Conversion of Some Azomethine Ylides Derived from 2-Cyano-1-imidoaziridines into Imines

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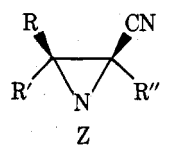
Thermolysis of 2,3-diaryl-2-cyano-1-imidoaziridines, prepared by the reaction of an imidonitrene with α-cyanostilbenes, gives imines. The likely mechanism involves an azomethine ylide. The imido group of this ylide undergoes 1–2 shift from nitrogen atom to carbon atom, with a high degree of intramolecularity.

N-Imidoaziridines are easily prepared by lead tetraacetate oxidation of *N*-aminoimides, in the presence of alkenes.[1-5] Thermolysis of *N*-imidoaziridines **1**, R = Ph; R′ = H; R″ = CO_2Me or COPh, leads to azomethine ylides which undergo cycloaddition reaction with a dipolarophile or rearrange to give oxazoles.[6] We describe here a new reaction given by aziridines **1**, **2**, and **3**.[7]



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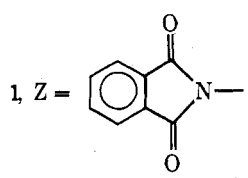
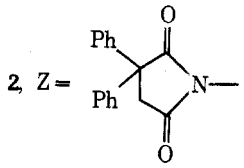
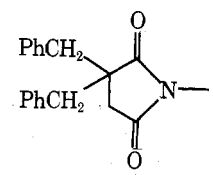


1, Z =

a, R = R″ = Ph; R′ = H
b, R = Ph; R′ = H; R″ = *p*-$MeOC_6H_4$
c, R = *p*-$MeOC_6H_4$; R′ = H; R″ = Ph
d, R = *p*-ClC_6H_4; R″ = Ph; R′ = H
e, R = *p*-ClC_6H_4; R″ = *p*-$MeOC_6H_4$; R′ = H
f, R = R″ = CO_2Me; R′ = CN
g, R = R′ = R″ = CN



2, Z =

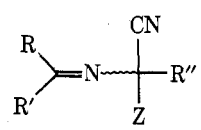


3, Z =

a, R = R″ = Ph; R′ = H
b, R = *p*-ClC_6H_4; R′ = H; R″ = Ph
R = *p*-ClC_6H_4; R′ = H; R″ = Ph

Results and Discussion

When dissolved in benzene or $CHCl_3$, at room temperature, aziridines **1**, **2**, or **3** are quantitatively converted to imines **4** and **5**.



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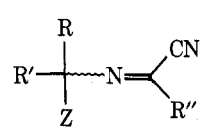

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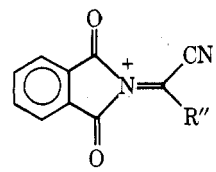
The rearrangement of aziridines **1c** and **1g** occurs so rapidly that these aziridines have not been isolated, but only the corresponding imines **4** and **5** have been obtained. The structures of the imines are confirmed by spectroscopic data. The NMR spectrum of **4** shows resonance at δ about 8.8 ppm, in agreement with the presence of the vinyl proton,[16] and the mass spectrum of **4**, Z = phthalimido, had a peak attributable to fragment **6**. The ir spectrum of isomer **5** exhibits a band at



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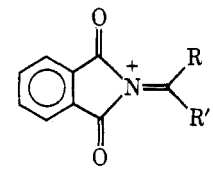

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about 2215 cm^{-1} (C≡N stretching vibration) and the peak of fragment **7** appears in the mass spectrum of **5**, Z = phthalimido.

Hydrolysis of imines **4** and **5**, R′ = H, Z = phthalimido, using hydrochloric acid solution gives RCHO, R″CO_2H, ZH, NH_4Cl, and HCN.

The relative yields of imines **4** and **5** in the decomposition of aziridines **1** (Table I) depends on the nature of the substituents R and R″.

We interpret these results by postulating formation of an azomethine ylide **8** in the first reaction step. Indeed, the C–C bond of the aziridine ring is weakened by substituents, particularly by the CN group.[6,17] Ylide **8** can be trapped by MeOH.[10] Thus, **1a** dissolved in a mixture of $CHCl_3$ (⅔) and MeOH (⅓) gives imine **9** (30%) in addition to **4** and **5** (70%) at room temperature. The conversion to imines **4** and **5** is slowed down when the solvent polarity increases: it is twice as fast in benzene as in acetonitrile at the same temperature. Therefore, the rate-determining step is not the formation of the ylide which involves an increase in charge separation, and which is favored by a polar solvent.

In the presence of diphenylsuccinimidate anion in tenfold excess aziridine **1d** gives only **4d** and **5d**, Z = phthalimido (**4d** and **5d**, Z = diphenylsuccinimido, are not detected). The diphenylsuccinimidate anion does not play any part in the transposition. This means that either the ion pair **11** (analogous to the salt referred to in order to explain the solvolysis of 1-chloroaziridines[8,9]) is not an intermediate or that ion pair is so tight that it does not react with external nucleophile.

This reaction which is of the Stevens type (1–2 migration of Z) could be explained by a radical mechanism (Scheme I). In favor of this mechanism, we must notice that the energy of

Table I. Reaction Products of 1 [a]

Aziridines	Yield of **4**, %	Yield of **5**, %
1a	48	52
1b	67	33
1c	0	100
1d	15	85
1e	58	42
1f, 1g [b]	50	50

[a] Yields determined by NMR (solvent $CDCl_3$). [b] These aziridines are symmetrical.

Table II. Spectroscopic Data of Aziridines

Aziridine	Yield, %	Mp, °C	$\nu_{C\equiv N}$	$\nu_{C=O}$	$\nu_{C=O}$	δ_{OMe}	δ_{CH}
1a	61	149 dec	2242	1771	1717		5.70 (s)
1b	95	150 dec	2248	1772	1710	3.71 (s)	5.57 (s)
1d	60	143 dec	2240	1772	1708		5.62 (s)
1e	95	135 dec	2235	1768	1710	3.72 (s)	5.55 (s)
1f	60	130 dec		1760	1728	4.04 (s)	
2a	48	160 dec	2240	1770	1700	3.19[a] (s)	5.64 (s)
2b	50	155 dec	2245	1771	1703	3.17[a] (s)	5.57 (s)
3	34	105 dec	2250	1780	1708	2.22[b] (q)	5.30 (s)

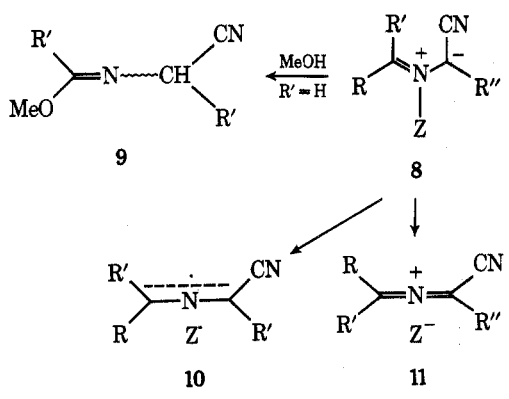
[a] δ_{CH_2} succinimido ring. [b] δ_{PhCH_2}, q, J = 18 Hz.

Table III. NMR and Ir Spectral Data for Imines 4, R′ = H

R	R″	Z	Mp, °C	$\nu_{C=O}$	$\nu_{C=N}$	δ_{OMe} or δ_{CH_2}	$\delta_{CH=N}$
Ph	Ph	Phthalimido	167	1776, 1720	1640		8.91 (s)
Ph	*p*-$MeOC_6H_4$	Phthalimido	*a*	1776, 1725	1640	3.87 (s)	8.85 (s)
p-$MeOC_6H_4$	Ph	Phthalimido	156	1777, 1727	1633	3.83 (s)	8.78 (s)
p-ClC_6H_4	Ph	Phthalimido	145	1782, 1730	1642		8.84 (s)
p-ClC_6H_4	*p*-$MeOC_6H_4$	Phthalimido	*a*			3.84 (s)	8.84 (s)
p-ClC_6H_4	Ph	Diphenylsuccinimido	190	1776, 1718	1632	3.47[b] (s)	8.78 (s)
Ph	Ph	Diphenylsuccinimido	*a*			3.45[b] (s)	8.80 (s)
p-ClC_6H_4	Ph	Dibenzylsuccinimido	147	1776, 1716	1640	2.68[b] (s)	8.61 (s)

[a] Nonpurified. [b] δ_{CH_2} succinimido ring.

Scheme I



the N–N bond is weaker (161 kJ)[18] than that of the C–N bond (292 kJ).

When the reaction was carried out with a mixture of aziridines **3** and **2a** or a mixture of **1a** and **2b**, cross products were not detected, although the rates of decomposition are of the same order of magnitude. Moreover, the lack of CINDP, the absence of ESR signal, and the fact that the yields of imines **4** and **5** are not altered by the presence of CBr_4 are evidence against a radical pair mechanism, though the radical pair **10** can react exclusively inside a solvent cage.[11,12]

Although an ionic process and a radical process cannot be definitely dismissed, all of the negative evidence presented for this rearrangement seems to be most consistent with a concerted mechanism.[13] These reactions provide the first example of 1–2 shift of a substituent fixed on nitrogen toward the neighboring carbon atom in an azomethine ylide. They permit an easy access to functionalized imines.

Experimental Section

The NMR (δ, $CDCl_3$, Me_4Si as internal standard) and ir (Nujol, ν) spectra (Tables II–IV) were recorded on a JEOL MH 100 spectrometer and on a Perkin-Elmer 225 spectrometer, respectively. The mass spectra (Table V) were measured on a Varian MAT 311 spectrometer. The melting points were determined on the Kofler apparatus. The observed values of C, H, N analyses for all new compounds isolated agreed within 0.4% with the calculated values.

The cyanostilbenes were prepared by the method of Frost[14] and (MeOCO)(CN)C=C(CN)CO_2Me by the procedure of Ireland and Pizey.[15]

Aziridines. The aziridines **1**, **2**, and **3** were obtained by oxidation of the corresponding *N*-aminoimide with $Pb(OAc)_4$ in the presence of the suitable alkene.[5] It is necessary to extract the aziridines quickly from the reactive medium because of their instability in solvents.

Transposition of Aziridines into Imines 4 and 5. A solution of 2 g of aziridines in 30 ml of $CHCl_3$ was left at room temperature for 24 h. The solvent was removed. The imines **4** and **5** were separated by fractional crystallization in ether.

Hydrolysis of Imines 4, R = *p*-ClC_6H_4; R′ = H; R″ = Ph; Z = Phthalimido, and 5, R = Ph; R′ = H; R″ = *p*-$MeOC_6H_4$; Z = Phthalimido. Imine (0.25×10^{-2} mol) suspended in 10 ml of a hydroalcoholic solution at 50% M in HCl was heated with reflux for 30 min. The medium became homogeneous when hot. The solution was cooled, the phthalimide was filtered off, and ethanol was removed. The aqueous layer was extracted with $CHCl_3$ and the organic layer obtained was extracted with 1 M $NaHCO_3$. Benzoic acid (with imine **4**) or *p*-methoxybenzoic acid (imine **5**) crystallized after acidification of the aqueous layer. The organic layer was extracted with 1 M soda and the $CHCl_3$ was removed. The ir and NMR spectra of the oil obtained were characteristic of *p*-chlorobenzaldehyde (imine **4**) or benzaldehyde (imine **5**). Phthalimide crystallized from the soda when acidified. The NH_4^+ cation was traced in the aqueous solution.

Decomposition of 1a in the Presence of MeOH. Aziridine **1a** (2 g) was dissolved in a mixture of $CHCl_3$ (48 ml) and MeOH (24 ml). The solution was left at room temperature for 18 h; then the solvent was removed under vacuum. The residual solid was extracted with 50 ml of ether. The solution was washed with diluted aqueous soda. Imines **4** and **5** crystallized first (yield 70%) from ether. Imine **8** slowly crystallized from the filtrate to yield white crystals (30%): mp 78 °C (ether); ir 2230, 1645 cm^{-1}; NMR δ 3.92 (s, 3 H), 5.31 (s, 1 H), 7.1–8.0 (m, 10 H); mass spectrum *m/e* (rel intensity) 250 (23), 249 (26), 235 (26), 218 (8), 157 (12), 116 (61), 105 (100).

Thermolysis of 1d in the Presence of the α,α-Diphenylsuccinimidyl Anion. Aziridine **1d** (400 mg, 1 mmol) was added to 10 mmol of sodium α,α-diphenylsuccinimidate (prepared by the reaction of 240 mg of NaH on 2.51 g of α,α-diphenylsuccinimide) in 30 ml of dry THF. After 15 h at room temperature, the solvent was removed and

Table IV. NMR and Ir Spectral Data for Imines 5

R	R′	R″	Z	Mp, °C	$\nu_{C\equiv N}$	$\nu_{C=O}$	δ_{OMe}
Ph	H	Ph	Phthalimido	141	2216	1768, 1712	
Ph	H	p-$MeOC_6H_4$	Phthalimido	136	2215	1764, 1708	3.85 s
p-ClC_6H_4	H	Ph	Phthalimido	198	2218	1763, 1708	
p-ClC_6H_4	H	p-$MeOC_6H_4$	Phthalimido	125	2218	1768, 1716	3.87 s
CN	CN	CN	Phthalimido	195	2214, 2210, 2198	1804, 1769, 1759	
CO_2Me	CN	CO_2Me	Phthalimido	171	2200	1796, 1788	4.00 (s), 3.94 (s)[a]
						1748, 1702	3.76 (s), 3.87 (s)

[a] Two isomers, syn and anti.

Table V. Mass Spectral Data for Imines, *m/e* (Relative Intensity)

Imine	R	R′	R″	Z	
4	Ph	H	Ph	Phthalimido	365 (M^+, 5), 261 (100), 236 (6), 218 (55), 190 (6), 158 (23), 147 (14)
4	p-$MeOC_6H_4$	H	Ph	Phthalimido	395 (M^+, 11), 278 (7), 261 (74), 248 (100), 233 (31), 203 (19), 158 (17), 147 (32)
4	p-ClC_6H_4	H	Ph	Phthalimido	401 (14), 399 (5) (M^+), 272 (12), 270 (35), 261 (100), 254 (38), 252 (66), 236 (5), 217 (10), 190 (10), 158 (25), 147 (15)
4	p-ClC_6H_4	H	Ph	Diphenyl-succinimido	505 (1), 503 (3), (M^+), 366 (7), 253 (48), 252 (44), 250 (47), 208 (56), 190 (14), 180 (100), 165 (51)
5	Ph	H	p-$MeOC_6H_4$	Phthalimido	395 (M^+, 32), 248 (77), 236 (100), 147 (14), 146 (38), 145 (58)
5	p-ClC_6H_4	H	Ph	Phthalimido	401 (11), 399 (31) (M^+), 272 (33), 270 (90), 261 (42), 254 (37), 252 (100), 217 (17), 190 (9), 158 (12), 147 (18)
5	CN	CN	CN	Phthalimido	288 (M^+, 18) 236 (4), 210 (33), 147 (14), 130 (52), 104 (100)
5	CO_2Me	CN	CO_2Me	Phthalimido	354 (M^+, 10), 295 (2), 243 (2), 147 (100)

the NMR spectrum of the crude product showed the presence of imine **4** (R = p-ClC_6H_4; R″ = Ph; R′ = H; Z = phthalimido) only.

Thermolysis of a Mixture of Aziridines 1. An equimolar solution (0.4 M) of aziridines **2a** and **3** in $CDCl_3$ was left at room temperature for 15 h. The NMR spectrum of this solution exhibited the characteristic absorption peaks of the two corresponding imines **4**. The lack of cross products was checked by adding reference samples to NMR solution. A similar result was reached when a mixture of aziridines **1a** and **2b** or a mixture of aziridines **3** and **1a** was thermolyzed.

Influence of the Solvent on the Transposition Rates of Aziridine 2b. A solution (0.4 M) of aziridine **2b** in the solvent was prepared in a flask, immersed in a thermostat (41 °C) at the initial time of the reaction. A small amount of the reaction mixture was taken out from the flask and the ratios of the products were determined from the integrated values on NMR spectra, at a given time.

Time, min	Solvent	Yield, %, in 4
41	$CDCl_3$	40
42	C_6D_6	42
44	CH_3CN	27

Registry No.—**1a,** 49678-78-6; **1b,** 53903-71-2; **1d,** 58747-23-2; **1e,** 53903-72-3; **1f,** 58747-24-3; **2a,** 58747-25-4; **2b,** 58747-26-5; **3,** 58747-27-6; **4a,** 58747-28-7; **4b,** 58747-29-8; **4c,** 58747-30-1; **4d,** 58747-31-2; **4e,** 58747-32-3; **4f,** 53903-75-6; **4g,** 53903-73-4; **4h,** 58784-34-2; **5a,** 58747-33-4; **5b,** 58784-35-3; **5c,** 58747-34-5; **5d,** 58747-35-6; **5e,** 58747-36-7; **5f,** 58747-37-8; sodium α,α-diphenylsuccinimidate, 58747-38-9.

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