (20) occurs at a C–N bond. Although this difference can not be satisfactorily accounted for at present, the relief of strain in these bicyclic intermediates must be the major driving force for the reactions.

EXPERIMENTAL

N.m.r. spectra were run at 60 Hz for solutions in [$^2H_6$]dimethyl sulphoxide with tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi RMU 7 spectrometer at 70 eV (direct inlet system; source temperature *ca.* 150°). Analyses were carried out at the Department of Pharmacy, Kyoto University. Light petroleum had b.p. 30—70°.

[12] O. Widman, *Ber.*, 1893, **26**, 2612.
[13] J. P. Horwitz, 'Heterocyclic Compounds,' ed. R. C. Elderfield, vol. 7, Wiley, New York, 1961, p. 720.
[14] A. N. Kost and I. I. Grandberg, *Adv. Heterocyclic Chem.*, 1966, **6**, 347; K.-H. Wunsche and A. J. Boulton, *ibid.*, 1967, **8**, 277; A. J. Boulton, A. R. Katritzky, and A. Majd Hamid, *J. Chem. Soc.* (*C*), 1967, 2005; D. N. McGregor, U. Corbin, J. E. Swigor, and L. C. Cheney. *Tetrahedron*, 1969, **25**, 389; K. Kotera, Y. Takano, A. Matsuura, and K. Kitahonoki, *ibid.*, 1970, **26**, 539.
[15] T. L. Jacobs, 'Heterocyclic Compounds,' ed. R. C. Elderfield, vol. 5, Wiley, New York, 1957, p. 149.

Benzoylphenylacetonitrile.—This was prepared as described [16] (commercial sodium ethoxide was used without further drying), but in better yield (35%) than reported,[16] m.p. 98—100° (from acetic acid) (lit.,[17] m.p. 91—92°) (Found: C, 81·3; H, 5·0; N, 6·25. Calc. for $C_{15}H_{11}NO$: C, 81·4; H, 5·0; N, 6·3%).

p-*Toluoylphenylacetonitrile*.—Commercial sodium ethoxide (13·3 g, 0·196 mol) was added to a solution of ethyl *p*-toluate (31·2 g, 0·196 mol) and benzyl cyanide (22·9 g, 0·196 mol) in anhydrous ether (150 ml) and the mixture was stirred for 2 h at room temperature. After 5 days, water (100 ml) was added to this mixture and the aqueous solution was acidified. Organic material was extracted into ether (2 × 50 ml) and the extracts were dried ($CaCl_2$). Evaporation left an oil, which solidified and was recrystallised from benzene–hexane (12·9 g; 28% yield). Further recrystallisation gave pale yellow *rods*, m.p. 103—105° (Found: C, 81·6; H, 5·55; N, 5·8. $C_{16}H_{13}NO$ requires C, 81·7; H, 5·6; N, 5·95%).

p-*Chlorobenzoylphenylacetonitrile*.—This was prepared similarly in 36% yield as *plates* [from benzene–light petroleum (100—120°)], m.p. 98—100° (Found: C, 70·15; H, 4·05; N, 5·45. $C_{15}H_{10}ClNO$ requires C, 70·45; H, 3·9; N, 5·5%).

5-*Amino*-3,4-*diphenylisoxazole* (1; R = H).—Preparation [16] of this compound was modified as follows. Hydroxylamine hydrochloride (2·3 g) was added to a solution of benzoylphenylacetonitrile (5·2 g) in pyridine (13 ml) and the mixture was kept overnight. It was then heated on a steam-bath for 15 min and poured on ice–water, affording a solid. Two recrystallisations from aqueous ethanol gave rods (3·9 g, 70%), m.p. 162—162·5° (lit.,[16] m.p. 160—162°), $\lambda_{max.}$ (EtOH) 229 (log ε 4·31) and 264 nm (4·11).

By the same procedure 5-*amino*-3-p-*chlorophenyl*-4-*phenylisoxazole* (1; R = Cl) [68% yield, m.p. 133—134° (from aqueous methanol) (Found: C, 66·7; H, 3·9; N, 10·25. $C_{15}H_{11}ClN_2O$ requires C, 66·55; H, 4·1; N, 10·35%), $\lambda_{max.}$ 240 nm (log ε 4·23) and 270sh] and 5-*amino*-4-*phenyl*-3-p-*tolylisoxazole* (1; R = Me) [53% yield, m.p. 137° (from benzene–hexane) (Found: C, 77·0; H, 5·6; N, 11·25. $C_{16}H_{14}N_2O$ requires C, 76·8; H, 5·6; N, 11·2%), $\lambda_{max.}$ (EtOH) 236 nm (log ε 4·24) and 265sh] were prepared.

2,3-*Diphenyl*-2H-*azirine*-2-*carboxamide* (2; R = H).—(*a*) The isoxazole (1; R = H) (3·0 g) was heated under reflux in tetralin (150 ml) for 2 h. Next day the precipitate was collected and washed with light petroleum, giving the *azirine* (2·2 g, 73%) as needles, m.p. 181—182° (from carbon tetrachloride) (Found: C, 76·1; H, 5·0; N, 11·95. $C_{15}H_{12}N_2O$ requires C, 76·25; H, 5·1; N, 11·9%), $\lambda_{max.}$ (EtOH) 245 nm (log ε 4·21), $\nu_{max.}$ ($CHCl_3$) 3520 and 3420 (NH_2), 1758 (C=N), and 1683 (C=O) cm^{-1}. The yield was 18% after 6 h under reflux. With the same ratio of (1; R = H) to solvent, the following results were obtained (with the last two solvents the product had to be isolated by removal of the solvent *in vacuo*).

Solvent	Reflux time *t*/h	Yield (%)
Decalin	2	86
o-Dichlorobenzene	2	64
Dimethylformamide	2	50
Bis-(2-methoxyethyl) ether	12	36

(*b*) The isoxazole (1; R = H) (0·52 g) in ether (550 ml) was irradiated with a Pyrex-filtered high-pressure mercury lamp (100 W) for 90 min, a yellow colour developing within a few min. The solvent was removed and the tenacious orange gum was washed with ether, leaving an insoluble material (0·04 g, 8%) which was purified as before, m.p. 182°.

3-p-*Chlorophenyl*-2-*phenyl*-2H-*azirine*-2-*carboxamide* (2; R = Cl).—The isoxazole (1; R = Cl) (2·0 g) was heated under reflux in tetralin (100 ml) for 1 h. The solvent was removed *in vacuo*, and light petroleum (100 ml) was added to the residue. The mixture separated; the solvent was removed by decantation to leave an oil, which gave crystals (0·423 g) on trituration with ethanol (2 ml). The petroleum solution was concentrated to *ca.* 50 ml, to give a small amount of sticky solid. This was filtered off and washed twice with ethanol (1 ml). The combined materials (0·720 g, 36%) crystallised from heptane as *needles*, m.p. 119—121° (Found: C, 66·7; H, 4·3; N, 10·4. $C_{15}H_{11}ClN_2O$ requires C, 66·55; H, 4·1; N, 10·35%), $\lambda_{max.}$ (EtOH) 258 nm (log ε 4·34), $\nu_{max.}$ ($CHCl_3$) 3520 and 3410 (NH_2), 1756 (C=N), and 1682 (C=O) cm^{-1}. This azirine was obtained in 23% yield by heating (1; R = Cl) (2·0 g) under reflux in decalin (100 ml) for 90 min.

2-*Phenyl*-3-p-*tolyl*-2H-*azirine*-2-*carboxamide* (2; R = Me).—The isoxazole (1; R = Me) (4·0 g) was heated under reflux in decalin (200 ml) for 45 min with stirring. The temperature was lowered to 90° and light petroleum (100—120°) (300 ml) was slowly added, whereupon solids were precipitated. These were collected (2·1 g, 52%) (a small amount of a red gum stuck to the walls) and recrystallised from heptane. An analytical sample was obtained as pale yellow *needles*, m.p. 129—130° [from cyclohexane (charcoal)] (Found: C, 76·9; H, 5·9; N, 11·2. $C_{16}H_{14}N_2O$ requires C, 76·8; H, 5·6; N, 11·2%), $\lambda_{max.}$ (EtOH) 258 nm (log ε 4·25), $\nu_{max.}$ ($CHCl_3$) 3500 and 3390 (NH_2), 1752 (C=N), and 1680 (C=O) cm^{-1}.

Reaction of the Azirine (2; R = H) *with Hydrazine*.—Hydrazine hydrate (80%) (1·0 ml) was added to a solution of (2; R = H) (0·70 g) in methanol (30 ml) and this mixture was kept at room temperature for 3 h; the solution became yellow ($\lambda_{max.}$ 304 nm) within a few min. The solvent was evaporated off and the residue triturated with ether (10 ml) to give solids which were chromatographed on silica gel. Elution with ether gave the *triazin*-6-*one* (3; R = H) (0·28 g, 38%) as rods, m.p. 203—204° (from ethyl acetate–hexane) (Found: C, 72·2; H, 5·2; N, 17·1; O, 6·4. $C_{15}H_{13}N_3O$ requires C, 71·7; H, 5·2; N, 16·7; O, 6·4%), $\lambda_{max.}$ (EtOH) 228 (log ε 4·31) and 304 nm (3·90). Elution with ether–methanol (2 : 1) afforded the *aziridine* (7; R = H) (0·07 g, 9%) as rods, m.p. 186—187° (from benzene) (Found: C, 67·1; H, 6·0; N, 20·95. $C_{15}H_{16}N_4O$ requires C, 67·1; H, 6·0; N, 20·9%), $\nu_{max.}$ (Nujol) 3430, 3390, 3350, 3270, and 3140 (NH_2 and NH) and 1678 (C=O) cm^{-1}.

The Reaction of the Azirine (2; R = Cl) *with Hydrazine*.—A solution of the azirine (0·420 g) in methanol (15 ml) was mixed with hydrazine hydrate (80%) (0·5 ml); an absorption at 310 nm developed within a few min. This mixture was heated under reflux for 2 h and the solvent was evaporated off. The residue was washed with ether and chromatographed on silica gel. Elution with ether gave the *triazin*-6-*one* (3; R = Cl) (0·160 g, 36%) as plates, m.p. 231—232° (from benzene) (Found: C, 63·1;

[16] R. von Walther and L. Schickler, *J. prakt. Chem.*, 1897, **55**, 305.

[17] W. Wislicenus, E. Eichert, and M. Marquardt, *Annalen*, 1924, **436**, 88.

H, 4·0; Cl, 12·6; N, 14·5. $C_{15}H_{12}ClN_3O$ requires C, 63·05; H, 4·2; Cl, 12·4; N, 14·7%), $\lambda_{max.}$ (EtOH) 236 (log ε 4·43) and 310 nm (4·06), $\nu_{max.}$ (Nujol) 3200 (NH) and 1650 (C=O) cm^{-1}, τ 4·97 (1H, d, *J* 2 Hz, changed into a singlet on deuteriation), 2·62 (5H, s), 2·48 (2H, d, *J* 8 Hz), 2·13 (2H, d, *J* 8 Hz), 1·85 (1H, broad d, *J* 2 Hz), exchangeable), and −0·76 (1H, s, exchangeable). When the reaction was carried out at room temperature, the yield of (3; R = Cl) was 37%.

The Reaction of the Azirine (2; R = Me) *with Hydrazine.*—A solution of the azirine (0·890 g) in methanol (20 ml) was mixed with hydrazine hydrate (80%) (1·3 ml) and kept for 2 h at room temperature, during which time crystals (0·230 g) were deposited. These were filtered off; concentration of the filtrate gave an additional crop and the combined materials (3; R = Me) (0·380 g, 40%) crystallised from benzene as rectangular *plates*, m.p. 246—248° (Found: C, 72·6; H, 5·8; N, 15·8; O, 6·2. $C_{16}H_{15}N_3O$ requires C, 72·4; H, 5·7; N, 15·8; O, 6·0%), $\lambda_{max.}$ (EtOH) 233 (log ε 4·31) and 303 nm (3·96), $\nu_{max.}$ (Nujol) 3300sh and 3150 (NH), and 1663 (C=O) cm^{-1}, τ 7·71 (3H, s), 4·99 (1H, d, *J* 2 Hz, changed into a singlet on deuteriation), 2·63 (5H, s), 2·72 (2H, d, *J* 8 Hz), 2·25 (2H, d, *J* 8 Hz), 1·98 (1H, d, *J* 2 Hz, exchangeable), and −0·68 (1H, s, exchangeable). The filtrate was evaporated to dryness and the residue was chromatographed on silica gel. Elution with ether gave a product unidentified as yet, and subsequent elution with ether–methanol (2 : 1) gave the *aziridine* (7; R = Me) (0·083 g, 8%) as prisms, m.p. 157—159° (from ethyl acetate–hexane) (Found: C, 67·9; H, 6·5; N, 19·6. $C_{16}H_{18}N_4O$ requires C, 68·1; H, 6·4; N, 19·85%), $\nu_{max.}$ (Nujol) 3430, 3390, 3280, and 3160 (NH_2 and NH) and 1678 (C=O) cm^{-1}.

The Reaction of the Azirine (2; R = H) *with Phenylhydrazine.*—The azirine (2; R = H) (1·6 g) and phenylhydrazine (1·5 ml) were heated in methanol (30 ml) for 5 h. The solvent was removed and 2N-hydrochloric acid (30 ml) was added to the residue. Extraction with ether and evaporation of the extract gave an oil, which afforded crystals (10) (0·16 g, 7%) on trituration with methanol (3 ml). Recrystallisation from benzene–hexane gave *rods*, m.p. 228—229° (Found: C, 77·3; H, 5·3; N, 12·6. $C_{21}H_{17}N_3O$ requires C, 77·0; H, 5·2; N, 12·8%), $\lambda_{max.}$ (EtOH) 227 (log ε 4·40), 261 (4·09), and 308 nm (3·93), $\nu_{max.}$ (Nujol) 3280 (NH) and 1650 (C=O) cm^{-1}. The ether-insoluble material (0·50 g) was a complex mixture (t.l.c.) and was discarded.

The Reaction of the Azirine (13; R^1 = Cl, R^2 = OMe) *with Hydrazine.*—Hydrazine hydrate (80%) (0·3 ml) was added to a solution of the azirine (0·47 g) in methanol (3 ml); a reddish-violet colour developed immediately. The mixture was left for 15 min at room temperature and evaporated to dryness, leaving a solid [0·40 g, $\lambda_{max.}$ (EtOH) 260 and *ca.* 310sh nm]. Three recrystallisations from n-butanol gave (17; R = Cl) as red *needles*, m.p. 265—267° (decomp.) (single product, as shown by t.l.c.; dried at 80° and 3 mmHg) (Found: C, 53·4; H, 3·65; Cl, 16·7; N, 16·9. $C_{18}H_{11}Cl_2N_5O_2,0·5H_2O$ requires C, 52·8; H, 3·0; Cl, 17·3; N, 17·1%), $\lambda_{max.}$ (EtOH) 211 (log ε 4·40), 245 (4·42), 371 (4·07), and 454 nm (4·10) (addition of 0·1N-sodium hydroxide changed the absorptions to 255, 349, 430, and 557 nm).

The Reaction of the Azirine (13; R^1 = H, R^2 = OMe) *with Hydrazine.*—By a similar method, compound (17; R = H) was obtained from (13; R^1 = H, R_2 = OMe) as red *needles*, m.p. 250—252° (decomp.) (from ethanol) (single product as shown by t.l.c.) (Found: C, 62·65; H, 4·9; N, 19·4. $C_{18}H_{13}N_5O_2,H_2O$ requires C, 61·9; H, 4·3; N, 20·05%), $\lambda_{max.}$ (EtOH) 237 (log ε 4·41), 371 (4·21), and 455 nm (4·21) [addition of 0·1N-sodium hydroxide gave a purple colour ($\lambda_{max.}$ 247, 348, 425, and 558 nm)]. Reduction of the coloured solution with sodium dithionite gave a colourless solution.

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