Hz, exchangeable with D_2O, NH), 5.47 (s, 1 H, H-2′), 5.32 (s, 1 H, H-5′), 2.78 (d, 3 H, J = 5.2 Hz, collapses to singlet with D_2O, $NHCH_3$), 2.65 (s, 3 H, $=NCH_3$); ^1H NMR ($CDCl_3$) δ 7.30–6.70 (m, 8 H, acridine protons), 6.25 (d, 1 H, J = 5.3 Hz, exchangeable with D_2O, NH), 5.63 (s, 1 H, H-2′), 5.35 (s, 1 H, H-5′), 5.30 (s, 1 H, H-5′), 5.30 (s, 1 H, exchangeable with D_2O, OH), 2.92 (d, 3 H, J = 5.3 Hz, collapses to singlet with D_2O, $NHCH_3$), 2.74 (s, 3 H, $=NCH_3$). Anal. Calcd for $C_{21}H_{18}N_4O$: C, 73.65; H, 5.30; N, 16.36. Found: C, 73.20; H, 4.96; N, 15.98.

Later eluates gave **N(4′)-(9-acridinyl)-6′-(methylamino)-3′-methoxy-1′,4′-benzoquinone imine (18f)** (50 mg, 22%) as a black solid: mp 193–194 °C (from EtOAc); ^1H NMR ($CDCl_3$) δ 8.20–7.40 (m, 8 H, acridine protons), 6.00 (s, 1 H, H-2′), 5.63 (d, 1 H, J = 5.0 Hz, exchangeable with D_2O, NH), 4.55 (s, 1 H, H-5′), 4.05 (s, 3 H, OCH_3), 2.35 (d, 3 H, J = 5.0 Hz, collapses to singlet with D_2O, $NHCH_3$). Anal. Calcd for $C_{21}H_{17}N_3O_2$: C, 73.5; H, 5.00; N, 12.2. Found: C, 73.21; H, 4.72; N, 12.11. Further elution with EtOAc/MeOH (10:1) gave reduced starting material **4** (110 mg, 52%), identified by TLC and mixed melting point.

With longer reaction time (5 min), under similar conditions, the following product distribution was obtained: **18g** (45% yield); **18f** (trace amount); and reduced starting material **4** (50%).

B. Quinone Diimine 7. Similar treatment of **7** (300 mg, 0.77 mmol) gave a major product (TLC), which was unstable and decomposed when purification by chromatography was attempted.

Acknowledgment. This work was supported by the Auckland Division of the Cancer Society of New Zealand and by the Medical Research Council of New Zealand.

Registry No. 1, 51264-14-3; 2, 51264-17-6; 3, 53478-38-9; 4, 106063-42-7; 5, 117252-48-9; 5·HCl, 117252-64-9; 6, 61421-83-8; 7, 117252-49-0; 8, 117252-50-3; 9, 106063-38-1; 10, 117252-51-4; 11, 117252-52-5; 12, 106063-36-9; 17a, 117252-53-6; 17b, 117252-55-8; 17c, 117252-56-9; 17d, 117252-61-6; 18a, 117252-54-7; 18b, 117252-57-0; 18c, 117252-58-1; 18d, 117252-60-5; 18e, 117252-59-2; 18f, 117252-62-7; 18g, 117252-63-8; 4-nitro-2-methoxyphenol, 3251-56-7; 9-chloroacridine, 1207-69-8.

Thermolysis of 7-(Acylamino)-7-azabenzonorbornadienes and 1-(Acylamino)aziridines. Generation and Trapping of Monosubstituted Azamines[1]

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The thermolysis of 7-[[[(9-fluorenylmethyl)oxy]carbonyl]amino]- and 7-(benzoylamino)-7-azabenzonorbornadienes (**2a** and **2b**) in various solvents has been studied. In the absence of an olefinic trapping agent the major products other than naphthalene are the corresponding hydrazides **6a,b**. In cyclohexene as solvent, the aziridines **7a,b** are formed, suggesting that the azamine **3** is ejected and captured by the olefin. For the olefin *cis*-4-methyl-2-pentene, the reaction occurs with greater than 95% stereoselectivity in further agreement with a labile azamine intermediate. This represents the first demonstration that a monosubstituted azamine has independent existence and reacts with olefin faster than it undergoes 1,2-hydrogen shift. Synthesis of the related 7-phthalimido-7-azabenzonorbornadiene (**17**) was achieved via rearrangement of the corresponding isophthalimide derivative **18**, which could be obtained by reaction of phthaloyl chloride with hydrazine **1**. Thermolysis of **17** caused fragmentation to naphthalene and phthaloylazamine **13** as shown by trapping of the latter. This reaction represents a new thermal source of transient species **13**. For synthetic purposes more practical intermediates for the generation of **3** are the aziridines **21** and **22**. The cis analogues (**23**) of **21** proved to be relatively stable thermally. A new route is presented for the synthesis of 1-amino-*cis*-2,3-diphenylaziridine.

In a previous paper, the use of 7-[[[(9-fluorenylmethyl)oxy]carbonyl]amino]-7-azabenzonorbornadiene (**2a**) as a storage form of the thermally sensitive hydrazine **1** was reported.[2] Although **2a** could be obtained as a crystalline solid and was far easier to handle ($t_{1/2}$ 70 min, $CDCl_3$, 37 °C) than oily **1** ($t_{1/2}$ 15 min, $CDCl_3$, 37 °C), it decomposed at its melting point (84 °C) or upon standing in solution at room temperature for several hours. Since the thermal decomposition of **2a** was accompanied by the formation of naphthalene (85%), it became of interest to determine whether the initial reaction involved fragmentation to the azamine **3**. Along with naphthalene, hydrazide **6a** was isolated from all such decompositions carried out in a variety of neutral solvents. Formation of **6a** can be rationalized as arising from capture of **3** by initial reactant **2** via adduct **4**, extrusion of **5**, and subsequent loss of nitrogen (Scheme I). Analogy for such extrusion reactions is available in the fragmentation of related ylides[3] and amine oxides.[4,5]

More direct evidence for the finite existence of **3** was sought by olefin trapping reactions. Indeed, thermolysis of **2a** in cyclohexene at 55 °C led to the isolation in 44% yield of aziridine **7a**, the structure of which was established by its alternate synthesis by reaction of authentic **9**[6] with

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(3) Gribble, G. W.; Allen, R. W.; LeHoullier, C. S.; Eaton, J. T.; Easton, N. R., Jr.; Slayton, R. I.; Sibi, M. P. *J. Org. Chem.* **1981**, *46*, 1025.

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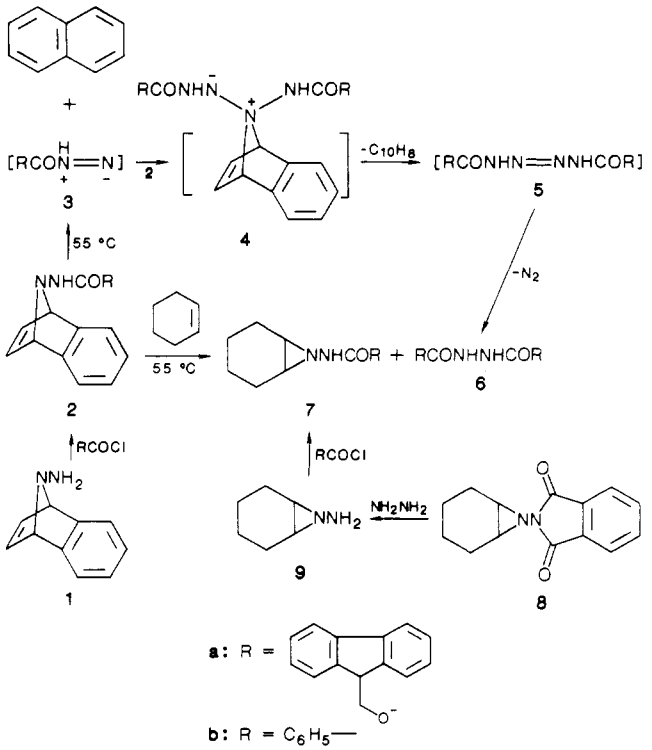
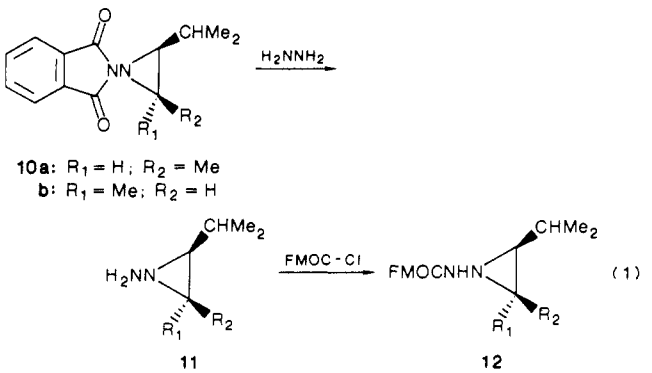
0022-3263/88/1953-6047$01.50/0

Scheme I



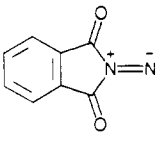
9-fluorenylmethyl chloroformate.[7] In agreement with the nitrene-like behavior of **3**, capture by *cis*-4-methyl-2-pentene proved to be stereospecific. Authentic samples of the expected cis and trans adducts (**12a,b**) were first synthesized from the known phthalimido derivatives (**10a,b**)[8] by treatment with hydrazine followed by appropriate acylation. Hydrazides **12a,b** could be readily distinguished by ^{1}H NMR analysis, particularly in the region from δ 0.9 to 1.1 ppm. Both isomers were shown to be stable in toluene at 45 °C for at least 4 h. Thermolysis of **2a** in 50% *cis*-4-methyl-2-pentene in toluene at 45 °C was complete after 4 h to give **12a** (cis) in 28% yield. On the basis of comparison with artificially prepared standard mixtures, the minimum cis/trans ratio was 95/5.



This is the first example of the olefin trapping of a monosubstituted azamine and, if the species involved is truly free, demonstrates that 1,2-hydrogen migration, either intra- or intermolecularly, is slow relative to reaction with cyclohexene. On the other hand a one- or multistep transfer of the elements of **3** from **2** to cyclohexene is conceivable. Evidence on this point is not available but might be obtainable by application of a Rebek three-phase test.[9] Previously, high activation energies have been calculated for the related 1,2-H shift from azamine to diimide, although a bimolecular transition state is said to be facile.[10] In the presence of an olefin (cyclohexene, *cis*-4-methyl-2-pentene) no bis[[(9-fluorenylmethyl)oxy]-carbonyl]hydrazine (**6**) is isolated, although TLC examination of the crude reaction mixture suggested the presence of trace amounts of this compound.

The corresponding *N*-benzoyl derivative of 7-amino-7-azabenzonorbornadiene (**2b**) proved to be much less stable than **2a** ($t_{1/2}$ <10 min in $CDCl_3$ at 37 °C) and a completely pure sample could not be obtained. Violent decomposition took place at the melting point (87 °C), and ^{1}H NMR analysis under ordinary conditions in $CDCl_3$ was attended by immediate gas evolution and precipitation of 1,2-dibenzoylhydrazine (**6b**). Heating a suspension of hydrazide **2b** in cyclohexene at 55 °C for 30 min gave 47% of **6b** and only 18% of the cyclohexene adduct **7b**.

In contrast to monoacyl azamines such as **3**, numerous 1,1-disubstituted analogues have been generated and captured. The corresponding phthaloyl derivative **13** has an extensive history, being of both theoretical and practical synthetic interest.[11] In early studies this transient species



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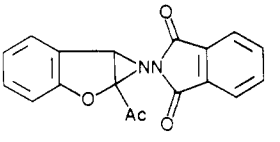

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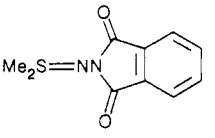
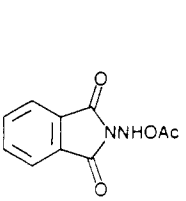


15

was assumed to be generated and trapped by the oxidation of *N*-aminophthalimide by means of lead tetraacetate in the presence of various olefins. For some reactions the presence of excess oxidant or acetic acid is deleterious, yet there are only a few thermal sources of phthaloylazamine (**13**). Two examples are **14**[12a] and **15**.[12b] Recently Atkinson and Kelly[13] isolated an *N*-acetoxyhydrazine **16**, which acts to transfer phthaloylazamine (**13**) to olefins stereospecifically. It was suggested that aziridination processes



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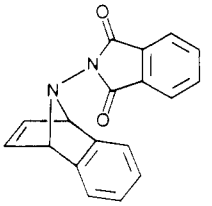

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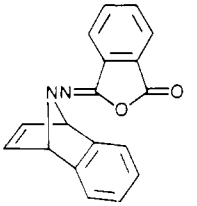

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involving **16** resemble the peracid oxidation of olefins and that under the normal Rees' aziridination conditions the

(7) Carpino, L. A.; Han, G. Y. *J. Am. Chem. Soc.* **1970**, *92*, 5748; *J. Org. Chem.* **1972**, *37*, 3404.
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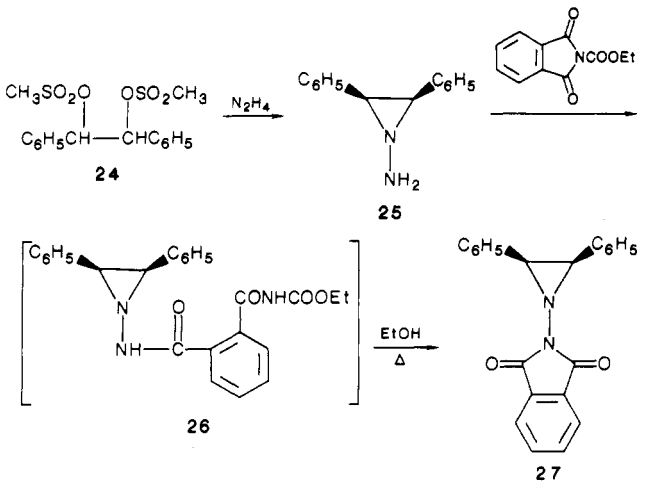
(10) (a) Kemper, M. J. H.; Buck, H. M. *Can. J. Chem.* **1981**, *59*, 3044. (b) Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 225.
(11) (a) Anderson, D. J.; Gilchrist, T. L.; Horwell, D. C.; Rees, C. W. *J. Chem. Soc. C* **1970**, 576. (b) Atkinson, R. S. In *Azides and Nitrenes. Reactivity and Utility*; Lwowski, W., Ed.; Academic: New York, 1984; p 247.
(12) (a) Jones, D. W. *Chem. Commun.* **1972**, 884. (b) Edwards, M.; Gilchrist, T. L.; Harris, C. J.; Rees, C. W. *J. Chem. Res., Synop.* **1979**, 114.
(13) Atkinson, R. S.; Kelly, B. J. *Chem. Commun.* **1987**, 1362.

Scheme II

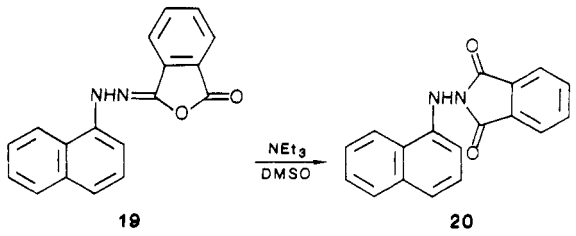


existence of free **13** is unlikely. In order to further establish the generality of 7-amino-7-azanorbornadienes as thermal sources of azamines, the phthaloyl derivative **17** was sought. Reaction of phthaloyl chloride with **1** gave not **17** but an isomeric compound established on the basis of IR, ^1H NMR and ^{13}C NMR spectroscopy to be the corresponding isophthalimide **18**.

Although early reports are somewhat confusing, the generality of the reaction of amines with phthaloyl chloride to give isophthalimides has recently been established.[14] Detailed analyses of the kinetics of the rearrangement of various isophthalimides to their normal isomers by means of nucleophilic reagents have been reported.[15] Compound **18** proved to be relatively stable thermally. Upon attempting to determine a half-life for its fragmentation in an NMR tube in $CDCl_3$ at 37 °C, slow decomposition was noted ($t_{1/2}$ >100 h) with the appearance of a new broad ^1H NMR peak at δ 6.05. After 10 days the intensities of the bridgehead peak of **18** at δ 5.63 and the new peak were about equal. In DMSO in the presence of triethylamine, build up of the δ 6.05 absorption was more rapid and indeed after 24 h a 74% yield of a compound was isolated, which proved to be the desired phthalimido derivative **17**. IR and ^1H and ^{13}C NMR spectral data are consistent with the normal structure. No invertomers were noted at room temperature for either **17** or **18**. Attempts to obtain **17** directly by reaction of **1** with *N*-carbethoxyphthalimide[16] or *o*-carbomethoxybenzoyl chloride[17] failed to give either **17** or **18**. The presumed intermediate monoacylhydrazine may have been too unstable to survive the reaction conditions. Although far more stable than **2a** or **2b**, phthalimide **17**, upon thermolysis in cyclohexene–toluene (1:1) at 105 °C over a period of 24 h, led to the isolation of both naphthalene and adduct **8** (59%). The stereospecificity of the reaction with *cis*-4-methyl-2-pentene (cis adduct, 33%) was such that the cis/trans ratio was at least 96/4.

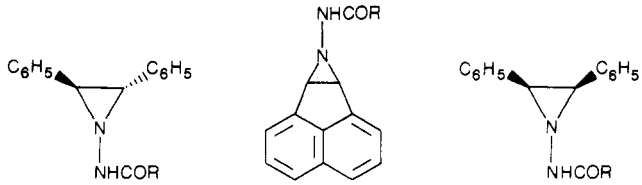
The exact nature of the extrusion process, which occurs upon heating **2a,b** and **17**, is not clear. Most likely it is either a concerted cheletropic fragmentation or a two-step radical process. In related systems incorporating other 7-hetero substituents (RN, SiR_2, GeR_2, POR, etc.) there is evidence for both modes of reaction.[5]

Thermolysis of **18** in benzene gave naphthalene and variable amounts of a compound identified as the ring-opened product **19**. An authentic sample of **19** was obtained by reaction of 1-naphthylhydrazine and phthaloyl chloride (74%). Isoimide **19** was isomerized to the known[18] phthalimide **20** by the method described earlier (eq 2).



(2)

Because the 7-(acylamino)-7-azabenzonorbornadienes **2** are relatively inaccessible (five-step synthesis) this route to the generation of monoacylazamines **3** is of limited practical synthetic applicability. More readily available thermal precursors of **3** are the *N*-(acylamino)aziridines **21** and **22**, which undergo thermolysis to **2** at 25–60 °C (Tables I and II). In the presence of cyclohexene or *cis*-4-methyl-2-pentene the expected adducts **7** and **12a** (from **21a**) are obtained. The related *cis*-2,3-diphenyl analogues



21, R as in Scheme I **22**, R as in Scheme I **23**

23 (R = C_6H_5, CH_3, FMO) proved to be thermally stable and did not eject the azamine fragment under any conditions examined. Whereas **21** (R = C_6H_5), the least stable of the compounds synthesized, exhibits a half-life of less than 15 min in $CDCl_3$ at 37 °C and is difficult to handle under ordinary conditions, compounds **23** (R = C_6H_5 or CH_3) have been stored at room temperature for over 15 years without change. The instability of **21** (R = C_6H_5) parallels the marked instability previously observed for **2b**. Derivatives of **22** are significantly more stable than analogous derivatives of **21**.

Hydrazides **21–23** were prepared by acylation of the free aminoaziridines, which are easily obtained by the standard Rees technique[23] (lead tetraacetate oxidation in the presence of olefin followed by hydrazine deblocking). 1-Amino-*cis*-2,3-diphenylaziridine (**25**) was also synthesized by a modification of Paulsen's technique[24] involving alkylation of hydrazine by means of *meso*-hydrobenzoin dimesylate **24** (Scheme II). Structure **25** was established as the three-ring rather than the four-ring analogue by

(14) (a) Ganin, E. V.; Anikin, V. F.; Rozynov, B. V.; Makarov, V. F.; Kamalov, G. L. *J. Org. Chem. (USSR)* **1985**, *21*, 142. (b) Ganin, E. V.; Makarov, V. F.; Nikitin, V. I. *J. Org. Chem. (USSR)* **1986**, *21*, 2209. (c) Ganin, E. V.; Makarov, V. F.; Rozynov, B. V. *J. Org. Chem. (USSR)* **1985**, *21*, 1772.

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(19) Melting points and boiling points are uncorrected. Infrared spectra were taken on Perkin-Elmer 237B and 1310 spectrometers. ^1H NMR spectra were obtained on Perkin-Elmer R-12 (60 MHz) or R-32 (90 MHz) spectrometers or Varian XL-200 (200 MHz) or XL-300 (300 MHz) instruments. ^{13}C NMR spectra were recorded on Bruker HX-90, Varian XL-200 or XL-300 instruments. TLC was performed on aluminum-backed Merck silica gel 60, F_{254} plates. Elemental analyses were performed at the University of Massachusetts Microanalytical Laboratory under the direction of Greg Dabkowski.

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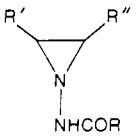
Table I. Synthesis[a] and Characterization of 1-(Acylamino)aziridines



compd	R	R′	R″	yield, %	mp (solv), °C	NMR (solv), δ	mol formula	analytical data calcd/found
1[b]	FMO	*cis*-C_6H_5	C_6H_5	80	165.5–167 dec (EtOAc/hexane)	($CDCl_3$–DMSO-d_6) 3.57 (s, 2, ring CH), 4.10–4.55 (m, 3, $CHCH_2$), 6.95–7.85 (m, 18, aryl), 8.85 (br s, 1, NH)	$C_{29}H_{24}N_2O_2$	C, 80.52; H, 5.60; N, 6.48 C, 80.33; H, 5.69; N, 6.49
2	FMO	*trans*-C_6H_5	C_6H_5	73	99–100.5 dec (CH_2Cl_2/hexane)	($CDCl_3$) 3.55 (q, 2, ring CH), 4.0–4.5 (m, 3, $CHCH_2$), 5.73 (br s, 1, NH), 7.0–7.9 (m, 18, aryl)	$C_{29}H_{24}N_2O_2$	C, 80.52; H, 5.60; N, 6.48 C, 80.25; H, 5.57; N, 6.33
3	C_6H_5	*cis*-C_6H_5	C_6H_5	97	151.5–152 dec (Me_2CO)	(acetone-d_6) 3.75 (s, 2, ring CH), 7.05–7.48 (m, 13, aryl), 7.89 (d, 2, *o*-Bz), 9.73 (s, 1, NH)[c]	$C_{21}H_{18}N_2O$	C, 80.25; H, 5.73; N, 8.92 C, 80.14; H, 5.79; N, 8.82
4[d]	C_6H_5	*trans*-C_6H_5	C_6H_5	14	60–63 dec (CH_2Cl_2/hexane)	($CDCl_3$) 3.80 (q, 2, ring CH), 7.0–7.8 (m, 15, aryl)		
5	CH_3	*cis*-C_6H_5	C_6H_5	90	165–166 dec (Me_2CO)[e]	($CDCl_3$) 1.98 (minor) and 2.41 (major) (s, totalling 3 H, CH_3), 3.55 (major) and 3.62 (minor) (s, totalling 2 H, ring CH), 7.15–7.26 (m, 10, aryl), 8.15 (s, 1, NH)	$C_{16}H_{16}N_2O$	C, 76.19; H, 6.35; N, 11.11 C, 76.44; H, 6.77; N, 10.75

[a] The cis derivatives were generally acylated in CH_2Cl_2 or $CHCl_3$ at 0 °C; the trans isomers at −50 to −40 °C with C_5H_5N or NEt_3 as base with the appropriate acid chloride or anhydride. [b] In this case a two-phase system involving ether and aqueous Na_2CO_3 was used for acylation via FMOC-Cl. [c] ^{13}C NMR (acetone-d_6) δ 53.2 (aziridine ring C), 165.5 (C=O); IR (Nujol) 1645 cm^{-1} (C=O). [d] Ether was used as solvent in this case with a second equivalent of aminoaziridine being used to absorb HCl from Bz-Cl. The *N*-benzoyl derivative was difficult to handle, a solution in $CDCl_3$ depositing *N,N′*-dibenzoylhydrazine within 5 min at 37 °C. An attempt to obtain an analytically pure sample was not successful. [e] Recrystallization from EtOAc gave a polymorphic modification, mp 177–178 °C dec.

Table II. Thermolysis of *N*-(Acylamino)aziridines[a]

run	compd	solvent	temp, °C	time, h	products (%)[b]
1	**21a**	cyclohexene	55	5.5	**7a** (58)
2	**21a**	*cis*-4-methyl-2-pentene/$C_6H_5CH_3$ (1:1)	45	4.0	**12a** (76)[c]
3	**21a**	CH_2Cl_2	25	24	FMOC-NHNH-FMOC (25) *trans*-C_6H_5CH=CHC_6H_5 (91)
4	**21b**	$CDCl_3$	37	0.25	$C_6H_5CONHNHCOC_6H_5$ (21)

[a] Decompositions were carried out as described in the Experimental Section for the corresponding acenaphthyleneimine derivatives. [b] *trans*-Stilbene could be isolated in each case in moderate-to-good yields. An example is given in run 3. [c] None of the corresponding trans isomer could be detected by TLC or ^1H NMR analysis. Comparison with standard mixtures of the cis and trans isomers showed that the cis/trans ratio was at least 96/4.

reaction with *N*-carbethoxyphthalimide[16] followed by warming of crude intermediate **26** in ethanol to give phthalimido derivative **27**, also obtainable unequivocally via the Rees' technique. Thermolysis of the free aminoaziridines, 1-amino-2,3-*cis*- and -*trans*-diphenylaziridine, has been the subject of previous reports.[6,25,26] In the case of free *N*-aminoacenaphthyleneimine, decomposition in chloroform at room temperature over a period of 150 h gave in 84% yield a 35/65 mixture of acenaphthylene and acenaphthene. In the same solvent at reflux for $1^1/_2$ h the ratio of the two hydrocarbons was reversed (70/30).

Experimental Section[19]

Thermolysis of 7-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (2a) in Cyclohexene. A suspension of 0.256 g of hydrazide **2a** in 35 mL of dry cyclohexene was stirred in an oil bath under N_2 at 55 °C for $5^1/_2$ h. A 10-cm Vigreaux column was attached, and most of the cyclohexene was removed by distillation at atmospheric pressure. Remaining cyclohexene was removed in vacuo at room temperature to give a partially solidified oil. Column chromatography of the residue using 20 g of silica gel (60–200 mesh) with elution by CH_2Cl_2 gave 0.069 g (71%) of naphthalene. The eluent was changed to 10–40% Et_2O in CH_2Cl_2, which gave 0.109 g (48%) of a white solid, mp 156–158 °C dec. Recrystallization from $CHCl_3$–Skellysolve F gave 0.099 g (44%) of a white solid, mp 163–165 °C dec, identified as FMOC hydrazide **7a** on the basis of spectral comparison with an authentic sample (mp 163.5–165 °C dec), which had been prepared from hydrazine **9** and FMOC-Cl (see below).

Thermolysis of 7-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (2a) in *cis*-4-Methyl-2-pentene/Toluene. A suspension of 0.295 g of hydrazide **2a** in 5.0 mL of dry toluene and 5.0 mL of *cis*-4-methyl-2-pentene was stirred under N_2 in an oil bath at 45 °C for 4 h. The solvent was evaporated in vacuo at 25 °C, a few milliliters of CCl_4 were added, and the process was repeated several times to give a partially solidified oil. TLC analysis (40% EtOAc in hexene) of the residue showed the presence of the *cis*-aziridine **12a** (R_f 0.31) but none of the trans isomer **12b** (R_f 0.23). Peaks in the ^1H NMR spectrum due to impurities near δ 1.0 prevented

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a minimum *cis*-/*trans*-aziridine ratio from being determined at this stage. Column chromatography on 15 g of silica gel (100–200 mesh, packed in CH_2Cl_2) with elution by 15% Et_2O in CH_2Cl_2 gave 0.072 g (28%) of **12a** (cis/trans ratio > 95/5). Recrystallization from 50% Et_2O in hexane gave 0.033 g (13%) of an off-white solid, mp 135–145 °C dec, identified by spectral comparison with an authentic sample, mp 154.5–155.5 °C dec, obtained by acylation of **11a** (see below). It was shown that the *trans*-aziridine **12b** could be recovered quantitatively when subjected to the conditions of this experiment.

Thermolysis of 7-[[[(9-Fluorenylmethyl)oxy]carbonyl]-amino]-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (2a) in CH_2Cl_2. A solution of 0.477 g of hydrazine **2a** in 5.0 mL of dry CH_2Cl_2 was allowed to stand at room temperature under N_2 for 22 h when TLC analysis showed the absence of starting material. Evaporation gave a solid, which was chromatographed on 3.0 g of silica gel (60–200 mesh) with elution by Skellysolve F. Eluent was evaporated to give 0.136 g (85%) of naphthalene, mp 79.0–81.0 °C. Elution by ether gave a semisolid, which was rechromatographed with elution by 3% Et_2O in CH_2Cl_2, resulting in a solid that was recrystallized from CH_2Cl_2–Skellysolve F to give 0.068 g (23%) of 1,2-bis(FMOC)hydrazine **6a** as a white solid, mp 198–200.5 °C dec (lit.[7] mp 202 °C dec), identified by spectral comparison with an authentic sample.

Thermolysis of 7-(Benzoylamino)-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (2b) in CH_2Cl_2. A solution of 0.313 g of **2b** in 5.0 mL of dry CH_2Cl_2 was allowed to stand at room temperature under N_2 for 3 h. Workup as described for the FMOC analogue gave naphthalene (61%), *N,N'*-dibenzoylhydrazine (35%) (mp 241.5–244 °C, lit.[20] mp 241 °C), and *N'*-benzoyl-α-naphthylhydrazine (25%), mp 177–182 °C dec, identified by comparison with an authentic sample, mp 191–192.5 °C (lit.[21] mp 184 °C).

Thermolysis of 7-Phthalimido-2,3-benzo-7-azabicyclo-[2.2.1]hepta-2,5-diene (17) in Cyclohexene/Toluene. A solution of 90.7 mg of **17** in 4.0 mL of 50% cyclohexene in toluene was heated at 105 °C with stirring in an oil bath for 24 h. Solvent was removed, and the residue was flash chromatographed on silica with elution by EtOAc/hexane (1:4), collecting material corresponding to R_f 0.25. Evaporation of solvent gave 58.1 mg of a tacky solid, which was dissolved in 0.5 mL of CH_2Cl_2, and 10 mL of hexane was added. Cooling to −20 °C overnight gave 45.1 mg (59%) of the adduct **8** as a yellow solid, mp 133–135 °C (lit.[6] mp 137 °C). Imide **8** was shown to be stable under the conditions described.

Thermolysis of 7-Phthalimido-2,3-benzo-7-azabicyclo-[2.2.1]hepta-2,5-diene (17) in *cis*-4-Methyl-2-pentene/Toluene. A solution of 0.325 g of phthalimide **17** in 5.0 mL of dry toluene and 0.766 g of *cis*-4-methyl-2-pentene was heated under N_2 in an oil bath at 105 °C with stirring for 34 h. The solvent was evaporated with the aid of a water aspirator, a few milliliters of CCl_4 were added, and the process was repeated several times to give a red-orange semisolid. ^1H NMR analysis (90 MHz) of the residue showed that the ratio of *cis*- to *trans*-aziridines **10a** and **10b** was at least 96:4, respectively, as determined by comparison with spectra taken of standard mixtures.

Column chromatography on 18 g of silica gel (100–200 mesh) with elution by 3% Et_2O in CH_2Cl_2 gave 0.090 g (33%) of a yellow-orange oil, which eventually solidified and was identified as *cis*-aziridine **10a** on the basis of spectral comparison with an authentic sample.[8]

***trans*-1-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-2-isopropyl-3-methylaziridine (12b).** A solution of 1.079 g of *trans*-phthalimide **10b** in 10 mL of hydrazine hydrate was stirred at room temperature for 30 min. The resulting solution was extracted with three 10-mL portions of Et_2O, the combined extracts were washed with 2.0 mL of saturated NaCl solution, dried, and filtered. The solution thus obtained was treated with 0.60 mL of Et_3N and cooled with stirring to −45 to −40 °C. A solution of 0.686 g of FMOC-Cl in 5.0 mL of Et_2O was added dropwise over a 3-min period. Stirring at this temperature was continued for 30 min, during which time a white precipitate separated. The mixture was warmed to 0 °C for 5 min, and 15 mL of H_2O was added followed by warming to room temperature and addition of 25 mL of CH_2Cl_2 and 10 mL of Et_2O. The organic layer was separated, and the aqueous layer was extracted with 15 mL of Et_2O. The combined organic extracts were dried and evaporated in vacuo at room temperature to give a white solid. The crude hydrazide was dissolved in 15 mL of warm EtOAc, 35 mL of hexane was added, and the solution was cooled to −20 °C. The precipitate was collected by filtration, washed with cold hexane, and air-dried to give 0.421 g (47%, based on FMOC-Cl) of the trans hydrazide **12b** as a white powdery solid, mp 131–133 °C dec. Recrystallization from warm EtOAc/hexane raised the melting point to 133–135 °C dec: ^1H NMR (90 MHz, $CDCl_3$) δ 0.93 (d, J = 6 Hz, 3, CH_3 of i-Pr), 1.07 (d, J = 6 Hz, 3, second CH_3 of i-Pr), 1.18–1.90 (m, 5, ring CH_3 + ring CH + CH of i-Pr), 1.90–2.25 (m, 1, ring CH), 4.10–4.65 (m, 3, $CHCH_2$), 5.90 (br s, 1, NH, D_2O exchangeable), 7.15–7.85 (m, 8, aromatic); IR (KBr) 3200 (NH), 1715, 1695 cm^{-1} (C=O).

A further recrystallization from the same solvent system provided the analytical sample, mp 138–139 °C dec. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.96; H, 7.20; N, 8.33. Found: C, 75.10; H, 7.32; N, 8.32.

***cis*-1-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-2-isopropyl-3-methylaziridine (12a).** Obtained by a procedure similar to that described for the corresponding trans isomer in a yield of 82% as a fluffy white solid, mp 153–155 °C dec: ^1H NMR (90 MHz, $CDCl_3$) δ 0.90 (d, J = 6 Hz, 3, CH_3 of i-Pr), 1.10–1.75 (m, 8, ring CH_3 + second CH_3 of i-Pr + ring H + CH of i-Pr), 1.85–2.15 (m, 1, ring H), 4.10–4.55 (m, 3, $CHCH_2$), 6.20 (br s, 1, NH, D_2O exchangeable), 7.15–7.90 (m, 8, aromatic); IR (KBr) 3240 (NH), 1700 cm^{-1} (C=O). The analytical sample was prepared by two precipitations from EtOAc/hexane, mp 154.5–155.5 °C dec. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.96; H, 7.20; N, 8.33. Found: C, 74.85; H, 7.42; N, 8.17.

7-(Benzoylamino)-7-azabicyclo[4.1.0]heptane (7b). A two-phase system containing 0.141 g of hydrazine **9** in 4.0 mL of Et_2O and 0.20 g of KOH in 3.0 mL of H_2O was stirred at 0 °C. Over a 2-min period a solution of 0.186 g of benzoyl chloride in 1.0 mL of Et_2O was added dropwise, and stirring was continued at 0 °C for 30 min. To the resulting suspension was added 5.0 mL of hexane, and after being stirred for 10 min the mixture was filtered and the solid was washed with water. After air-drying, 0.132 g (49%) of the hydrazide was obtained as a white powder, mp 150–151 °C dec. Recrystallization from EtOAc gave 0.112 g (41%) of the pure hydrazide as small white crystals, mp 152–154.5 °C dec: ^1H NMR (90 MHz, $CDCl_3$–Me_2SO-d_6) δ 1.00–1.50 (br m, 4, CH_2CH_2), 1.60–2.10 (br m, 4, CH_2), 2.20–2.40 (m, 2, CHCH), 7.20–7.65 (m, 3, meta plus para aromatic), 7.70–8.10 (m, 2, ortho aromatic), 9.75 (br s, 1, NH, D_2O exchangeable); IR (KBr) 3205 (NH), 1635 (sh), and 1625 cm^{-1} (C=O).

The same compound was obtained in 18% yield along with 47% of **6b** upon thermolysis of **2b** in cyclohexene. Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.18; H, 7.47; N, 12.95. Found: C, 71.98; H, 7.56; N, 13.20.

7-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-7-azabicyclo[4.1.0]heptane (7a). A two-phase system containing 0.216 g of hydrazine **9** in 10 mL of Et_2O and 0.30 g of Na_2CO_3 in 5.0 mL of H_2O was stirred at 0 °C. Over a 6-min period a solution of 0.499 g of FMOC-Cl in 10 mL of Et_2O was added dropwise, and the solution was stirred at 0 °C for 15 min and at room temperature for 15 min. Recrystallization of the precipitated solid from Skellysolve B gave 0.551 g (85%) of the hydrazide as a white powdery solid: mp 160–162 °C dec; ^1H NMR ($CDCl_3$) δ 0.95–1.45 (br m, 4, CH_2CH_2), 1.55–1.95 (br m, 4, CH_2) overlapping with peak at 1.95–2.20, 1.95–2.20 (br m, 2, CHCH) overlapping with peak at 1.55–1.95, 4.00–4.60 (m, 3, $CHCH_2$), 6.30 (br s, 1, NH, D_2O exchangeable), 7.05–7.95 (m, 8, aromatic); IR (KBr) 3245 (NH), 1695 cm^{-1} (C=O). The analytical sample was precipitated twice from EtOAc/hexane, mp 163.5–165 °C dec. Anal. Calcd for $C_{21}H_{22}N_2O_2$: C, 75.41; H, 6.64; N, 8.38. Found: C, 75.22; H, 6.64; N, 8.26.

7-Isophthalimido-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (18). A solution of 7.00 g of 7-azabenzonorbornadiene in 85 mL of Et_2O was converted to **1** as previously described.[2] The ice-cold solution of the hydrazine was filtered at 0 °C into a stirred mixture of 2.00 g of phthaloyl chloride, 10 mL of Et_2O, and 40 mL of 10% Na_2CO_3. The precipitated amine salt (13.4 g) was washed with 40 mL of cold Et_2O, and the washings were combined with the filtrate. After the mixture had been stirred for 3 h at 0 °C, 60 mL of CH_2Cl_2 and 40 mL of H_2O were added, and the

mixture was warmed to room temperature to dissolve a precipitate. After the organic layer had been separated the aqueous portion was extracted with 50 mL of Et_2O. The combined organic layers were dried and evaporated in vacuo at 25 °C to give a yellow-brown oil, which was dissolved in 30 mL of 95% EtOH and cooled to −20 °C overnight. Filtration of the precipitated solid followed by washing with cold 95% EtOH and air-drying gave 0.871 g (25%, based on MSH) of the isoimide as a yellow solid, mp 115–119 °C dec. Reprecipitation by dissolving the solid in 4 mL of CH_2Cl_2, adding 20 mL of 95% EtOH, and cooling to −20 °C gave 0.739 g (21%) of the pure isoimide as tiny yellow needles, mp 130–132 °C dec: ^1H NMR ($CDCl_3$) δ 5.63 (t, 2, bridgehead), 6.80–8.00 (m, 10, olefinic + aromatic); ^{13}C NMR (50.3 MHz, $CDCl_3$, 20 °C) δ 73.1 (bridgehead), 121.7, 122.0, 125.0, 125.1, 130.9, 134.9, 136.6, 140.2, 141.0, 147.2, 164.4 (C=O); IR (KBr) 1845 (w), 1790 (s), 1650 (m) cm^{-1} (C=O). The analytical sample was precipitated from CH_2Cl_2/Skellysolve F, mp 129–131 °C dec. Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.98; H, 4.20; N, 9.72. Found: C, 74.81; H, 4.17; N, 9.80.

7-Phthalimido-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (17). A mixture of 3.0 mL of DMSO, 0.50 mL of Et_3N, and 0.265 g of isophthalimide **18** was stirred at room temperature until the solid dissolved. The solution was allowed to stand for 24 h, 10 mL of CH_2Cl_2 was added, the solution was cooled in an ice bath with stirring, and 15 mL of H_2O was added. After separation of layers, the aqueous portion was washed with an additional 5 mL of CH_2Cl_2. The combined organic extracts were dried and evaporated under reduced pressure at room temperature to give a yellow-orange solid. The crude imide was dissolved in 1.0 mL of CH_2Cl_2, 7.0 mL of 95% EtOH was added, and the solution was allowed to stand at −20 °C overnight. The precipitated solid was filtered, washed with cold 95% EtOH, and air-dried to give 0.195 g (74%) of the imide as tiny yellow needles: mp 141–143 °C dec; ^1H NMR ($CDCl_3$) δ 6.05 (br s, 2, bridgehead), 6.65–7.55 (m, 6, olefinic + aromatic), 7.70 (br s, 4, phthalimido aromatic); ^{13}C NMR (50.3 MHz, $CDCl_3$, 46 °C) δ 71.2 (bridgehead), 123.0, 126.2, 131.0, 134.1, 140.5, 146.2 (br), 165.6 (C=O); IR (KBr) 1765 (w), 1700 (s) cm^{-1} (C=O). The analytical sample was prepared by precipitation from $CHCl_3$/hexane and cooling to −20 °C, mp 142–144 °C dec. Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.98; H, 4.20; N, 9.72. Found: C, 74.78; H, 4.23; N, 9.69.

***N*-Isophthalimido-1-aminonaphthalene (19).** A two-phase system consisting of 0.329 g of 1-naphthylhydrazine hydrochloride,[22] 15 mL of Et_2O, and 0.70 g of K_2CO_3 in 10 mL of H_2O was cooled with stirring to 0 °C. Over a period of 1 min a solution of 0.378 g of phthaloyl chloride in 5.0 mL of Et_2O was introduced in two portions. After being stirred at 0 °C for 30 min the mixture was filtered, and the solid was washed with H_2O followed by cold Et_2O. Air-drying gave 0.401 g (82%) of the crude isoimide, mp 218–232 °C dec. After dissolution in 50 mL of boiling $CHCl_3$ and filtration to remove a trace of insoluble solid, the volume was reduced to 25 mL, and 95% EtOH (25 mL) was added. Cooling to −20 °C followed by filtration and washing with cold 95% EtOH gave 0.361 g (74%) of the isoimide as a yellow-orange powder: mp 228–234 °C dec; ^1H NMR (90 MHz, $CDCl_3$) δ 7.35–8.10 (m, 10, aromatic), 8.55 (br s, 1, NH, slowly D_2O exchangeable); IR (KBr) 3350 (NH), 1785 (s), and 1660 (w to m) cm^{-1} (C=O). The analytical sample was prepared by an additional precipitation from CH_2Cl_2/hexane, mp 231.5–234.0 °C dec. The same compound was obtained in variable yield (0–24%) along with naphthalene upon refluxing a dilute solution (3%) of **18** in benzene for 24 h. Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.98; H, 4.20; N, 9.72. Found: C, 74.91; H, 4.07; N, 9.59.

***N*-Phthalimido-1-aminonaphthalene (20).** A mixture of 6.0 mL of DMSO, 1.0 mL of Et_3N, and 0.196 g of isophthalimide **19** was stirred at room temperature for 24 h. Twenty milliliters of CH_2Cl_2 was added, the solution was cooled in an ice bath with stirring, and 20 mL of cold H_2O was added. The organic layer was separated and washed with 20 mL of cold H_2O. The combined aqueous portions were washed with 10 mL of CH_2Cl_2, and the extracts were added to the previous organic extract. After drying, the extracts were evaporated in vacuo to give a partially solidified oil, which was treated with 8.0 mL of 95% EtOH with stirring, and the mixture was cooled to −20 °C. The precipitated solid was filtered by suction, washed with cold 95% EtOH, and allowed to air-dry to give 0.108 g (55%) of a yellow solid, mp 188–194 °C. Recrystallization was accomplished by dissolving in the minimum amount of hot CH_2Cl_2 followed by addition of 4.0 mL of 95% EtOH and cooling to −20 °C. Filtration, washing with a little cold 95% EtOH, and air-drying gave 0.088 g (45%) of the phthalhydrazide as a yellow powder, mp 217–221 °C (lit.[18] mp 215–216 °C), identified by melting point and IR spectral comparison with data obtained from an authentic sample.[18]

7-(Benzoylamino)-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (2b). A solution of 3.245 g of 7-azabenzonorbornadiene in 40 mL of Et_2O was converted to **1** as described previously. The initial suspension was filtered through an ice-jacketed frit into a stirred mixture of 0.793 g of benzoyl chloride, 5 mL of Et_2O, and 25 mL of 4% Na_2CO_3 solution, which was held at 0 °C. The precipitated amine salt was washed with 15 mL of cold Et_2O, and the washings were added to the filtrate. A white solid precipitated within a few minutes. Stirring at 0 °C was continued for 15 min, and 30 mL of cold hexane was added. After a 5-min period the entire mixture was suction filtered, and the solid was washed thoroughly with cold water followed by a small amount of cold MeOH. After being briefly dried in air the solid was dried to constant weight in vacuo (vacuum pump) to give 0.703 g (47%) of the hydrazide as a white powder: mp 87 °C dec; ^1H NMR (300 MHz, 20 °C, $CDCl_3$) δ 4.84 (br s, major) and 5.05 (br s, minor) totalling 2 H (bridgeheads of two invertomers), 6.75–8.15 (m, 12, olefinic + aromatic + NH); the ratio of the two invertomers as determined by integration of the peaks at δ 4.84 and 5.05 was 2:1; IR (KBr) 3330 (NH), 1680 cm^{-1} (C=O).

Due to its instability, this compound was not further purified but instead was used directly in thermolysis studies. It was characterized as the *O*-benzoyl derivative, which was obtained by treatment with benzoyl chloride in THF at −50 °C in the presence of KOBu-*t*. The isoimide was obtained as a white powder by precipitation from methylene dichloride/hexane at −20 °C: mp 105–106 °C; ^1H NMR ($CDCl_3$) δ 5.26 (t, 2, bridgehead), 6.75–7.85 (m, 14, olefinic + aromatic), 8.15–8.40 (m, 2, aromatic); ^{13}C NMR (50.3 MHz, $CDCl_3$, 31 °C) δ 72.9 (bridgehead), 121.9, 125.1, 126.5, 128.4, 128.8, 130.2, 130.4, 131.6, 134.2, 140.7, 144.9, 147.5, 162.5 (C=O); IR (KBr) 1735 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.66; H, 4.96; N, 7.65. Found: C, 78.55; H, 4.76; N, 7.58.

***N*-Phthalimidoacenaphthyleneimine.** A suspension of 4.56 g of acenaphthylene in 100 mL of CH_2Cl_2 was stirred and cooled in an ice bath while a solution of 13.3 g of $Pb(OAc)_4$ in 50 mL of CH_2Cl_2 was added dropwise. After 4 h at room temperature 120 mL of H_2O was added, and the mixture was stirred until the solid dissolved. The organic layer was washed twice with 120-mL portions of H_2O and once with 100 mL of saturated NaCl solution, dried ($MgSO_4$), and rotovaped to dryness. The residue was recrystallized from acetone to give 4.3 g (46%) of the imide as a yellow solid: mp 190–192 °C dec; IR ($CHCl_3$); 1760, 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 4.72 (s, 2, aziridine CH), 7.22–7.95 (m, 10, aryl); ^{13}C NMR ($CDCl_3$) δ 51.2 (aziridine C), 164.8 (C=O); MS (80 eV), *m/e* (RA) 312 (M^+, 100), 166 (100), 152 (53), 104 (68). Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.89; H, 3.87; N, 8.97. Found: C, 76.72; H, 3.61; N, 8.97.

***N*-Aminoacenaphthyleneimine.** A mixture of 3.14 g of *N*-phthalimidoacenaphthyleneimine, 150 mL of 95% EtOH, and 0.72 g of 95% hydrazine was stirred for $2^1/_2$ h in an ice bath, and the precipitated solid was filtered and washed with 10 mL of cold (0 °C) 95% EtOH. The combined filtrates were evaporated to a volume of about 30 mL, poured into 200 mL of H_2O, and extracted with three 75-mL portions of ether. The ether extracts were washed with 2 N KOH, H_2O, and saturated NaCl. Following drying ($MgSO_4$), rotary evaporation gave a brown solid, which was recrystallized from ligroin–ether (5:1, bp 67–71 °C) to give 1.05 g (57.6%) of the aziridine as a yellow solid: mp 81–83 °C (dec); IR ($CHCl_3$) 3320 cm^{-1} (NH_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.7 (br s, 2, NH_2), 3.73 (s, 2, aziridine CH), 7.43 (t, 2, 3-aryl), 7.55 (d, 2, aryl), 7.65 (d, 2, aryl); ^{13}C NMR ($CDCl_3$) δ 52.2 (aziridine C); MS (80 eV), *m/e* (RA) 182 (M^+, 2.1), 153 (55), 152 (100), 151 (47), 150 (31). Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.12; H, 5.52; N, 15.38. Found: C, 79.08; H, 5.62; N, 15.52.

***N*-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-acenaphthyleneimine (22a).** A solution of 194 mg of *N*-aminoacenaphthylenimine and 130 μL of pyridine in 10 mL of CH_2Cl_2 was cooled to −30 °C, and a solution of 275 mg of

FMOC-Cl[7] in 5 mL of CH_2Cl_2 added via cannula with stirring. After 10 min at −30 °C and 30 min at 0 °C the precipitate was filtered, washed with MeOH, and dried in vacuo to give 311 mg (73%) of the hydrazide as a white powder, mp 163 °C dec. The analytical sample was prepared by briefly warming a suspension in acetone, filtering, and cooling at −20 °C to give a white solid: mp 165 °C dec; IR (Nujol) 1692 cm^{-1} (C=O); ^1H NMR (DMSO-d_6, 300 MHz) δ 4.15 (s, 2, aziridine CH), 4.23 (t, 1, fluorene 9-H), 4.36 (d, 2, CH_2), 7.2–8.0 (m, 14, aryl), 9.22 (br s, 1, NH). Anal. Calcd for $C_{27}H_{20}N_2O_2$: C, 80.16; H, 4.99; N, 6.93. Found: C, 80.23; H, 5.01; N, 6.82.

***N*-(Benzoylamino)acenaphthyleneimine (22b).** A solution of 460 mg of *N*-aminoacenaphthyleneimine in 15 mL of dry THF was cooled to −50 °C, and with stirring over 2 min a solution of 570 mg of benzoic anhydride in 3 mL of ether was added via cannula. After 5 min at −50 °C the mixture was warmed to 0 °C over 30 min, and the precipitate was filtered, washed with both ether and MeOH, and dried in vacuo to give 517 mg (72%) of the hydrazide as a white powder, mp 126 °C dec. The analytical sample was prepared as given for the FMOC analogue: mp 130 °C dec; IR (Nujol) 1639 cm^{-1} (C=O); ^1H NMR (DMSO-d_6, 300 MHz) δ 4.35 (s, 2, aziridine CH), 7.4–7.85 (m, H, aryl), 10.3 (br s, 1, NH). Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.79. Found: C, 79.52; H, 4.68; N, 9.79.

***meso*-Hydrobenzoin Dimesylate.** To a solution of 30 g of *meso*-hydrobenzoin[27] in 600 mL of dry pyridine there was added 64.5 mL of methanesulfonyl chloride over a period of 10 min with stirring and cooling in an ice bath. After 30 min, 18 mL of H_2O was added, stirring was continued for 2 h, and the mixture was poured into 1000 mL of $CHCl_3$; the resulting suspension filtered and washed twice each with H_2O, acetone, and ether. Recrystallization from acetone gave 26.8 g (52.5%) of the sulfonate as white crystals, mp 120 °C dec; IR (Nujol) 1355, 1180 cm^{-1} (SO_2). Anal. Calcd for $C_{16}H_{18}O_6S_2$: C, 51.87; H. 4.90; O, 25.92. Found: C, 52.05; H, 4.95; O, 25.90.

1-Amino-*cis*-2,3-diphenylaziridine. A suspension of 4.0 g of *meso*-hydrobenzoin dimesylate in 75 mL of 95% hydrazine was heated with stirring under N_2 to an internal temperature of 60–65 °C (optimum temperature 62 °C) for 24 h. Hexane (200 mL) was added, stirring was continued for 30 min, the hexane was decanted, and the residue was extracted with three 50-mL portions of hexane. The combined hexane extracts were dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was recrystallized from hexane to give 0.8–1.02 g (35–45%) of the aminoaziridine as white crystals, mp 100–104 °C. The analytical sample (pentane) had mp 110–111 °C: ^1H NMR ($CDCl_3$) δ 3.14 (s, 2, CH), 3.8 (br s, 2, NH), 7.12 (s, 10, aryl). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.33. Found: C, 80.03; H, 6.81; N, 13.23.

1-Phthalimido-*cis*-2,3-diphenylaziridine. A solution of 0.22 g of **25** dissolved in 10 mL of CH_2Cl_2 was treated with 0.23 g of *N*-carbethoxyphthalimide.[16] After the mixture was stirred at room temperature for 1 h, evaporation in vacuo gave a white residue, which was washed with ether and recrystallized from EtOAc–Et_2O to give 0.3 g (67%) of phthalhydrazide **26** as colorless needles. The crude product [Anal. Calcd for $C_{25}H_{23}N_3O_4$: C, 69.93; H, 5.36. Found: C, 70.40; H, 5.58] was refluxed in ethanol for 2 h, the mixture was evaporated in vacuo, and the residue was washed with Et_2O and recrystallized from hexane–Et_2O to give 0.15 g of the phthalimido derivative **27** as pale yellow needles, mp 125–126 °C, identified by mixture melting point and comparison of IR and ^1H NMR spectra with the sample obtained[6] by oxidation of *N*-aminophthalimide by $Pb(OAc)_4$ in the presence of *cis*-stilbene.

Thermolysis of *N*-[[[(9-Fluorenylmethyl)oxy]carbonyl]-amino]acenaphthyleneimine in Cyclohexene/Benzene. A suspension of 198 mg of hydrazide **22a** in 20 mL of cyclohexene/benzene (1:1) was stirred under N_2 at 60 °C for 16 h. The solid eventually dissolved. Removal of solvent gave a residue, which by flash chromatography on silica gel with elution by hexane gave a yellow material, which was rechromatographed in the same way to give 66.5 mg (89%) of acenaphthylene, mp 88–92 °C, identified by IR and ^1H NMR spectral comparison. Switching to elution by 10% ether in CH_2Cl_2 gave 91.1 mg of material, which was rechromatographed with 40% EtOAc in hexane to give 75.0 mg (46%) of cyclohexyl hydrazide **7a** as a fluffy white solid, mp 161–165 °C dec, identified on the basis of IR and ^1H NMR spectral comparison with an authentic sample (see above). Only traces of *N,N'*-bis(FMOC)hydrazine were detected in the reaction mixture by TLC analysis.

Thermolysis of *N*-(Benzoylamino)acenaphtheneimine in Cyclohexene/Benzene. A suspension of 288 mg of hydrazide **22b** in 20 mL of cyclohexene/benzene (1:1) was stirred under N_2 at 55–60 °C for 7 h. Complete solution never occurred. The suspension was cooled and filtered to give 39.5 mg (33%) of 1,2-dibenzoylhydrazine, mp 241–243 °C (lit.[20] mp 241 °C), identified by IR spectral comparison with an authentic sample. Flash chromatography as described for the analogous FMOC derivative gave 131.7 mg (86%) of acenaphthylene, mp 91–93 °C, and 17.5 mg (8%) of cyclohexylhydrazide **7b**, mp 147–151 °C, identified by comparison with an authentic sample prepared by benzoylation of the corresponding free aminoaziridine (see above). For thermolyses of other compounds, see Table II.

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The Unusual Reactivity of 9,9'-Dianthrylcarbene[1]

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9,9'-Dianthrylcarbene was investigated by using laser flash photolysis, conventional flash photolysis, and optical modulation spectroscopy. Its optical absorption spectrum was characterized by two strong bands at 355 nm (ε 3.9×10^4 M^{-1} cm^{-1}) and at 445 nm (ε 2.9×10^4 M^{-1} cm^{-1}). Although the carbene has a triplet ground state, the rate constant for its spin-allowed reaction with oxygen was ca. 5×10^5 M^{-1} s^{-1}, yet it underwent self-reaction at the diffusion-controlled limit. These unusual kinetic properties stem from the fact that the carbene has a structure in which the unpaired electrons are highly delocalized.

There has been a great deal of theoretical[2-4] and experimental[5-11] interest in the way that carbene structures affect the energy separation between the triplet and singlet electronic states. We have recently shown that increasing

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