Preparation, Mass Spectra, and Acid-catalysed Rearrangement of Aryl-substituted Azetidin-2-ones

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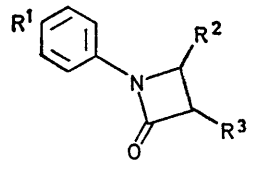
Several acid-catalysed reactions of aryl-substituted azetidin-2-ones are described. Thus 1,3,4-triphenylazetidin-2-one underwent rearrangement in concentrated sulphuric acid to yield the isomeric 3,4-dihydro-3,4-diphenylquinolin-2(1*H*)-one; however, reaction in toluene with boron trifluoride as catalyst yielded *N*,2,3-triphenyl-3-(4-tolyl)propionamide, a toluene adduct. 1,4-Diphenylazetidin-2-one underwent similar reactions, but when the rearrangement was performed in chlorobenzene the isomeric cinnamanilide was obtained. In contrast, treatment of 1,3,3,4,4-pentaphenylazetidin-2-one with boron trifluoride in toluene caused a fission reaction and α-phenylbenzylideneaniline and diphenylacetic acid were isolated, whereas 1,3,4,4-tetraphenylazetidin-2-one yielded 2,3-diphenylindene by extrusion of a molecule of aniline. The mass spectra of several aryl-substituted azetidin-2-ones are discussed in terms of the principal decomposition modes which yield ions due to keten, anil, olefin, and isocyanate fragments.

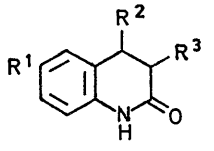
MANY varied rearrangements of derivatives of azetidin-2-ones are now known, although the majority of these have been demonstrated with the reactive penicillin nucleus. Rearrangements of monocyclic azetidin-2-ones include epimerisation,[1] ring fission,[2] ring expansion,[3] a Cope-type reaction,[4] and rearrangements of amino-azetidinones.[5] Further, it has been shown that 1,4-diphenylazetidin-2-one, on treatment with concentrated sulphuric acid, yields 3,4-dihydro-4-phenylquinolin-2(1*H*)-one [6] (formation of a 4,4a-bond), whereas 1,3,3,4,4-pentaphenylazetidin-2-one gives 3,4-dihydro-1,3,3,4-tetraphenylquinolin-2(1*H*)-one [7] (formation of a 1,8a-bond). We have now shown that, depending upon the reaction conditions and the substituents present in the azetidinone ring, acid-catalysed rearrangement may proceed by any of several pathways.

Treatment of 1-(4-methoxyphenyl)-4-phenylazetidin-2-one (1) with concentrated sulphuric acid at room temperature for 16 h yielded the isomeric 6-methoxy-4-phenylquinolin-2(1*H*)-one (2), identical with a sample prepared from 4'-methoxycinnamanilide and polyphosphoric acid.[8] This reaction may involve *O*-protonation which initiates 3,4-bond fission; the resulting intermediate then cyclises to yield the quinolinone *via* the stabilised benzylic carbonium ion. The course of the reaction was unchanged when trisubstituted compounds were used, and 1,3,4-triphenyl- (3) and 1-(4-chlorophenyl)-3,4-diphenyl-azetidin-2-ones (5) underwent similar reactions to yield the corresponding quinolinones, (4) and (6).

It has been shown [6] that, when no cyclisation takes place, olefins which are isomeric with the azetidinone may be isolated; in attempts to isolate intermediates from the cyclisation reactions, the reaction conditions were varied. Initial attempts to catalyse the rearrangement with a



(1) R^1 = OMe, R^2 = Ph, R^3 = H
(3) R^1 = H, R^2 = R^3 = Ph
(5) R^1 = Cl, R^2 = R^3 = Ph

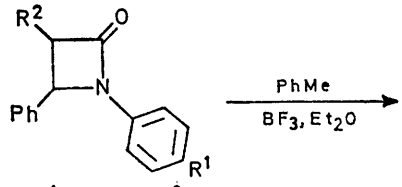


(2) R^1 = OMe, R^2 = Ph, R^3 = H
(4) R^1 = H, R^2 = R^3 = Ph
(6) R^1 = Cl, R^2 = R^3 = Ph

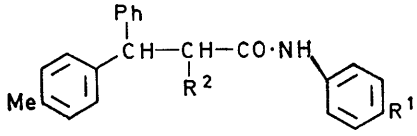
Lewis acid (boron trifluoride–diethyl ether complex) in chloroform were unsuccessful (starting material was recovered) but when toluene was used as solvent reaction occurred. Thus 1-(4-methoxyphenyl)-3,4-diphenylaze-

[1] A. K. Bose, C. S. Narayanan, and M. S. Manhas, *Chem. Comm.*, 1970, 975.
[2] L. Paquette, M. Wyuratt, and G. Allen, *J. Amer. Chem. Soc.*, 1970, **92**, 1763; M. Fischer, *Chem. Ber.*, 1968, **101**, 2669.
[3] D. Barman, *Angew. Chem. Internat. Edn.*, 1969, **8**, 892; T. Doyle and T. Conway, *Tetrahedron Letters*, 1969, 1889.
[4] H. Schinabel, *Angew. Chem. Internat. Edn.*, 1969, **8**, 922.
[5] C. W. Bird and J. D. Twibell, *J. Chem. Soc.* (*C*), 1971, 3155.
[6] I. Knunyants and N. Gambaryan, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1957, **7**, 834.
[7] S. Sarel, E. Breuer, J. T. Klug, and Y. Fattal, *Israel J. Chem.*, 1966, **4**, 233.
[8] R. Conley and W. Knopka, *J. Org. Chem.*, 1964, **29**, 496.

tidin-2-one (1), boron trifluoride, and toluene, heated under reflux, yielded a colourless product [*m/e* 421 (M^+)], which, however, was not isomeric with the azetidinone [*m/e* 329 (M^+)]. This mass difference (equivalent to a toluene molecule), the presence of an extra methyl resonance (τ 7·8) in the ^{1}H n.m.r. spectrum, and the increase in the vicinal coupling constant of the azetidinone ring protons from 2·5 (cyclic *trans*) to 12 Hz (acyclic *anti*) rather than the 6 Hz found for the 3,4-diphenylquinolinone (4) suggested that an intermolecular

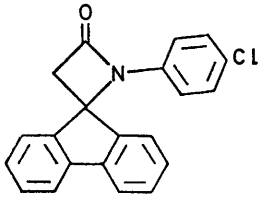


(7) R^1 = OMe, R^2 = Ph
(9) R^1 = R^2 = H
(11) R^1 = H, R^2 = Ph



(8) R^1 = OMe, R^2 = Ph
(10) R^1 = R^2 = H
(12) R^1 = H, R^2 = Ph

reaction with solvent had occurred to yield *N*-(4-methoxyphenyl)-2,3-diphenyl-3-(4-tolyl)propionamide (8). 1,4-Diphenyl- (9) and 1,3,4-triphenyl-azetidinone (11), and the spirofluorene (13) similarly yielded ring-opened β-(4-tolyl) amides [(10), (12), and (14)]. The use



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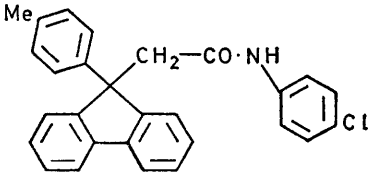


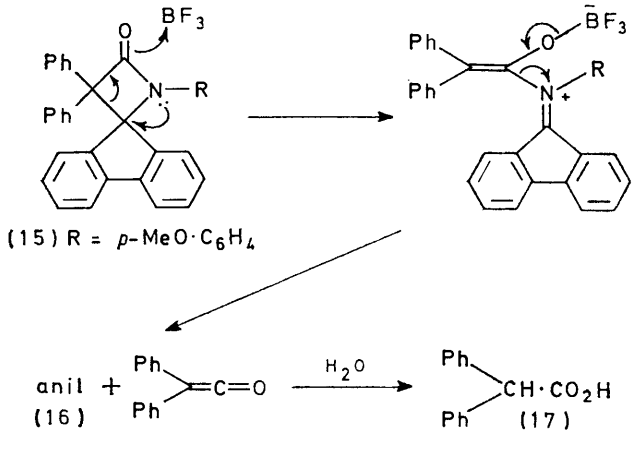
(14)

of other reactive aromatic solvents furnished similar products and in this way 1,4-diphenylazetidin-2-one (9) and anisole yielded 3-(4-methoxyphenyl)-*N*,3-diphenyl-propionamide.

The formulation of these reaction products as ring-opened amides which had undergone electrophilic substitution by an aromatic solvent prompted an investigation of the reaction in an inert solvent. 1,4-Diphenylazetidin-2-one and boron trifluoride in chlorobenzene yielded a product without solvent incorporation which was isomeric with both azetidinone and quinolinone, and which was shown to be cinnamanilide. Under the conditions of the foregoing experiments, cinnamanilide did not react with toluene to yield the (4-tolyl)propionamide, a fact which precludes the intermediacy of olefins in those reactions.

Treatment of 1,3,3,4,4-pentaphenylazetidin-2-one with toluene and boron trifluoride, however, did not yield the expected fully-substituted propionamide, but gave a mixture of α-phenylbenzylideneaniline and diphenylacetic acid. The latter probably results from reaction of the initially formed diphenylketen, for the presence of ethanol leads to the isolation of ethyl diphenylacetate. The reaction of 1'-(4-methoxyphenyl)-3',3'-diphenylfluorene-9-spiro-2'-azetidin-4'-one (15), another fully substituted compound, followed a similar pathway to yield the corresponding anil (16) and diphenylacetic acid (17). This type of fission reaction appears to be limited to fully substituted azetidinones in which substituents at C-3 and C-4 are eclipsed. This will exert considerable strain on the C(3)–C(4) bond and it is probable that the relief of this strain is the driving force for reaction, rather than the production of the stabilised carbonium ion observed previously.

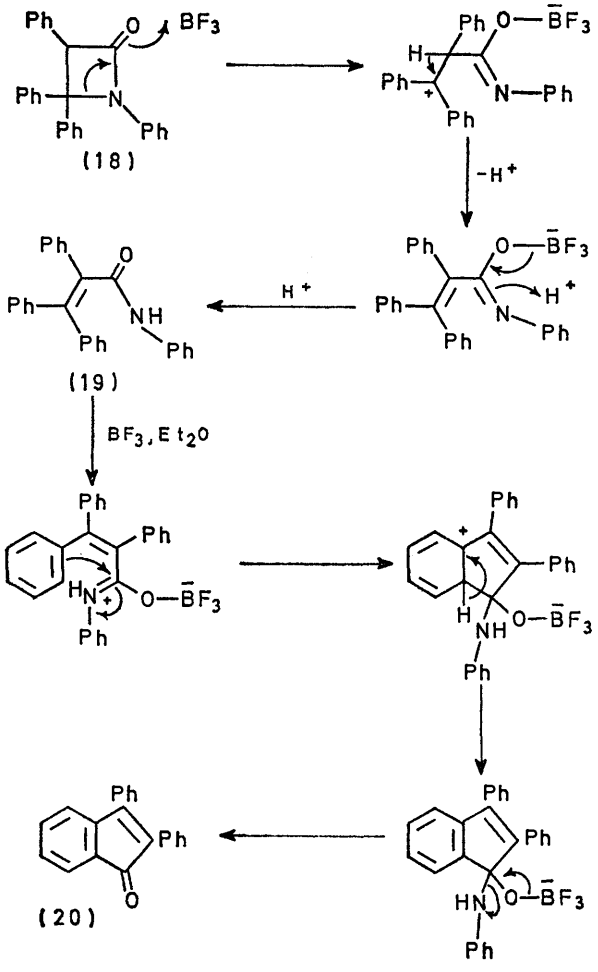
A further reaction in which no solvent incorporation was observed owing to an alternative mode of reaction being available was found with 1,3,4,4-tetraphenylazetidin-2-one (18). Treatment of this compound with toluene and boron trifluoride yielded a red crystalline compound in good yield. The i.r. spectrum (ν_{CO} 1700 cm^{-1}) indicated that this was not an amide, nor indeed would such an intense chromophore be expected from a toluene adduct, and the ^{1}H n.m.r. spectrum indicated the presence of aromatic protons only. The product was eventually shown to be 2,3-diphenylindenone [9] (20) [*m/e* 282 (M^+)] produced from the azetidinone by the expulsion of aniline. This result may be explained in terms of initial production of a stabilised carbonium ion



resulting in the rapid formation of an olefin (19) by β-proton loss (Scheme 1). Evidence which indicated the importance of the formation of a stabilised ion was obtained in a similar reaction of 1,3,3,4-tetraphenylazetidin-2-one. Treatment of this compound with

[9] D. Curtin and J. Kauer, *J. Org. Chem.*, 1960, **25**, 880.

toluene and boron trifluoride also yielded 2,3-diphenylindenone, but in poor yield, and starting material was recovered. This reaction probably entails ring opening



SCHEME 1

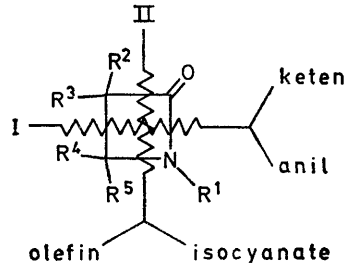
followed by a 1,2-phenyl shift with subsequent proton loss to yield the acrylamide (19).

The azetidinones used in this study were prepared by known [2 + 2] cycloaddition reactions of an anil and a keten.[10] The keten was isolated pure (diphenylketen), or was generated and used immediately (keten), or was generated *in situ* (phenylketen). The azetidinones (20)—(22) were obtained readily from anils derived from 2-, 3-, and 4-aminopyridines and diphenylketen, as were compounds (23) and (25) from this keten and 4-chloro- and 4-nitro-benzylideneaniline, despite reports to the contrary.[11]

The Table records the mass spectral fragmentation of a series of aryl-substituted azetidin-2-ones. The molecular ion is usually weak or absent and in general two distinct modes of decomposition were found. These may be considered as the reverse of possible [2 + 2] cycloadditions *via* which the azetidinones may be synthesised (see Figure).[12-15] Thus fission by pathway I leads to fragment ions due to a keten and an anil whereas pathway II produces olefin and isocyanate residues. Usually all four of these possible decomposition ions are observed, but the intensity is dependent upon the nature of substitution. The extrusion of CO from the molecular ion was an alternative mode of fragmentation but this usually accounted for only a small proportion of the total ion current.

The mass spectra of the 3,3-diphenylazetidinones (Table) were qualitatively similar and showed typical fragmentation pathways. Thus 1,3,3,4,4-tetraphenylazetidin-2-one (32) showed a weak (3%) molecular ion (*m/e* 375) and principal decomposition *via* pathway I (Scheme 2) to yield the diphenylketen radical ion (*m/e* 194, base peak) and the benzylideneaniline radical ion (*m/e* 181). The former underwent further decomposition by successive losses of CO and H to yield the second most abundant ion (*m/e* 165). The first of these transitions (194 — CO) generated an intense metastable ion (*m** 141·9) which was an extremely characteristic feature of the mass spectra of all of the 3,3-diphenylazetidin-2-ones examined. The benzylideneaniline radical ion (*m/e* 181) also underwent further decomposition by loss of H (*m/e* 180) or phenyl radical (*m/e* 104). The alternative mode of fission (pathway II) was a relatively minor process yielding fragments corresponding to the olefin (*m/e* 256) and phenyl isocyanate (*m/e* 119). Decomposition of the molecular ion *via* CO loss yielded a weak (1%) ion (*m/e* 347).

Halogen substitution in the 4-phenyl group (23) had little effect upon the fragmentation pattern but the keten residue then accounted for more of the total ion current *via* pathway I and a small reduction in intensity of the olefin peak was apparent. However, with the 4-(4-nitrophenyl) derivative (25), although pathway I *via* the diphenylketen radical ion (*m/e* 194) was still



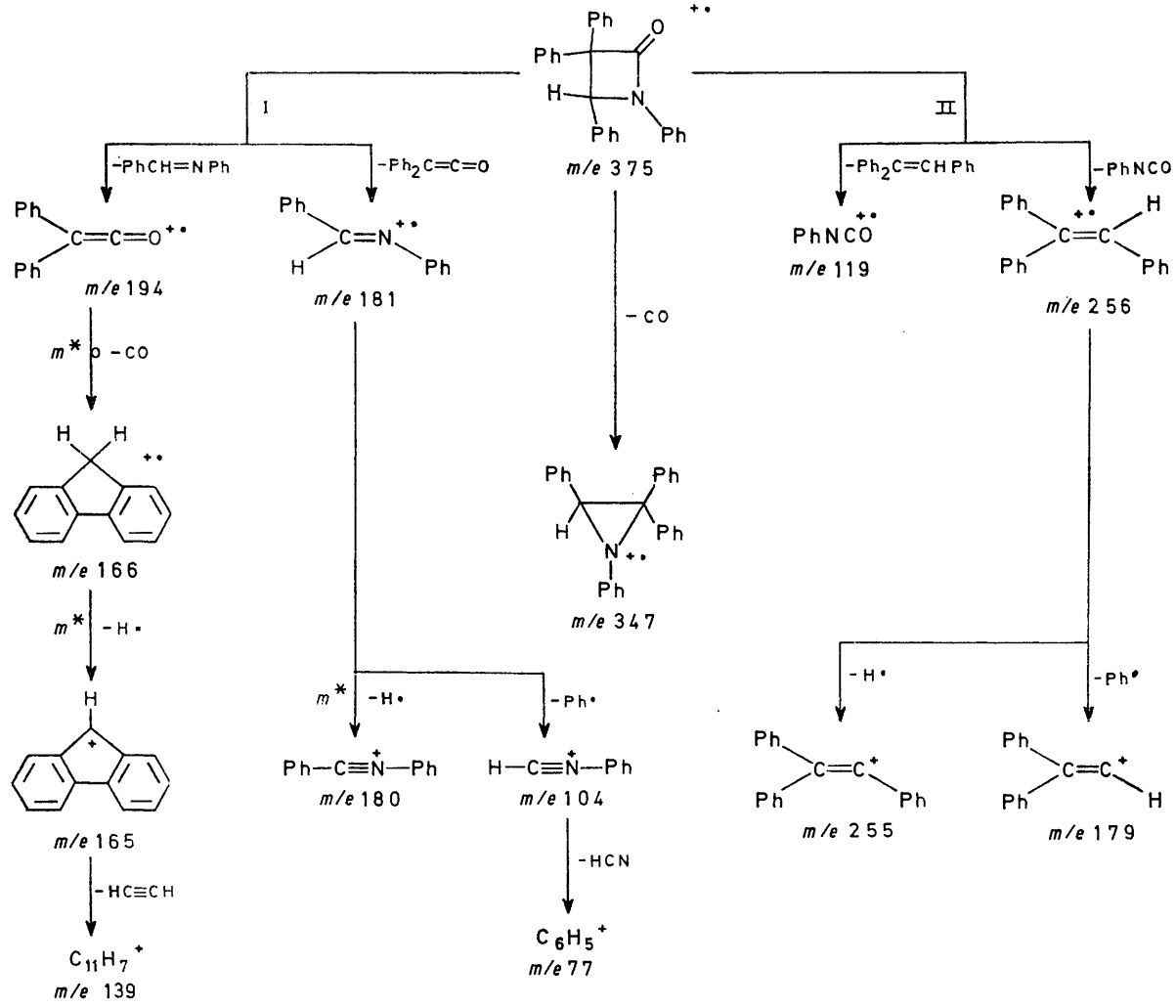
the preferred mode of decomposition, a major fragment (76%) was then due to the olefin radical ion (*m/e* 301). This trend was continued in the decomposition of the isomeric 4-(*x*-pyridyl)azetidinones (20)—(22) and al-

[10] J. A. Moore in ' Heterocyclic Compounds with Three- and Four-Membered Rings,' part 2, ed. A. Weissberger, Interscience, New York, 1964, p. 885.
[11] R. Pfleger and A. Jager, *Chem. Ber.*, 1957, **90**, 2460.
[12] H. E. Audier, M. Fetizon, H. B. Kagan, and J. L. Luche, *Bull. Soc. chim. France*, 1967, 2297.
[13] M. B. Jackson, T. Spotwood, and J. H. Bowie, *Org. Mass Spectrometry*, 1968, **1**, 857.
[14] A. K. Bose and I. Kugajevsky, *Tetrahedron*, 1967, **23**, 957.
[15] L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 942.

Mass spectral fragmentation of aryl-substituted azetidin-2-ones

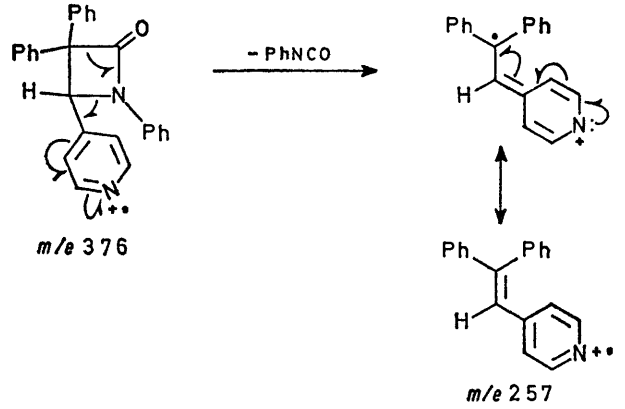
Compound no.	Substituents *					Fragment ions [*m/e* (%)]					
	R^1	R^2	R^3	R^4	R^5	M^+	$R^4R^5C{=}C{=}O^{+\cdot}$	$R^4R^5C{=}N^{+\cdot}R^1$	$R^4R^5C{=}C^{+\cdot}R^2R^3$	$R^1NCO^{+\cdot}$	Base peak
	Ph	Ph	Ph	Ph	Ph	451 (1)	194 (49)	257 (53)	332 (1)	119 (1)	165
	Ph	Ph	Ph	Ph	H	375 (2)	194 (100)	181 (40)	256 (44)	119 (3)	194
(33)	Ph	Ph	Ph	2-Pyridyl	H	376 (9)	194 (33)	182 (6)	257 (100)	119 (2)	257
(21)	Ph	Ph	Ph	3-Pyridyl	H	376 (9)	194 (100)	182 (17)	257 (56)	119 (3)	194
(22)	Ph	Ph	Ph	4-Pyridyl	H	376 (3)	194 (53)	182 (10)	257 (100)	119 (3)	257
(23)	Ph	Ph	Ph	$4\text{-}ClC_6H_4$	H	409 (1)	194 (100)	215 (17)	290 (23)	119 (1)	194
(24)	Ph	Ph	Ph	$4\text{-}FC_6H_4$	H	393 (2)	194 (100)	199 (25)	274 (32)	119 (1)	194
(25)	Ph	Ph	Ph	$4\text{-}NO_2\cdot C_6H_4$	H	420 (1)	194 (100)	226 (11)	301 (76)	119 (3)	194
(26)	3-Pyridyl	Ph	Ph	Ph	H	376 (3)	194 (100)	182 (9)	256 (26)	120 (1)	194
(27)	4-Pyridyl	Ph	Ph	Ph	H	376 (11)	194 (100)	182 (7)	256 (26)	120 (1)	194
(15)	Ph	Ph	Ph	Fluorene-9-spiro		449 (1)	194 (3)	255 (19)	330 (1)	119 (1)	167
(28)	$4\text{-}MeO\cdot C_6H_4$	Ph	Ph	Fluorene-9-spiro		479 (—)	194 (6)	285 (100)	330 (—)	149 (3)	285
(3)	Ph	Ph	H	Ph	H	299 (1)	118 (1)	181 (26)	180 (100)	119 (1)	180
(29)	$4\text{-}ClC_6H_4$	Ph	H	Ph	H	333 (1)	118 (17)	215 (16)	180 (100)	153 (—)	180
(7)	$4\text{-}MeO\cdot C_6H_4$	Ph	H	Ph	H	329 (1)	118 (3)	211 (24)	180 (100)	149 (15)	180
(30)	$4\text{-}ClC_6H_4$	Ph	H	Fluorene-9-spiro		407 (4)	118 (3)	289 (100)	254 (7)	153 (2)	289
	Ph	Ph	H	Ph	Ph	327 (—)	118 (—)	257 (100)	256 (28)	119 (21)	257
(13)	$4\text{-}ClC_6H_4$	H	H	Fluorene-9-spiro		329 (2)	42 (—)	289 (2)	178 (100)	153 (9)	178
(9)	Ph	H	H	Ph	H	223 (10)	42 (—)	181 (9)	104 (100)	119 (10)	104

* See Figure.



SCHEME 2

though pathway I (base peaks *m/e* 194) remained the predominant mode of fragmentation in the 4-(3-pyridyl)-azetidinone (21), with the 4-(2- and 4-pyridyl) isomers (20) and (22) pathway II was the source of the base peak (*m/e* 257). This effect may be due to the presence of a new centre with a low ionisation potential, *i.e.* the 2- or 4-pyridyl residue, which controls subsequent fragmentation (Scheme 3).



SCHEME 3

In the mass spectra of those azetidinones with only one 3-phenyl substituent pathway I no longer appeared to be a major decomposition route. In contrast, for the 3,3-diphenyl compounds fission in this direction resulted in the anil fragment carrying most of the ion current. Thus the mass spectrum of 1,3,4-triphenylazetidinone (11) showed a weak (1%) molecular ion (*m/e* 299) which underwent decomposition to yield the benzylideneaniline radical ion (*m/e* 181) and the base peak at *m/e* 180. This latter ion was formulated as the stilbene radical ion and showed characteristic loss of methyl.[16] A further source of this ion (*m/e* 180), however, is hydrogen loss from the anil residue (*m/e* 181); this was confirmed by high resolution mass measurement. No such ambiguity was possible with 1-(4-chlorophenyl)-3,4-diphenylazetidin-2-one (29) and the base peak (*m/e* 180) was clearly due to the olefin residue.

The spectra of 4,4-disubstituted azetidinones, which may be regarded as formally derived from the anils of ketones, showed enhanced decomposition *via* this anil fragment presumably due to the extra stabilisation caused by the second aromatic substituent, and pathway I was the major route of decomposition of 1,3,3,4,4-pentaphenylazetidin-2-one (31).

EXPERIMENTAL

^{1}H N.m.r. spectra were determined for solutions in deuteriochloroform with a Varian A60A spectrometer (tetramethylsilane as internal reference). I.r. spectra were obtained with Unicam SP 200 spectrophotometer and mass spectra with an A.E.I. MS9 spectrometer (ionising voltage 70 eV, trap current 100 μA, accelerating voltage 8 kV); samples were introduced through the heated inlet system at 150°.

3,3-*Diphenylazetidin*-2-*ones*

4-(4-*Chlorophenyl*)-1,3,3-*triphenylazetidin*-2-*one* (23).—A solution of diphenylketen [17] (5·0 g) in dry ether (30 cm^3) was slowly added to a stirred solution of 4-chlorobenzylideneaniline (5·0 g) in dry ether (30 cm^3). The precipitate crystallised from methanol to yield the *azetidin*-2-*one* (5·3 g, 56%) as needles, m.p. 157—158° (Found: C, 79·1; H, 5·1; Cl, 8·9; N, 3·6. $C_{27}H_{20}ClNO$ requires C, 79·2; H, 4·9; Cl, 8·7; N, 3·4%), $\nu_{max.}$ 3050, 1750 (C=O), 1603, 1510 (aromatic nucleus), 1395, 1100, and 1020 cm^{-1}, τ ($CDCl_3$) 2·3—2·9 (19H, m, Ph) and 4·2 (1H, s, 4-H).

The following compounds were similarly prepared: 3,3,4-*triphenyl*-1-(3-*pyridyl*)*azetidin*-2-*one* (26) (7·9 g, 77%) as needles, m.p. 177—178° [from 3-benzylideneaminopyridine (5·0 g)] (Found: C, 82·3; H, 5·3; N, 7·3. $C_{26}H_{20}N_2O$ requires C, 83·0; H, 5·3; N, 7·3%), $\nu_{max.}$ 3050, 1750 (C=O), 1600, 1490, 1450, 1390, and 1150 cm^{-1}, τ ($CDCl_2$) 1·4 (1H, d, *J* 2 Hz, pyridyl 2-H), 1·6 (1H, d, *J* 5 Hz, pyridyl 6-H), 2·2—3·1 (17H, m, Ph and pyridyl 4- and 5-H), and 4·15 (1H, s, 4-H); 3,3,4-*triphenyl*-1-(4-*pyridyl*)*azetidin*-2-*one* (27) from 3-benzylideneaminopyridine (5·0 g) (yield 7·1 g, 69%) as needles, m.p. 158—159° (from methanol) (Found: M^+ 376·157034. $C_{26}H_{20}N_2O$ requires *M*, 376·157555), $\nu_{max.}$ 3050, 1760 (C=O), 1603, 1510, 1390, and 1150 cm^{-1}, τ ($CDCl_3$) 1·6 (2H, d, *J* 5 Hz, pyridyl 2- and 6-H), 2·2—3·1 (17H, m, Ph and pyridyl 3- and 5-H), and 4·15 (1H, s, 4-H); 1,3,3-*triphenyl*-4-(2-*pyridyl*)*azetidin*-2-*one* (33) from 2-pyridylmethyleneaniline (3·0 g) (yield 1·33 g, 21·4%) as needles, m.p. 162—164° (from methanol) (Found: C, 83·1; H, 5·3; N, 7·4. $C_{26}H_{20}N_2O$ requires C, 83·0; H, 5·3; N, 7·3%), $\nu_{max.}$ 3050, 1750 (C=O), 1603, 1510, 1390, and 1150 cm^{-1}, τ ($CDCl_3$) 1·4 (1H, m, pyridyl 2-H), 2·1 (2H, m, pyridyl 4- and 5-H), 2·3—3·3 (16H, m, Ph and pyridyl 3-H), and 3·9 (1H, s, 4-H); 1,3,3-*triphenyl*-4-(3-*pyridyl*)*azetidin*-2-*one* (21) from 3-pyridylmethyleneaniline (3·0 g) (yield 1·42 g, 22·8%) as needles, m.p. 137—138° (from methanol) (Found: M^+ 376·157786. $C_{26}H_{20}N_2O$ requires *M*, 376·157555), $\nu_{max.}$ 3050, 1750 (C=O), 1603, 1510 (aromatic nucleus), 1390, and 1150 cm^{-1} τ ($CDCl_3$) 1·75 (2H, m, pyridyl 2- and 6-H), 2·45—3·2 (17H, m, Ph and pyridyl 4- and 5-H), and 4·35 (1H, s, 4-H) [in this reaction a quantity of diphenylacetanilide (0·25 g) was formed, m.p. 185—186° (Found: C, 83·6; H, 5·9; N, 4·9. Calc. for $C_{20}H_{17}NO$: C, 83·6; H, 6·0; N, 4·9%), $\nu_{max.}$ 3400, 3050, 1690, 1603, 1540, 1510, 1450, and 1120 cm^{-1}, τ ($CDCl_3$) 2·7 (15H, s, Ph) and 4·9 (1H, s, CH)]; 1,3,3-*triphenyl*-4-(4-*pyridyl*)*azetidin*-2-*one* (22) from 4-pyridylmethyleneaniline (3·0 g) (yield 3·8 g, 61·6%) as prisms, m.p. 147—148° [from petroleum (b.p. 60—80°)] (Found: C, 81·8; H, 5·4; N, 7·2%; M^+, 376·157005. $C_{26}H_{20}N_2O$ requires C, 83·0; H, 5·3; N, 7·5%; *M*, 376·157555), $\nu_{max.}$ 3050, 1750 (C=O), 1603, 1510, 1390, and 1150 cm^{-1}, τ ($CDCl_3$) 1·7 (2H, d, *J* 5 Hz, pyridyl 2- and 6-H), 2·3—3·1 (17H, m, Ph and pyridyl 3- and 5-H), and 4·25 (1H, s, 4-H); 4-(4-*nitrophenyl*)-1,3,3-*triphenylazetidin*-2-*one* (25) from 4-nitrobenzylideneaniline (4·0 g) (yield 6·1 g, 81%) as yellow needles, m.p. 180—181° (from methanol) (Found: C, 77·6; H, 4·6; N, 6·7. $C_{27}H_{20}N_2O_3$ requires C, 77·2; H, 4·8; N, 6·7%), $\nu_{max.}$ 3050, 1750 (C=O), 1603, 1540, 1510, 1390, 1350, 1150, 1110, and 860 cm^{-1}, τ ($CDCl_3$) 2·3 (2H, d, *J* 9 Hz, 2- and

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[17] L. I. Smith and H. H. Hoehn, *Org. Synth.*, Coll. Vol. III, 1955, 356.

6-H of nitrophenyl), 2·5—3·2 (17H, m, Ph and 3- and 5-H of nitrophenyl), and 4·2 (1H, s, 4-H); 4-(4-*fluorophenyl*)-1,3,3-*triphenylazetidin*-2-*one* (24) from 4-fluorobenzylideneaniline (3·0 g) (yield 3·5 g, 59%) as needles, m.p. 189—190° (from methanol) (Found: C, 82·0; H, 5·2; N, 3·4. $C_{27}H_{20}FNO$ requires C, 82·9; H, 5·1; N, 3·6%), $\nu_{max.}$ 3050, 1750 (C=O), 1603, 1510, 1390, 1240, 1150, and 850 cm^{-1}, τ ($CDCl_3$) 2·2—3·2 (19H, m, Ph) and 4·2 (1H, s, 4-H); 1′-(4-*chlorophenyl*)-3′,3′-*diphenylfluorene*-9-*spiro*-2′-*azetidin*-4′-*one* (30) from 4-chloro-*N*-fluoren-9-ylideneaniline (2·0 g) (yield 3·0 g, 91%) as prisms, m.p. 255—258° (from methanol) (Found: M^+, 483·136912. $C_{33}H_{22}ClNO$ requires M, 483·138983) (for ^{35}Cl), $\nu_{max.}$ 3100, 1750 (C=O), 1603, 1510, 1460, 1390, 1100, and 840 cm^{-1}; 1′,3′,3′-*triphenyfluorene*-9-*spiro*-2′-*azetidin*-4′-*one* (15) from fluoren-9-ylideneaniline (3·0 g) (yield 4·6 g, 87%) as prisms, m.p. 277—279° (from methanol) (Found: M^+, 449·175393. $C_{33}H_{23}NO$ requires M, 449·177955), $\nu_{max.}$ (Nujol) 1745 (C=O), 1603, 1510, 1250, 770, 750, 720, and 700 cm^{-1}; 1′-(4-*methoxyphenyl*)-3′,3′-*diphenylfluorene*-9-*spiro*-2′-*azetidin*-4′-*one* (28) from fluoren-9-ylidene-*p*-anisidine (1·0 g) (yield 1·54 g, 91%) as prisms, m.p. 240—242° (from methanol), $\nu_{max.}$ 3050, 2590 (OCH_3), 1740 (C=O), 1603, 1590, and 1510 (aromatic nucleus), 1450, 1380, 1250 (OCH_3), 1160, 1020, 830, 730, and 700 cm^{-1}, τ ($CDCl_3$) 2·3—3·7 (17H, m, Ph, fluorenyl and C_6H_4), and 6·55 (3H, s, OCH_3).

General Method for the Preparation of 3-*Phenylazetidin*-2-*ones*.—A stirred solution of the Schiff's base (0·16 mol), triethylamine (0·48 mol), and chloroform (50 cm^3) [18] was cooled to 0 °C and phenylacetyl chloride (0·32 mol) was added slowly. The mixture was allowed to attain room temperature during 1 h and then was washed with water (50 cm^3), dried ($MgSO_4$), and evaporated to low bulk. Trituration and crystallisation of the residual yellow oil yielded the 3-phenylazetidin-2-one.

1-(4-*Chlorophenyl*)-3,4-*diphenylazetidin*-2-*one* (29) was obtained from 4-chloro-*N*-benzylideneaniline (1·0 g), triethylamine (1·0 g), chloroform (25 cm^3), and phenylacetyl chloride (1·5 g) (yield 0·68 g, 44%) as needles, m.p. 148—150° (from methanol), $\nu_{max.}$ 3050, 1740 (C=O), 1505, 1135, 830, 750, and 700 cm^{-1}, τ ($CDCl_3$) 2·69—2·9 (14H, m, Ph), 5·1 (1H, d, J 2·5 Hz, 4-H), and 5·75 (1H, d, J 2·5 Hz, 3-H) (Found: C, 75·9; H, 4·9; N, 4·2%; M^+, 333·09100. $C_{21}H_{16}ClNO$ requires C, 75·7; H, 4·8; N, 4·2%; M, 333·092035). 1′-(4-*Chlorophenyl*)-3′-*phenylfluorene*-9-*spiro*-2′-*azetidin*-4′-*one* (30) was obtained from 4-chloro-*N*-fluoren-9-ylideneaniline (2·5 g) (yield 3·2 g, 89%) as prisms, m.p. 205° (from methanol–chloroform) (Found: C, 79·4; H, 4·5; N, 3·4. $C_{27}H_{18}ClNO$ requires C, 79·5; H, 4·4; N, 3·4%), $\nu_{max.}$ 3050, 1745 (C=O), 1603, 1500, 1460, 1390, 1100, 910, 830, and 720 cm^{-1}, τ ($CDCl_3$) 2·2—3·2 (17H, m, Ph) and 4·85 (1H, s, 3-H). 3-*Chloro*-1-(4-*methoxyphenyl*)-3,4-*diphenylazetidin*-2-*one* was obtained from benzylidene-*p*-anisidine (1·4 g, 0·066 mol), triethylamine (2·0 g, 0·2 mol), and chloroacetyl chloride (2·0 g, 0·1 mol) in chloroform (25 cm^3) (reaction for 15 h) (yield 1·0 g, 42%) as needles, m.p. 130—132° (from methanol) (Found: C, 72·2; H, 4·9; N, 3·6. $C_{22}H_{18}ClNO_2$ requires C, 72·6; H, 4·9; N, 3·8), $\nu_{max.}$ 3050, 2950, 1745, 1520, 1450, 1390, 1300, 1250, 1140, 1030, 830, 750, and 690 cm^{-1}, τ ($CDCl_3$) 2·5—3·3 (14H, m, Ph), 4·4 (1H, s, 4-H), and 6·25 (3H, s, OMe).

3′-*Chloro*-1′-(4-*methoxyphenyl*)-3′-*phenylfluorene*-9-*spiro*-2′-*azetidin*-4′-*one*. α-Chloroacetyl chloride (8·0 g) was added slowly to a cooled mixture of fluorenylidene-*p*-anisidine (5 g), triethylamine (5·0 g), and chloroform (120 cm^3). The solution was stirred at room temperature for 30 min to yield the *azetidin*-2-*one* (6·3 g, 82%) as prisms, m.p. 160—162° (from methanol) (Found: C, 76·7; H, 4·7; N, 3·1. $C_{28}H_{20}ClNO_2$ requires C, 76·9; H, 4·6; N, 3·2%), $\nu_{max.}$ 3100, 1770 (C=O), 1530, 1260, 840, and 750 cm^{-1}, τ ($CDCl_3$) 2·1—3·7 (17H, m, Ph, C_6H_4, and fluorenyl), and 6·4 (3H, s, OCH_3).

3′-*Chloro*-1′-(4-*methoxyphenyl*)*fluorene*-9-*spiro*-2′-*azetidin*-4′-*one*. Chloroacetyl chloride (1·0 g) was added slowly to a cooled, stirred solution of fluorenylidene-*p*-anisidine (1·35 g), chloroform (20 cm^3), and triethylamine (0·5 g) and the mixture was stirred for 10 min to yield the *azetidin*-2-*one* (1·02 g, 30%) as needles, m.p. 174—175° (from ethanol) (Found: C, 73·1; H, 4·6; N, 3·8. $C_{22}H_{16}ClNO_2$ requires C, 73·0; H, 4·4; N, 3·9%), $\nu_{max.}$ 3000 and 1760 (C=O) cm^{-1}, τ ($CDCl_3$) 2·2—2·85 (8H, m, fluorenyl), 2·9 (2H, d, J 9 Hz, 3- and 5-H of methoxyphenyl), 3·4 (2H, d, J 9 Hz, 2- and 6-H of methoxyphenyl), 4·7 (1H, s, 3-H), and 6·4 (3H, s, OCH_3).

Rearrangement Reactions

(a) *With Sulphuric Acid*.—3,4-*Dihydro*-3,4-*diphenylquinolin*-2(1H)-*one* (4). 1,3,4-Triphenylazetidin-2-one [11,19,20] (0·5 g) and concentrated sulphuric acid (4 cm^3) were stirred at room temperature for 2 h and then poured into iced water (50 cm^3). Extraction with chloroform (2 × 50 cm^3), drying ($MgSO_4$), and evaporation yielded the dihydro-2(1*H*)-quinolone (0·2 g, 40%) as needles, m.p. 200° (from methanol) (lit.,[21] 220°), $\nu_{max.}$ 3300, 3050, 1675 (C=O), 1600, 1530, 1450, 1320, 760, and 700 cm^{-1}, τ ($CDCl_3$) 2·5—3·2 (16H, m, Ph and C_6H_4), 5·55 (1H, d, J 6 Hz, 3-H), and 5·9 (1H, d, J 6 Hz, 4-H), (Found: M^+ 299·130931. Calc. for $C_{21}H_{17}NO$: M, 299·131007).

3,4-*Dihydro*-6-*methoxy*-4-*phenylquinolin*-2(1H)-*one* (2). 1-(4-Methoxyphenyl)-4-phenylazetidin-2-one (0·6 g) and concentrated sulphuric acid (4 cm^3) were mixed at room temperature for 16 h to yield the dihydro-2(1*H*)-quinolone (0·3 g, 50%) as needles, m.p. 154—155° (from chloroform) (lit.,[8] 155—156°), identical with a sample prepared from 4′-methoxycinnamanilide and polyphosphoric acid; $\nu_{max.}$ 3300, 2900, 1660 (C=O), 1510, 1240 (OCH_3), 830, and 700 cm^{-1}, τ ($CDCl_3$) 2·5—3·6 (8H, m, Ph and C_6H_3), 5·8 (1H, t, J 7 Hz, 4-H), 6·4 (3H, s, OCH_3), and 7·15 (2H, d, J 7 Hz, 3-H_2).

(b) *With Boron Trifluoride*.—*General method*. The azetidin-2-one and boron trifluoride–diethyl ether complex were heated together in a solvent for 60 h. Cooling, washing with water, drying ($MgSO_4$) and evaporation yielded the product. Purification was effected by trituration and crystallisation from aqueous ethanol.

N-(4-*Methoxyphenyl*)-2,3-*diphenyl*-3-(4-*tolyl*)*propionamide* (8). 1-(4-Methoxyphenyl)-3,4-diphenylazetidin-2-one (1·0 g), boron trifluoride–diethyl ether (1·0 cm^3), and toluene (100 cm^3) yielded the *propionamide* (0·45 g, 35%) as microprisms, m.p. 157—159° (from ethanol) (Found: C, 81·4; H, 6·6; N, 3·1%; M^+, 421·204224. $C_{29}H_{27}NO_2$ requires C, 82·6; H, 6·4; N, 3·3%; M, 421·204168), $\nu_{max.}$ 3300 (NH), 3050, 2950, 1650 (C=O), 1603, 1520, 1250 (OCH_3), 1170, 1040, 760, and 700 cm^{-1}, τ ($CDCl_3$) 2·1—3·1 (14H, m, Ph

[18] A. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 1964, (*a*) p. 372, (*b*) p. 773, (*c*) p. 779.
[19] W. Kirmse and L. Horner, *Chem. Ber.*, 1956, **89**, 2759.
[20] H. Staudinger, *Chem. Ber.*, 1917, **50**, 1035.
[21] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 2333.

and C_6H_4Me), 3·05 (2H, d, *J* 9 Hz, 3- and 5-H of C_6H_4OMe), 3·45 (2H, d, *J* 9 Hz, 2- and 6-H of C_6H_4OMe), 5·1 (1H, d, *J* 12 Hz, 2-H), 5·75 (1H, d, *J* 12 Hz, 3-H), 6·4 (3H, s, OCH_3), and 7·8 (3H, s, CH_3).

N,3-*Diphenyl*-3-(4-*tolyl*)*propionamide* (10). 1,4-Diphenylazetidin-2-one (1·0 g) and toluene (100 cm³) yielded the *propionamide* (0·6 g, 42·5%) as needles, m.p. 124—126° (from ethanol) (Found: C, 84·1; H, 6·7; N, 4·5. $C_{22}H_{21}NO$ requires C, 83·8; H, 6·7; N, 4·5%), $\nu_{max.}$ 3350, 1660 (C=O), 1603, 1555, 1450, 760, and 700 cm⁻¹, τ ($CDCl_3$) 2·9 (14H, d, Ph and C_6H_4), 5·45 (1H, t, *J* 8 Hz, 3-H), 7·0 (2H, d, *J* 8 Hz, 2-H_2), and 7·75 (3H, s, CH_3).

N,2,3-*Triphenyl*-3-(4-*tolyl*)*propionamide* (12). 1,3,4-Triphenylazetidin-2-one (1·0 g) and toluene (100 cm³) yielded the *propionamide* (0·54 g, 41%) as needles, m.p. 210° (from ethanol) (Found: M^+, 391·191751. $C_{28}H_{25}NO$ requires *M*, 391·193604), $\nu_{max.}$ 3350, 3100, 1665 (C=O), 1603, 1560, 1510, 1460, 860, and 710 cm⁻¹, τ ($CDCl_3$) 2·2—3·2 (19H, m, Ph and C_6H_4), 5·1 (1H, d, *J* 10 Hz, 2-H), 5·65 (1H, d, *J* 10 Hz, 3-H), and 7·8 (3H, s, CH_3).

N-(4-*Chlorophenyl*)-2-*phenyl*-2-[9-(4-*tolyl*)*fluoren*-9-*yl*]*acetamide* (14). 1'-(4-Chlorophenyl)-3'-phenylfluorene-9-spiro-2'-azetidin-4'-one (1·6 g), and toluene (100 cm³) yielded the *acetamide* (0·28 g, 17%) as buff microprisms, m.p. 210° (from ethanol) (Found: M^+, 499·170771. $C_{34}H_{26}ClNO$ requires *M*, 499·170282) (for ^{35}Cl), $\nu_{max.}$ 3250 (NH), 1650 (C=O), 1603, 1560, 1500, 1460, 1400, and 740 cm⁻¹, τ ($CDCl_3$) 2·3—3·5 (21H, m, Ph, 2 × C_6H_4, and fluorene), 4·9 (1H, s, 2-H), and 7·75 (3H, s, CH_3).

3-(4-*Methoxyphenyl*)-N,3-*diphenylpropionamide*. 1,4-Diphenylazetidin-2-one (0·3 g), boron trifluoride–diethyl ether (2·0 cm³), and anisole (100 cm³) were heated under reflux for 60 h. Cooling, washing with water (50 cm³), drying ($MgSO_4$) and evaporation yielded a red oil. Trituration and crystallisation yielded the *propionamide* (0·15 g, 34%) as needles, m.p. 160—162° (from ethanol) (Found: M^+, 331·156611. $C_{22}H_{21}NO_2$ requires *M*, 331·157220), $\nu_{max.}$ 3300, 3100, 1660 (C=O), 1603, 1560, 1520, 1460, 1260 (OCH_3), 770, and 700 cm⁻¹, τ ($CDCl_3$) 2·4—3·1 (14H, m, Ph and C_6H_4), 5·35 (1H, t, *J* 7 Hz, 3-H), 4·05 (3H, s, OCH_3), and 4·6 (2H, d, *J* 7 Hz, 2-H_2).

2,3-*Diphenylinden*-1-*one*. 1,3,4,4-Tetraphenylazetidin-2-one [11,19] (1·4 g), boron trifluoride–diethyl ether (2·0 cm³), and toluene (100 cm³) were heated together under reflux for 60 h. The solution was cooled, extracted with water (50 cm³), and dried ($MgSO_4$). Evaporation to low bulk yielded the inden-1-one (0·71 g, 67·5%) as red prisms, m.p. 152—154° (from ethanol) (lit.,[9] 151·5—152°) (Found: C, 89·1; H, 5·1. Calc. for $C_{21}H_{14}O$: C, 89·4; H, 5·0%), $\nu_{max.}$ 3100, 1710 (C=O), 1603, 1460, 1360, 770, and 710 cm⁻¹, τ ($CDCl_3$) 2·3—2·9 (14H, d, Ph and C_6H_4), M^+ 282. A similar experiment with 1,3,3,4-tetraphenylazetidin-2-one [19,22] also yielded 2,3-diphenylinden-1-one (5%), and starting material.

Reaction of Boron Trifluoride with 1,3,3,4,4-*Pentaphenylazetidin*-2-*one*.—1,3,3,4,4-Pentaphenylazetidin-2-one [23] (1·0 g), boron trifluoride–diethyl ether (2·0 cm³), and toluene (100 cm³) were heated under reflux for 60 h. The solution was cooled, washed with water (50 cm³), and dried. Evaporation yielded α-phenylbenzylideneaniline (0·4 g, 70%) as yellow plates, m.p. 107° (from ethanol) (lit.,[23] 106°), $\nu_{max.}$ 3100, 1630 (C=N), 1600, 1500, 1460, 1330, 1300, 790, and 710 cm⁻¹. The filtrate from the crystallisation was evaporated and the residue redissolved in chloroform (10 cm³). The solution was washed with 10% sodium hydroxide (10 cm³) and the aqueous layer neutralised with sulphuric acid. Filtration gave diphenylacetic acid (0·2 g, 43%) as needles, m.p. 146—147° (from water) (lit.,[18b] 145°), $\nu_{max.}$ 3100, 2950, 1705 (C=O), 1230, 950, 740, and 700 cm⁻¹. A further reaction of the azetidin-2-one with boron trifluoride in toluene was carried out with dry ethanol included in the reaction mixture. Ethyl diphenylacetate was isolated together with the Schiff's base; $\nu_{max.}$ 3050, 1730, 1603, 1510, 1460, 1200, 1150, 1020, 760, and 710 cm⁻¹, τ ($CDCl_3$) 2·7 (10H, s, Ph), 5·0 (1H, s, CH), 5·8 (2H, q, *J* 7 and 14 Hz, CH_2·CH_3), and 8·8 (3H, t, *J* 7 Hz, CH_2·CH_3).

Reaction of Boron Trifluoride with 1'-(4-*Methoxyphenyl*)-3',3'-*diphenylfluorene*-9-*spiro*-2'-*azetidin*-4'-*one* (28).—1'-(4-Methoxyphenyl)-3',3'-diphenylfluorene-9-spiro-2'-azetidin-4'-one (0·5 g), boron trifluoride–diethyl ether (1·0 cm³), and toluene (50 cm³) were heated under reflux for 60 h. The solution was cooled, washed with water (50 cm³), and extracted with 5% sodium hydroxide (50 cm³). The organic fraction contained unchanged azetidine-2-one and fluorenylidene-*p*-anisidine (0·12 g, 40%) as orange prisms, m.p. 136° (from ethanol), $\nu_{max.}$ 3050, 2950, 2850, 1640 (C=N), 1603, 1510, 1455, 1240 (OCH_3) 1100, 1040, 840, 800, and 735 cm⁻¹. Acidification of the basic fraction yielded diphenylacetic acid (0·15 g, 50%) as needles, m.p. 146° (from water), $\nu_{max.}$ 3100, 3000, 2750 (OH), 1710 (C=O), 1510, 1420, 1330, 1230, 950, 740, and 710 cm⁻¹.

Reaction of Boron Trifluoride with 1,4-*Diphenylazetidin*-2-*one*.—1,4-Diphenylazetidin-2-one (1·0 g), boron trifluoride–diethyl ether (1·0 cm³), and chlorobenzene (100 cm³) were heated together under reflux for 60 h. Cooling, washing with water (50 cm³), drying ($MgSO_4$) and evaporation yielded cinnamanilide (0·7 g, 70%) as needles, m.p. 153° (from chloroform) (lit.,[18c] 153°), identical with a sample prepared from aniline and cinnamoyl chloride; $\nu_{max.}$ 3000 (NH), 3050, 1665 (C=O), 1630 (C=C), 1600, 1550, 1510, 1450, 1350, 1190, 990, 770, and 700 cm⁻¹, τ ($CDCl_3$) 2·0—3·2 (10H, m, Ph), 2·3 (1H, d, *J* 16 Hz, =C*H*–CO), and 3·15 (1H, d, *J* 16 Hz, PhC*H*=).

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[3/1258 *Received*, 15*th June*, 1973]