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SYNTHESIS AND PHOTOLYSIS OF N-PHTHALIMIDOAZIRIDINES WITH ELECTRON-WITHDRAWING SUBSTITUENTS

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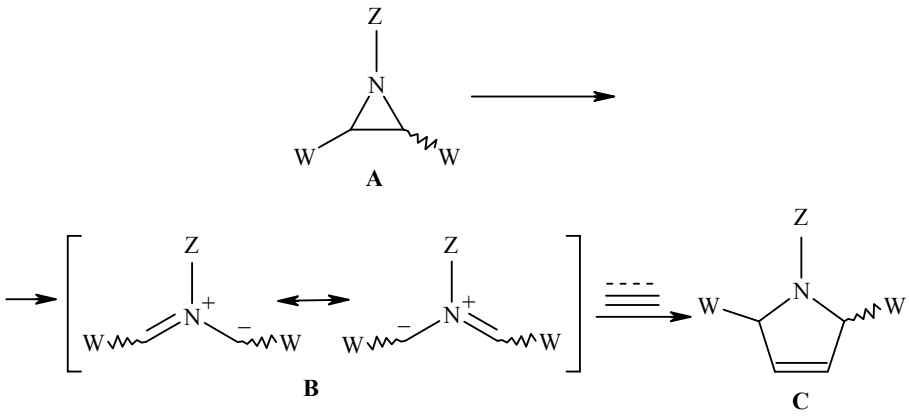
Mono-, bi-, tetra-, and pentacyclic N-phthalimidoaziridines with electron-withdrawing substituents in the three-membered ring have been obtained by the oxidative addition of N-aminophthalimide to dimethyl fumarate, ethyl cinnamate, N-phenyl- and N-benzylmaleimide, and endo-tricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione. Photolysis of 3-benzyl-6-phthalimido-3,6-diazabicyclo-[3.1.0]hexane-2,4-dione obtained in this way in the presence of dimethyl acetylenedicarboxylic acid (DMAD) gives in low yield the dimethyl ester of 3-benzyl-2,4-dioxo-8-phthalimido-3,8-diazabicyclo[3.2.1]oct-6-ene-6,7-dicarboxylic acid, the product of 1,3-dipolar cycloaddition to the N-phthalimidoazomethinylide formed as intermediate. However photolysis of this phthalimidoaziridine in the presence of other 1,3-dipolarophiles, like photolysis in the presence of DMAD of the remaining phalimidoaziridines, does not lead to a 1,3-dipolar cycloaddition product.

Keywords: azomethinylides, 1,3-dipoles, N-phthalimidoaziridines.

It was shown even in the sixties of the last century in the classical works of R. Huisgen that certain aziridines **A** under conditions of thermolysis or photolysis may stereospecifically be opened at a C–C bond giving octet-stabilized 1,3-dipoles, the azomethines **B** [1]. These reactive intermediates enter into various subsequent conversions, though their addition at the multiple bond of 1,3-dipolarophiles has undoubted preparative value as a general method of synthesizing five-membered nitrogen heterocycles of type **C** [1-3].



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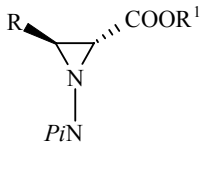
Opening of the three-membered ring at a C–C bond is alleviated in the presence of a substituent W on the carbon atoms, able to delocalize the partial negative charge on 1,3-dipoles **B**. For example, the readily available N-phthalimidoaziridines with three or four electron-withdrawing groups (CN, COR, Ph) just on slight heating (and even at room temperature!) in the presence of 1,3-dipolarophiles give good yields of products, the formation of which is treated as the result of an intra- (oxazolines, oxazoles) and/or intermolecular (pyrrolines, azetidines) conversion of the corresponding N-phthalimidoazomethinylides [4-6]. It was noted that the ability of substituents W to activate these processes falls in the series CN >> COR > COOR [4].

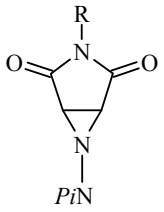
Since the interaction of N-phthalimidoazomethinylides with dipolarophiles permits in one stage the preparation of difficultly available derivatives of various N-aminoheterocycles, in our opinion, the alternative method of generating these 1,3-dipoles, *viz*. photolysis of N-phthalimidoaziridines, merits attention. First of all, if the opening of the aziridine ring in the azomethinylide is a coordinated process, then on thermolysis (conrotatory) and on photolysis (disrotatory) a given initial aziridine must give stereoisomeric 1,3-dipoles, and then diastereomeric cycloaddition products. Further, for bicyclic aziridines the permitted thermally conrotatory opening into cyclic azomethinylides is exclusively due to steric limitations, but the disrotatory process permitted on photolysis is impossible. Finally, it is possible to hope that photolytic opening of aziridines into azomethinylides can be successfully effected at a lower number (and strength) of the activating substituents in the three-membered ring.

However up to the present time the photolytic conversion of 1-(heteroaryl)aziridines is almost uninvestigated. It has only been reported that on photolysis of N-phthalimido- and N-(4-oxoquinazolin-3-yl)aziridines containing at the carbon atoms at least one substituent capable of conjugation (Ar, vinyl, COR), the three-membered ring is broken with fission of both C-N bonds [7]. A conjugated unsaturated compound is formed in this way and the corresponding N-heteroarylnitrene, which is successfully intercepted with a large excess of cyclohexene, or some other unsaturated substrate, added to the reaction mixture.

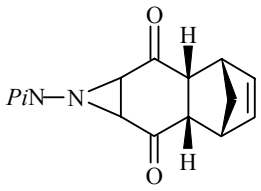
The aim of the present work began with the clarification of the possibility of photolytic opening of N-phthalimidoaziridines to the corresponding N-phthalimidoazomethinylides. The subjects of the investigation were the mono-, bi-, and tetracyclic aziridines **1-5**. In their selection we proceeded from the fact that there must be substituents capable of stabilizing the corresponding 1,3-dipole at both carbon atoms of the three-membered ring. In addition we wanted to study the effect on the course of the reaction of including the aziridine ring in a bicyclic system (compounds **3-5**), and also the possibility of intramolecular addition of azomethinylides at the spatially close double bond in compound **5**.



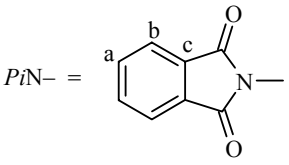
1, 2



3, 4



5

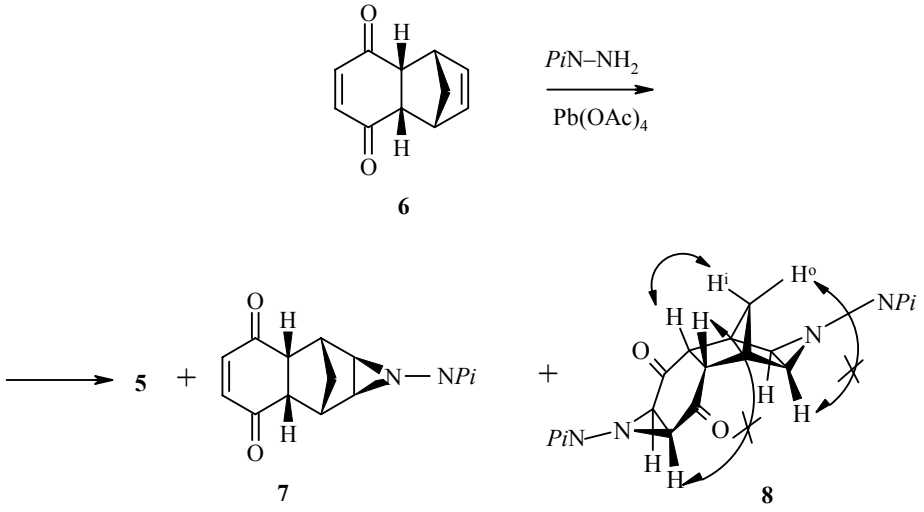


1 R = COOMe, R^1 = Me; **2** R = Ph, R^1 = Et; **3** R = Ph; **4** R = CH_2Ph

We expected to obtain all these compounds by the oxidative addition of N-aminophthalimide (*Pi*N-NH_2) to the appropriate unsaturated substrate, *viz*. dimethyl fumarate, ethyl cinnamate, N-phenyl- and N-benzylmaleimide, and to the monoadduct of quinone to cyclopentadiene, *endo*-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene-3,6-dione (**6**) [8, 9]. In spite of the enormous number of N-heteroarylaziridines synthesized in such a way [10-13], it turned out that of this selection only aziridine **1** and the methyl analog of compound **2** have been described up to the present time [13, 14].

As a result of the low stability of the strained three-membered ring oxidative addition of N-aminophthalimide to an unsaturated compound is usually carried out at reduced temperature. But at a temperature from -15 to -18°C reaction with dimethyl fumarate and N-benzylmaleimide leads to aziridines **1** and **4** in yields of 13-20% overall. Moreover at room temperature the yield of aziridine **1** grows to 85%. We also synthesized adducts **3** (37%) and **4** (56%) at room temperature. Aziridine **2** (51%) was obtained at 0°C, and the reaction with the tricyclic substrate was carried out at -10°C.

Oxidative addition of N-aminophthalimide and related N-aminoheterocycles to a conjugated multiple bond goes, as a rule, far more readily than to an unconjugated bond [10-13]. However in dienedione **6** the reactivity of the $C_{(9)}$–$C_{(10)}$ bond is increased due to its inclusion in a strained structure of the norbornene type. Consequently it is no wonder that from the reaction mixture, in addition to the main product, the desired phthalimidoaziridine **5**, the adduct **7** isomeric with it at the $C_{(9)}$–$C_{(10)}$ bond was isolated, and in spite of the appreciable excess of unsaturated substrate **6**, even the bisadduct **8**.



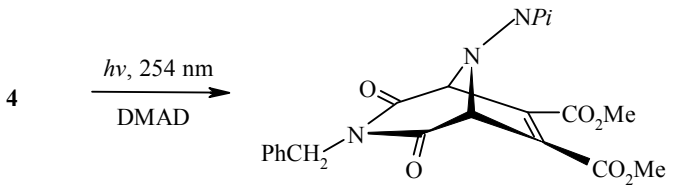
The characteristics of the previously known N-phthalimidoaziridine **1** were in good agreement with the literature [13]. The composition of compounds **2-5, 7, 8** obtained for the first time were confirmed by data of elemental analysis and/or mass spectrometry, and their structures by NMR spectroscopy. The regiomeric mono-adducts **5** and **7** were readily distinguished by the position of the signals of the remaining olefinic protons (5.99 and 6.75 ppm respectively) in their ^{1}H NMR spectra. Information on the spatial structure of diadduct **8** was given by its ^{1}H NOESY spectrum with a single cross peak between the high field (0.88) signal of one of the protons of the methylene bridge H-13 and the singlet at 3.37 ppm, which, allowing for the *endo* configuration of the initial compound **6**, we must assign to protons H-2,8. The absence of other cross peaks indicates the *exo* orientation of both aziridine fragments.

Since the formation of diadduct **8** must take place in stages, it is possible to assume that monoadducts **5** and **7** also have an *exo* linking of the aziridine ring with the remaining portion of the molecule. The size of the chemical shifts of the methylene protons proved to be a sensitive indicator of the spatial structure of these frame compounds. In the ^{1}H NMR spectrum of aziridine **5** they resonate at about 1.35 ppm, and the difference of their

chemical shifts is 0.06 ppm overall. For compounds **7** and **8** the closeness of the methylene bridge to the aziridine nitrogen atom is displayed as a large separation of the signals of these protons (Δδ 0.8-0.9 ppm) and it follows from the NOESY spectrum of diadduct **8** that strong deshielding of the proton adjacent to the three-membered ring and shielding of the remote proton occurs. The formation in the final reaction of *exo* products of the oxidative addition of N-aminophthalimide at the double bond of the tricyclic dienedione **6** is in good agreement with literature data on the analogous reaction with norbornadiene (ratio of *exo* and *endo* adducts was ~10:1) [15].

A known feature of N-aminoaziridine derivatives is the slow inversion in the NMR time scale of the aziridine nitrogen atom [16]. Consequently in the sole (as a result of degenerate inversion) invertomer of compound **1** the methoxycarbonyl groups are nonequivalent in the NMR spectra and the two protons of the three membered ring give a typical doublet of an AX system in the ^{1}H NMR spectrum [13]. In aziridine **2** the inversion is not a degenerate process and in its ^{1}H NMR spectrum signals are observed for the two forms in a ratio of ~15:1, the main, most preferred, is the invertomer with an *anti* disposition of the phenyl and phthalimide groups. In the bi- and polycyclic compounds **3, 5, 7, 8**, containing only *cis*-disubstituted aziridine fragments, the conformational equilibria are displaced to the side of the appreciably more stable invertomers with a *cis* orientation of the phthalimide group and the ring protons but in their NMR spectra only one set of signals is observed. The exception is the benzyl derivative **4**. In its ^{1}H NMR spectrum two small high field singlets are seen, which possibly should be treated as the signals of the second invertomer.

We carried out the first experiments on photolytic generation of N-phthalimidoazomethinylides in a quartz reactor, irradiating a solution of aziridine **4** in anhydrous dichloromethane with light from a high pressure mercury lamp (λ 254 nm) in the presence of DMAD. The progress of the conversion was checked by TLC, observing the slow weakening of the spot of the initial aziridine and the development of the sole new spot of the reaction product. The reaction proceeded without any appreciable discoloration, the solution remained transparent throughout the whole experiment. However at the end of photolysis, isolation from the reaction mixture of the bicyclic product of 1,3-dipolar cycloaddition, compound **9**, was successful in 4% overall yield. Replacement of dichloromethane by anhydrous 1,4-dioxane (see [2]) enabled the yield of adduct **9** to be increased to 13%, but we were unable to obtain a larger yield.



9

The low yield of compound **9** is probably linked with the fact that this compound is sensitive to hard ultraviolet, at the end of photolysis its spot on TLC usually began to fade. Consequently we attempted to carry out the reaction under milder conditions, using for activation of the phthalimidoaziridine **4** molecule the long-wave slope of its last absorption band. However irradiation of the same pair of reactants through a pyrex filter, i.e. with light of wavelength >300 nm, was unsuccessful. In the course of many hours generally no changes at all took place in the reaction mixture according to TLC data, and at the end of photolysis the initial aziridine **4** was isolated from it.

Photolysis of aziridine **4** in a quartz reactor in the presence of other 1,3-dipolarophiles (phenylmaleimide, dimethyl fumarate, dimethyl maleate, and ethyl vinyl ether) also gave no positive result. In the course of these experiments we observed only slow consumption (combustion) of compound **4**, not accompanied by the appearance of new spots on TLC. All attempts to isolate any individual substances from the oily residues after evaporation of the reaction mixtures proved to be unsuccessful.

In conclusion we have carried out photolysis of phthalimidiaziridines **1-3, 5** in a quartz reactor in the presence of DMAD. Aziridine **3** proved to be stable even under these conditions, and was isolated unchanged from the reaction mixture after many hours irradiation. In the remaining cases we observed (TLC) only slow breakdown of the initial aziridines without the appearance on the plates of new spots for any individual photolysis products.

To sum up, it is possible to state that in spite of the principle of the possibility of photochemical generation of N-phthalimidoazomethinylides from N-phthalimidoaziridines indicated by us, the synthetic application of this method seems extremely limited.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 (300 and 75 MHz respectively) instrument, for solutions in $CDCl_3$ or DMSO-d_6, internal standards were the signals of the residual protons (7.26 or 2.50 ppm) and carbon atoms (77.16 or 39.5 ppm) of the solvents. Electron impact (EI) mass spectra were obtained on a MX 1303 mass spectrometer. Mass spectra with ionization in the electrospray mode (ESI) were recorded on a Finnigan TSQ 700 triple quadrupole spectrometer. The UV spectrum of aziridine **4** was recorded on a Specord M 40 instrument. Elemental analysis was carried out on a Hewlett-Packard HP 185B automatic C,H,N analyzer. The composition of reaction mixtures, the fractions obtained on separating them, and the purity of the isolated preparations were checked by TLC on Polygram sil G/UV_{254} and Alugram sil G/UV_{254} plates (from Macherey-Nagel. N-Benzylmaleimide [17] and the monoadduct **6** of cyclopentadiene with benzoquinone [8,9] were obtained by the known methods.

Dimethyl Ester of (*E*)-1-Phthalimidoaziridine-2,3-dicarboxylic Acid (1). N-Aminophthalimide (486 mg, 3 mmol) and lead tetraacetate (1.33 g, 3 mmol) were added alternately in 10-15 mg portions during 40 min to a suspension of anhydrous potassium carbonate (1.3 g, 9.4 mmol) in a solution of dimethyl fumarate (432 mg, 3 mmol) in methylene chloride (40 ml) at 18-23°C. The reaction mixture was stirred for 1 h further, filtered through a thin layer of silica gel, and the solvent evaporated in vacuum. Aziridine **1** (775 mg, 85%) was obtained, the analytical characteristics of which agreed completely with the literature data of [13]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.60 (1H, d, *J* = 4.8, CH); 3.74 (3H, s, CH_3); 3.86 (3H, s, CH_3); 3.96 (1H, d, *J* = 4.8, CH); 7.65-7.79 (4H, m, *Pi*).

Ethyl Ester of (*E*)-3-Phenyl-1-phthalimidoaziridine-2-carboxylic Acid (2). N-Aminophthalimide (486 mg, 3 mmol) and lead tetraacetate (1.33 g, 3 mmol) were added alternately in 10-15 mg portions during 40 min to a suspension of anhydrous potassium carbonate (1.3 g, 9.4 mmol) in a mixture of ethyl cinnamate (792 mg, 4.5 mmol) and methylene chloride (40 ml) cooled to 0°C. The mixture was stirred for 1 h further, filtered through a thin layer of silica gel, and the solvent evaporated in vacuum. The oily residue was dissolved in ether (5 ml) and placed in the refrigerator. On the following day the precipitated solid was recrystallized from ethanol. Yellow crystals (514 mg, 51%) of mp 93°C were obtained. Signals were seen in the ^{1}H NMR spectrum for two invertomers in a ratio of ~15:1. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*,Hz): 1.28 (t, *J* = 7.2, CH_3 of main invertomer) and 1.38 (t, *J* = 7.2, CH_3 of minor invertomer), 3H in total; 3.51 (d, *J* = 5.0, H-2 main) and 4.06 (d, *J* = 5.5, H-3 minor) 1H in total; 4.18 (2H, q, *J* = 7.2, CH_2); 4.39 (d, *J* = 5.0, H-3 main) and 4.59 (d, *J* = 5.5, H-2 minor) 1H in total; 7.30-7.45 (3H, m, H-*m,p*), 7.45-7.50 (2H, m, H-*o*), 7.60-7.85 (4H, m, *Pi*). Assignment of the signals of the aziridine protons was made on the basis of the fact that the doublets of the H-3 proton were somewhat broader (and lower) than the corresponding signals of the H-2 proton due to the additional coupling with H-*o* of the adjacent phenyl substituent. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.07 (CH_3); 46.44 and 49.64 ($C_{(2,3)}$); 62.20 (CH_3); 123.23 ($C_{(b)}$); 127.37 and 128.77 ($C_{(o,m,p)}$); 130.43 ($C_{(a)}$); 134.14 ($C_{(c)}$); 134.71 ($C_{(i)}$); 164.76 (CO, *Pi*); 166.33 (CO). Mass spectrum (ESI), *m/z* (*I*, %); 391 (44) [M^++Na+CH_3OH], 359 (100) [M^++Na]. Found, %: C 67.82; H 4.86; N 8.27. $C_{19}H_{16}N_2O_4$. Calculated, %: C 67.85; H 4.79; N 8.23.

3-Phenyl-6-phthalimido-3,6-diazabicyclo[3.1.0]hexane-2,4-dione (3). N-Aminophthalimide (486 mg, 3 mmol) and lead tetraacetate (1.33 g, 3 mmol) were added alternately in 10-15 mg portions during 40 min to a suspension of anhydrous potassium carbonate (1.3 g, 9.4 mmol) in a solution of N-phenylmaleimide (5.9 mg, 3 mmol) in methylene chloride (40 ml) at room temperature. The mixture was stirred for 1 h further, diluted with dioxane (50 ml), heated to boiling, and filtered through a thin layer of silica gel. The solvent was evaporated in vacuum, the residue was rubbed with chloroform (5 ml), and the solid filtered off. After recrystallization from dioxane, white crystals (370 mg, 37%) of mp >235°C were obtained. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.52 (2H, s, NCH); 7.15-7.30 (2H, m, H-*o*); 7.35-7.55 (3H, m, H-*m,p*); 7.75-7.95 (4H, m, *Pi*). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 43.95 (NCH); 123.03 ($C_{(b)}$); 126.99 ($C_{(o)}$); 128.92 ($C_{(p)}$); 129.30 ($C_{(m)}$); 129.78 ($C_{(a)}$); 131.12 ($C_{(i)}$); 134.85 ($C_{(c)}$); 163.92 (CO, *Pi*). 169.07 (CO). Mass spectrum (ESI), *m/z* (*I*, %): 388 (35) [M^++Na+CH_3OH], 420 (100) [M^++Na+2CH_3OH]. Found, %: C 64.55; H 3.45; N 12.59. $C_{18}H_{11}N_3O_4$. Calculated, %: C 64.87; H 3.33; N 12.61.

3-Benzyl-6-phthalimido-3,6-diazabicyclo[3.1.0]hexane-2,4-dione (4) was synthesized analogously from N-benzylmaleimide (561 mg, 3 mmol). After recrystallization from a butanol–dioxane mixture colorless crystals (582 mg, 56%) of mp >235°C were obtained. UV spectrum (EtOH–dioxane, 39:1), λ_{max}, nm (log ε): 230 (4.22), 275 (3.93). Signals were seen in the ^{1}H NMR spectrum for two invertomers at a ratio of ~15:1. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.58 (s, CH, minor) and 4.36 (s, CH, main), total 2H; 4.16 (s, CH_2, minor) and 4.54 (s, CH_2 main), total 2H; 7.20-7.35 (5H, m, C_6H_5); 7.83 (4H, m, *Pi*). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 41.13 (CH_2); 43.63 (NCH); 123.27 ($C_{(b)}$); 127.44 and 128.70 ($C_{(o,m)}$); 127.74 ($C_{(p)}$); 129.76 ($C_{(a)}$); 134.82 ($C_{(c)}$); 135.52 ($C_{(i)}$); 163.91 (CO, *Pi*); 169.71 (CO). Mass spectrum (ESI), *m/z* (*I*, %): 434 (100) [M^++Na+2CH_3OH]; 402 (93) [M^++Na+CH_3OH], 370 (7) [M^++Na], 255 (13). Found, %: C 65.75; H 4.04; N 12.00. $C_{19}H_{13}N_3O_4$. Calculated, %: C 65.70; H 3.77; N 12.10.

Reaction with *endo*-Tricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione (6). N-Aminophthalimide (0.972 g, 6 mmol) and lead tetraacetate (2.66 g, 6 mmol) were added alternately in 10-15 mg portions during 1 h to a suspension of anhydrous potassium carbonate (2.6 g, 19 mmol) in a solution of diene **6** (1.74 g, 10 mmol) in methylene chloride (80 ml) cooled to -10°C. The mixture was stirred for 1 h further at room temperature, filtered through a thin layer of silica gel, and the solvent was removed in vacuum. The oily residue was mixed with ether (5 ml), and left at 0°C. On the following day the precipitated crystalline solid was separated on a column of silica gel (30 g) (gradient elution with a hexane–CH_2Cl_2 mixture, ratio 1:1 to 0:1). Aziridine **5** (280 mg, 14%) with R_f 0.4 in CH_2Cl_2, phthalimide (40 mg, 5%) with R_f 0.25, and diadduct **8** (45 mg, 3%) with R_f 0.15 were obtained. More ether (3 ml) was added to the mother liquor remaining after filtration, and the solution left for 1 week at 0°C. Recrystallization of the precipitated colorless crystals from methanol gave aziridine **7** (60 mg, 3%).

5-Phthalimido-5-tetracyclo[7.2.1.0^{2,8}.0^{4,6}]dodec-10-ene-3,7-dione (5). Mp 239-242°C. ^{1}H NMR spectrum (DMSO-d_6–CCl_4, 1:2), δ, ppm (*J*, Hz): 1.32 (1H, d, ^2J = 8.7, H); 1.38 (1H, d, ^2J = 8.7, H); 3.24 (2H, s, H-1,9); 3.51 (2H, s, H-2,8); 3.57 (2H, s, H-4,6); 5.99 (2H, s, H-10,11); 7.70-7.85 (4H, m, *Pi*). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 43.45 ($C_{(2,8)}$); 46.59 (CH_2); 50.85 ($C_{(1,9)}$ and $C_{(4,6)}$); 123.83 ($C_{(b)}$); 129.89 ($C_{(a)}$); 134.87 ($C_{(c)}$); 137.14 ($C_{(10,11)}$); 164.22 (CO, *Pi*); 201.80 (CO). Mass spectrum (ESI), *m/z* (*I*, %): 389 (100) [M^++Na+CH_3OH], 361 (25), 357 (75) [M^++Na], 323 (44), 304 (9), 291 (53). Found, %: C 68.16; H 4.16; N 8.26. $C_{19}H_{14}N_2O_4$. Calculated, %: C 68.26; H 4.22; N 8.38.

10-Phthalimido-10-azatetracyclo[6.3.1.0^{2,7}.0^{9,11}]dodec-4-ene-3,6-dione (7). Mp 205-208°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.01 (1H, d, ^2J = 11.0, H); 1.90 (1H, d, ^2J = 11.0, H); 2.82 (2H, s, H-2,7); 3.11 (2H, s, H-1,8); 3.51 (2H, s, H-9,11); 6.75 (2H, s, H-4,6); 7.60-7.80 (4H, m, *Pi*). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.09 (CH_2); 42.07, 42.23, and 49.46 ($C_{(1,8)}$, $C_{(2,7)}$, and $C_{(9,11)}$); 123.39 ($C_{(b)}$); 130.63 ($C_{(a)}$); 134.46 ($C_{(c)}$); 142.48 ($C_{(4,5)}$); 165.25 (CO, *Pi*); 198.63 (CO). Mass spectrum (ESI), *m/z* (*I*, %): 389 (24) [M^++Na+CH_3OH], 357 (100) [M^++Na], 304 (9). Found, %: C 68.34; H 4.20; N 8.14. $C_{19}H_{14}N_2O_4$. Calculated, %: C 68.26; H 4.22; N 8.38.

5,11-Diphthalimido-5,11-diazapentacyclo[7.3.1.$0^{2,8}$.$0^{4,6}$.$0^{10,12}$]tridecane-3,7-dione (8). Mp >235°C. ^{1}H NMR spectrum (mixture of DMSO-d_6–CCl_4, ~1:2), δ, ppm (*J*, Hz): 0.88 (1H, d, ^2J = 10.1, H-13*i*); 1.64 (1H, d, ^2J = 10.1, H-13*o*); 2.82 (2H, s, H-10,12); 3.13 (2H, s, H-1,9); 3.37 (2H, s, H-2,8); 3.76 (2H, s, H-4,6); 7.72 (4H, m, *Pi*); 7.81 (4H, m, *Pi*). ^{13}C NMR spectrum (mixture of DMSO-d_6–CCl_4, ~1:2), δ, ppm: 24.72 (CH_2); 37.49 ($C_{(1,9)}$); 41.39 ($C_{(2,8)}$); 49.22 ($C_{(4,6)}$); 52.36 ($C_{(10,12)}$); 122.28 and 122.89 ($C_{(b,b')}$); 129.53 and 129.82 ($C_{(a,a')}$); 133.69 and 134.16 ($C_{(c,c')}$); 162.90 and 163.92 (CO, *Pi*); 200.52 (CO). Mass spectrum (ESI), *m/z*, (*I*, %): 549.1 (100) [M^++Na+CH_3OH], 521 (59) [M^++Na+CH_3OH-CO], 517.1 (83) [M^++Na], 357.1 (12), 304.2 (27).

Photolysis of N-Phthalimidoaziridines (General Procedure). A solution of N-phthalimidoaziridine **1-5** (1 mmol) and dipolarophile (3-6 mmol) in anhydrous dioxane (30 ml) was placed in a cylindrical coaxial quartz reactor fitted with an internal water cooling jacket and a calcium chloride tube, and was irradiated for 8-12 h with a high pressure mercury lamp (125 W) set along the axis of the reactor while cooling with a water flow, periodically checking the composition of the reaction mixture by TLC.

Photolysis using longer wave radiation (λ >300 nm) was carried out in the same reactor but the mercury lamp was placed additionally in a pyrex glass tube.

Dimethyl Ester of 3-Benzyl-2,4-dioxo-8-phthalimido-3,8-diazatricyclo[3.2.1]-oct-6-ene-6,7-dicarboxylic Acid (9). A solution of aziridine **4** (347 mg, 1 mmol) and DMAD (0.37 ml, 426 mg, 3 mmol) in anhydrous dioxane (30 ml) was irradiated until the spot of the initial aziridine on TLC had mostly faded (8.5 h). The solution was diluted with a mixture of water (20 ml) and alcohol (20 ml), and the precipitated initial compound **4** was filtered off. The filtrate was evaporated to dryness in vacuum, the residue was dissolved in alcohol (3 ml), and ether (40 ml) was added. On the following day the precipitated solid aziridine **4** was filtered off, and added to the first portion. The total recovery of the initial aziridine **4** was 75 mg (22%). The filtrate was evaporated once again, the residue was dissolved in ether (3 ml), and placed in the refrigerator. On the following day the precipitated white crystals of compound **9** were filtered off; mp 167-170°C. Yield was 65 mg (10%; allowing for the recovery of initial aziridine 13%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.89 (6H, s, CH_3); 4.87 (2H, s, CH_2); 5.31 (2H, s, CH); 7.20-7.35 (5H, m, C_6H_5); 7.70-7.90 (4H, m, *Pi*). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 42.85 (CH_2); 53.57 (CH_3); 75.98 (CH); 124.41 ($C_{(b)}$); 128.02 ($C_{(p)}$); 128.16 and 129.01 ($C_{(o,m)}$); 129.84 ($C_{(a)}$); 135.39 ($C_{(c)}$); 136.19 ($C_{(i)}$); 141.36 (C=C); 161.81 (CO); 165.16 (CO, NCO); 165.80 (NCO). Mass spectrum (EI), *m/z*, (*I*, %): 489 (47) $[M]^+$, 328 (19) [M^+-*Pi*NNH], 297 (100) [M^+-*Pi*NNH-CH_3O], 214 (14), 147 (19) [*Pi*NH^+], 104 (39), 91 (53), 76 (39), 65 (14), 59 (19). Found, %: C 61.31; H 4.01; N 8.48. $C_{25}H_{19}N_3O_8$. Calculated, %: C 61.35; H 3.88; N 8.59.

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