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[3+2] Cycloadditions and Nucleophilic Additions of Aziridines under C-C and C-N Bond Cleavage[1]

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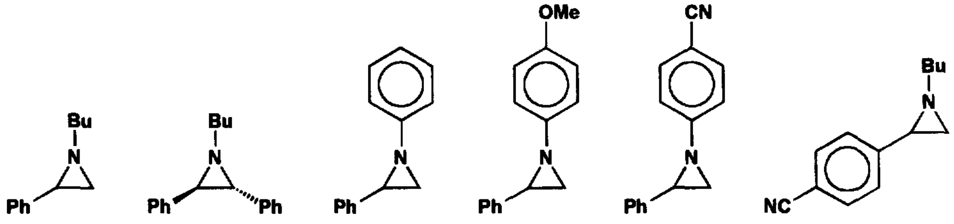
Abstract: Under PET conditions (photoinduced electron transfer) aziridines react with dipolarophiles in a [3+2] cycloaddition to form five-membered heterocycles. In this study we used mono- and disubstituted *N*-alkyl and *N*-arylaziridines. We noticed that the radical cation as intermediate reacts in a different manner to the classical azomethine ylide. Furthermore, under mild thermal conditions, aziridines react in acetonitrile in a formal [3+2] cycloaddition with activated acetylene derivatives under C-N bond cleavage. Using methanol as solvent, the intermediate is trapped leading to highly substituted enamines. A mechanism for this unexpected thermal reaction is proposed.

Aziridines and their reactions are of great interest because of their synthetic and pharmacological importance.[2] The [3+2] cycloaddition represents one of the most intensively studied conversions.[3] On irradiation or under thermal conditions the aziridine ring opens to the corresponding azomethine ylide which can be trapped in a [3+2] cycloaddition with various dipolarophiles, e. g. dimethyl acetylenedicarboxylate (DMAD), to form nitrogen-containing five-membered heterocycles.[4] Under PET conditions (photoinduced electron transfer)[5] the aziridine is oxidized to the corresponding radical cation which can react in a similar manner. Only reactions of *(Z)*-1-alkyl-2,3-diphenylaziridines are documented so far.[6,7,8] In this study we enlarge the synthetic application of the PET transformations and present a new thermal reaction under formal C-N bond cleavage of the aziridines.

The substrates examined in the present study are 1-butyl-2-phenylaziridine (**1**), *(E)*-1-butyl-2,3-diphenylaziridine (**2**), 1,2-diphenylaziridine (**3**), 1-(*p*-methoxyphenyl)-2-phenylaziridine (**4**), 1-(*p*-cyanophenyl)-2-phenylaziridine (**5**) and 1-butyl-2-(*p*-cyanophenyl)aziridine (**6**).



1 **2** **3** **4** **5** **6**

Scheme 1. Aziridines investigated in this study

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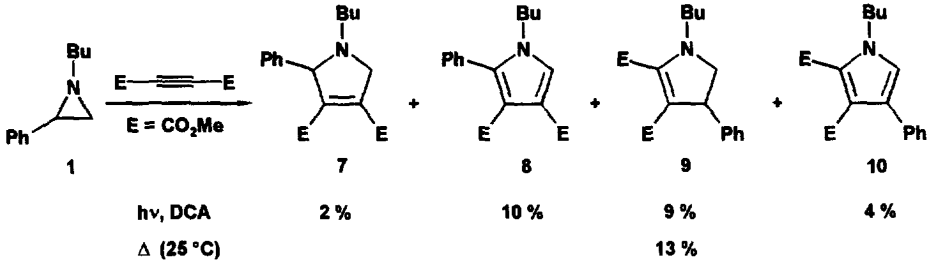
Photochemical Reactions

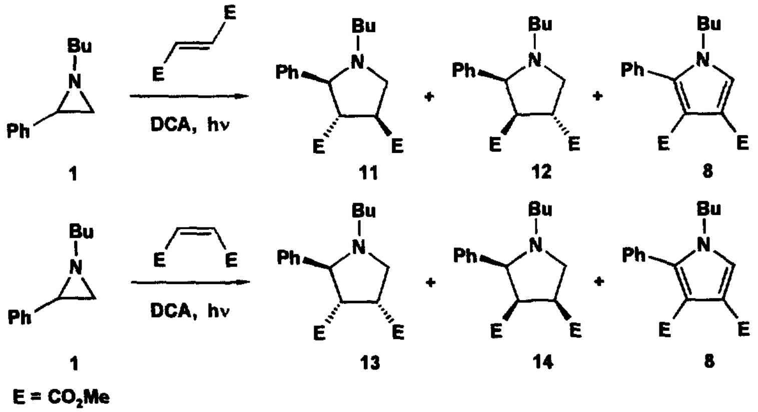
Concerning the [3+2] cycloadditions of aziridines under PET conditions (acetonitrile, 9,10-dicyanoanthracene (DCA), $\lambda = 419$ nm), we first studied a monosubstituted *N*-alkylaziridine (Scheme 2).[9]



Scheme 2. [3+2] Cycloadditions of 1-butyl-2-phenylaziridine (1) with DMAD

The reaction of 1-butyl-2-phenylaziridine (1) with DMAD under PET conditions revealed an unexpected result. Four products were formed. We isolated **7** in a yield of 2 % and the corresponding oxidation product **8** in yields of 10 %. The expected cleavage of the C-C bond of the aziridine is responsible for the formation of these heterocycles. Futhermore, we obtained **9** in a yield of 9 % and the corresponding oxidation product **10** in yields of 4 %. These products are formed in a formal [3+2] cycloaddition under cleavage of the C-N bond of the aziridine. At room temperature and without irradiation, we observed the same product **9** in a similar yield in the transformation of aziridine **1** with DMAD.

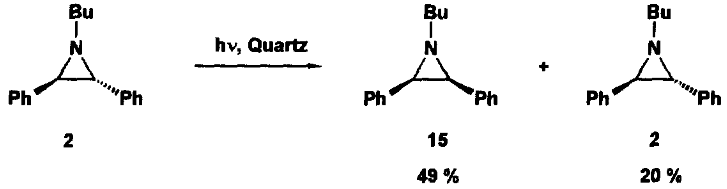
In accordance with the results of Laurent et al.[7], who investigated the reaction of the *tri*substituted aziridine **15**, the reaction of the *di*substituted aziridine **1** with dimethyl fumarate or dimethyl maleate as dipolarophile indicates a concerted reaction pathway (Scheme 3). In these cases a back electron transfer is postulated, i. e., the initially generated aziridine radical cation is converted to the corresponding azomethine ylide which reacts in a concerted manner. In the case of dimethyl fumarate, the two pyrrolidines **11** and **12** were built up in yields of 4 % each, retaining the stereochemistry of the alkene. In analogy, the reaction with dimethyl maleate afforded the pyrrolidines **13** and **14** in yields of 5 and 1 %. In both cases, traces of the pyrrol **8** were detected as oxidation product (GC).



Scheme 3. [3+2] Cycloadditions of 1-butyl-2-phenylaziridine (1) with dimethyl fumarate and maleate

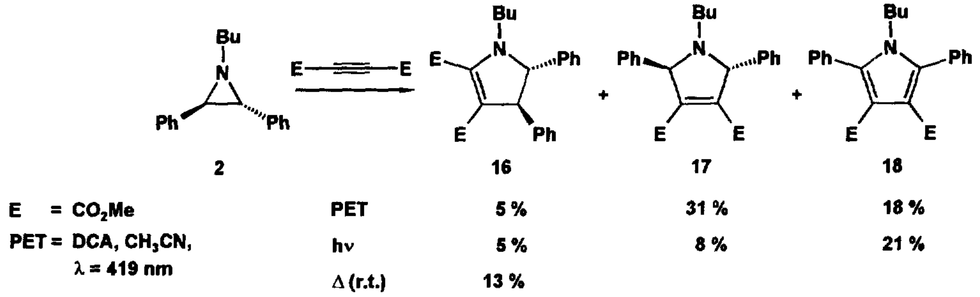
Because of the diminished reactivity of monosubstituted *N*-alkylaziridines compared with disubstituted *N*-alkylaziridines we used *(E)*-1-butyl-2,3-diphenylaziridine (**2**) for further investigations.

Under direct photolysis aziridine **2** undergoes isomerization (Scheme 4). In yields of almost 50 % the *cis* isomer **15** is formed beside the starting material (20 %). Longer irradiation time reduced the amount of the starting material but also decreased the yields of the *cis* isomer. Starting with the latter isomer, Laurent and coworkers[6] did not observe any isomerization due to the higher stability of the corresponding intermediate, the *cis* azomethine ylide[8c].



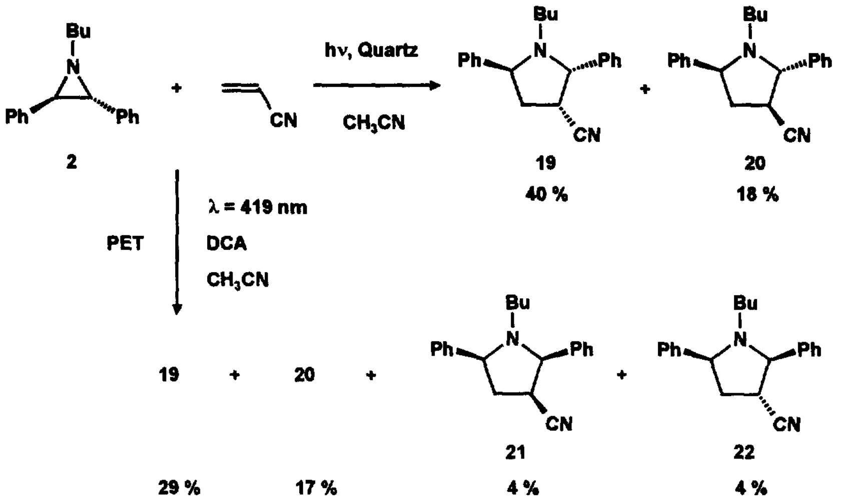
Scheme 4. Direct photolysis of *(E)*-1-butyl-2,3-diphenylaziridine (**2**)

The reaction of aziridine **2** with DMAD under PET conditions (Scheme 5) led to the unexpected dihydropyrrole **16** (5 %) under formal C-N bond cleavage of the aziridine. We also observed the expected dihydropyrrole **17** (31 %) and the corresponding pyrrole **18** (18 %) as oxidation product. Using direct photolysis, we got the same products in different yields. The dihydropyrrole **17** under C-C bond cleavage is built up in yields of 8 % and the corresponding pyrrole **18** in yields of 21 %. Only the yield of the unexpected dihydropyrrole **16**, based on a formal C-N bond cleavage, did not change. Because of the higher yields, in this case the aziridine radical cation, formed under PET conditions, is superior to the classical azomethine ylide generated under direct photolysis. Further investigations proved that the dihydropyrrole **16** is formed in a thermal side reaction. Without irradiation the yield of this product increased up to 13 %.



Scheme 5. [3+2] Cycloadditions of *(E)*-1-butyl-2,3-phenylaziridine (**2**) with DMAD

The conversion of *(Z)*-1-butyl-2,3-diphenylaziridine (**15**) with DMAD under PET conditions has been published by Laurent and coworkers.[6] In a ratio of 1:1 they obtained the dihydropyrrole **17** and the corresponding *cis* isomer. The authors proposed an aziridine radical cation as intermediate without any favoured stereochemistry. In contrast, the conversion of the *(E)*-aziridine **2** with DMAD under PET conditions is stereospecific, provided the pyrrole **18** is formed exclusively by oxidation of the dihydropyrrole **17** and not on the oxidation of the corresponding *cis* isomer.



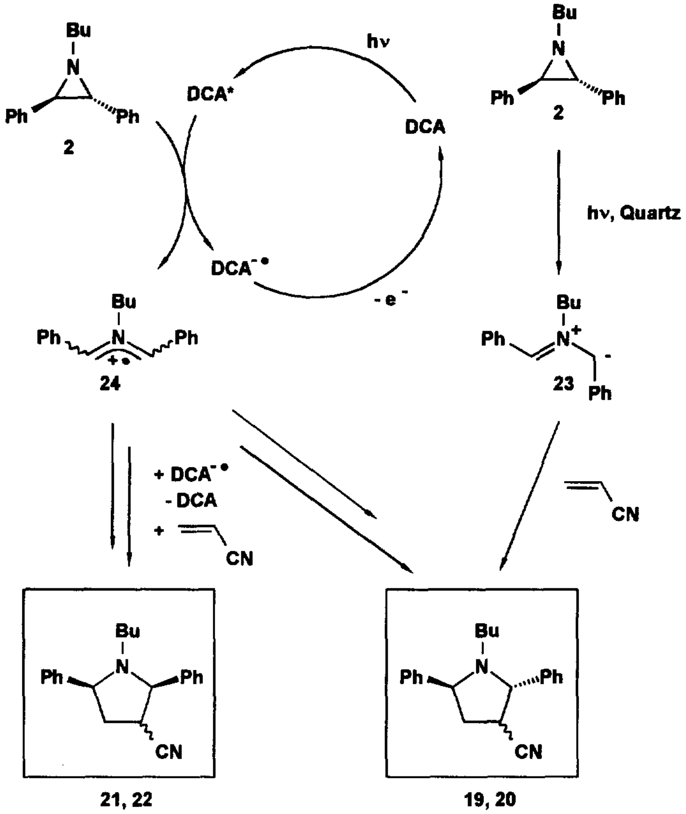
Scheme 6. [3+2] Cycloadditions of *(E)*-1-butyl-2,3-phenylaziridine (**2**) with acrylonitrile

Further investigations proved that, for the thermal side reaction, an activated triple bond is necessary. Therefore, with acrylonitrile as dipolarophile, we did not observe any thermal reaction (Scheme 6). Under direct photolysis we found two isomeric pyrrolidines **19** and **20** in yields of 40 and 18 %. In both products the phenyl groups are in the *trans* position. In pyrrolidine **19** the cyano group is standing *cis* to the phenyl group at C 2, in the case of pyrrolidine **20** it is in *trans* position. Using PET conditions we observed all possible isomeric pyrrolidines. The main products **19** and **20** were formed in yields of 29 and 17 % and the side products **21** and **22** in yields of about 4 % each. The side products are characterized by a *cis* position of the phenyl groups.

In accordance with Laurent et al.[6], we propose the following mechanism (Scheme 7). Under direct photolysis, the aziridine ring is opened in a disrotatory manner to build up the azomethine ylide **23** with the phenyl groups in the *trans* position. The *trans* azomethine ylide **23** is trapped with acrylonitrile in a stereospecific [3+2] cycloaddition leading to the corresponding pyrrolidines **19** and **20** with *trans*-configurated phenyl groups. Under PET conditions, first the sensitizer, 9,10-dicyanoanthracene, is electronically excited into its singlet state which then oxidizes the aziridine **2** to its radical cation **24**. **24** reacts under back electron transfer and [3+2] cycloaddition with acrylonitrile to give the four isomeric pyrrolidines **19** - **22**. The sequence of these steps is still unknown. However, the radical cation **24** has different properties compared to the azomethine ylide **23** and, consequently, the pyrrolidines **21** and **22** with the *cis* position of the phenyl groups are formed as well. Therefore, an isomerization step has to be involved. In the case of the azomethine ylide **23** this isomerization step is not observed.

In order to elucidate the influence of the back electron transfer we applied both, salt effects and the cosensitization process.[5c] However, when using a saturated lithium perchlorate solution in acetonitrile, no change of the product ratio was observed. The same is true with biphenyl as cosensitizer. Therefore, we assume that dissociation into separated radical ions is favoured even under standard PET conditions.

Under PET conditions no reaction is detected in the cases of 1-aryl-2-phenylaziridines **3** and **4**. The radical cations, formed of these aziridines under PET conditions, probably have a ring closed structure.[10] Therefore, a cycloaddition cannot take place.



Scheme 7. Proposed mechanism for the transformations under PET conditions

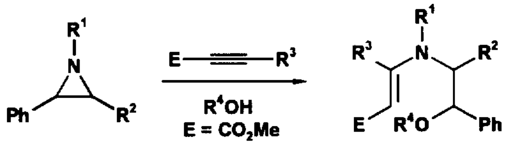
Thermal Reactions

In acetonitrile as solvent aziridines **1** and **2** also afforded the corresponding dihydropyrroles **9** and **16** based on a formal C-N bond cleavage up to 13 %. In the case of aziridine **2** the *trans* position of the phenyl substituents is retained in the five-membered heterocycle.

To elucidate the mechanism of this reaction, we used methanol as solvent (Table). In this case a 1:1:1 aziridine-acetylene-solvent addition product is formed. Aziridine **1** and DMAD in methanol gave **25a** in yields of 70 % (Entry a). Using methyl propiolate instead of DMAD (Entry b), the analogous product **25b** is formed in almost quantitative yields. In the case of the trisubstituted aziridine **2** the reaction occurred with similar efficiency (Entry c and d). In order to change the electron density at the nitrogen atom of the aziridine, we synthesized 1-aryl-2-phenyl substituted aziridines. The aziridine **3** reacted with both acetylene derivatives (Entry e and f) in yields of 84 % and 64 %, respectively. The reactions of aziridine **4** with enlarged electron density at the nitrogen atom only led to increased yields with methyl propiolate compared to the phenyl derivate (Entry h). Using aziridine **5** the electron density at the nitrogen atom is reduced. The reaction time is increased and the yields of the reaction with DMAD were diminished to 42 % (Entry i). The transformation with methyl propiolate (Entry k) led to yields lower than 10 %.

Due to the longer reaction times the nucleophilic addition of the 1-aryl-2-phenylaziridines compete with the nucleophilic ring opening of the aziridine ring by methanol. Nevertheless, the nucleophilic ring opening took place in yields about 10 %. The same amount is obtained in the reaction of the aziridines in methanol without any acetylenic component. Only in the case of the transformation of aziridine **5** with methyl propiolate, the reactivity of the aziridine is reduced in such a manner, that the nucleophilic ring opening is favoured.

Table: Thermal reactions of aziridines with acetylene derivatives in different solvents at r.t.

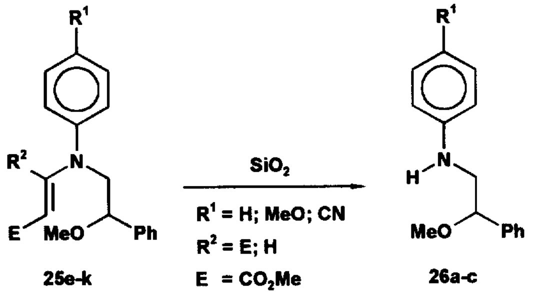


1-5 **25a-m**

Entry	Compd.	Solvent	R^1	R^2	R^3	R^4	Yield (%)
a	1	MeOH	Bu	H	E	Me	70
b	1	MeOH	Bu	H	H	Me	95
c	2	MeOH	Bu	Ph	E	Me	74
d	2	MeOH	Bu	Ph	H	Me	83
e	3	MeOH	Ph	H	E	Me	84
f	3	MeOH	Ph	H	H	Me	64
g	4	MeOH	*p*-MeOC$_6$H$_4$	H	E	Me	85
h	4	MeOH	*p*-MeOC$_6$H$_4$	H	H	Me	80
i	5	MeOH	*p*-CNOC$_6$H$_4$	H	E	Me	42
k	5	MeOH	*p*-CNOC$_6$H$_4$	H	H	Me	<10
l	1	CH$_3$CN:H$_2$O = 1:1	Bu	H	H	H	18
m	2	CH$_3$CN:H$_2$O = 9:1	Bu	Ph	H	H	29

In the cases of methyl propiolate (R^3 = H) as acetylenic compound, the coupling constant of the olefinic protones (J = 13 Hz) and increment calculations (δ_{trans}> 7.23 ppm vs. δ_{cis}> 6.60 ppm, measured δ = 7.35-7,85 ppm for 3-H) indicate a *trans* configuration. In analogy, the corresponding products formed with DMAD (R^3 = E) are supposed to be maleate derivatives.

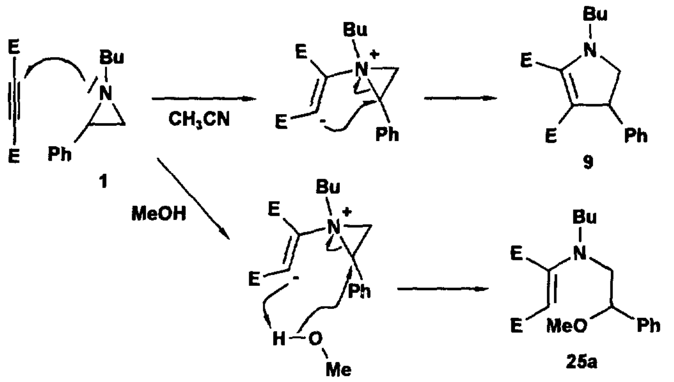
The products of the reactions with 1-aryl-2-phenyl substituted aziridines are less stable than in the case of 1-alkyl substitution. On silica gel we observed the decomposition of the highly substituted enamines **25e-k** to (2-methoxy)-2-(phenylethyl)arylamines (**26a-c**), however, the products are stable on neutral aluminium oxide (Scheme 8).



Scheme 8. Decomposition of the enamines **25** on silica gel

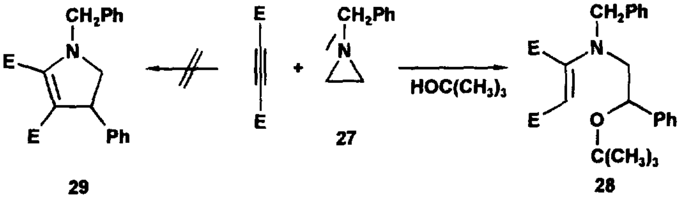
Changing the solvent to a mixture of acetonitrile and water (1:1) the reaction of aziridine **1** led to **25l** in yields of 18 % (Entry l). With a mixture of acetonitrile and water (9:1) aziridine **2** afforded **25m** in yields of 29 % (Entry m). The reaction conditions have not been optimized so far. Nevertheless, this method provides the opportunity to introduce further functionalizations.

Concerning the mechanism we propose a nucleophilic attack of the lone electron pair at the nitrogen atom of the aziridine **1** to one of the acetylenic carbon centers (Scheme 9). The resulting intermediate has a positive charge at the nitrogen atom and a negative charge on the acetylenic unit. Because of the retention of the relative stereochemistry during product formation we assume that the aziridine ring has not been opened in this step. In acetonitrile as solvent the negative center opens the aziridine ring by intramolecular nucleophilic substitution forming the corresponding five-membered heterocycle **9**. In presence of methanol (or in a mixture of water and acetonitrile), the negative charge is trapped by a proton while the methoxy group (or hydroxyl group) opens the aziridine ring by intermolecular nucleophilic substitution. The 1:1:1 aziridine-acetylene-solvent adduct **25a** is formed in high up to quantitative yields.



Scheme 9. Proposed mechanism for the formal [3+2] cycloaddition of aziridines to acetylenic derivatives

This mechanism is in agreement with an early investigation of Winterfeldt and Dillinger.[11] They observed a *single* analogous reaction of aziridine **27** with DMAD in *tert*-butanol (Scheme 10) leading to the ring opened butyl ether **28**. The corresponding dihydropyrrole **29** was not observed at that time. In this paper we provide an access to the corresponding dihydropyrrole by changing the solvent from an alcohol to acetonitrile.

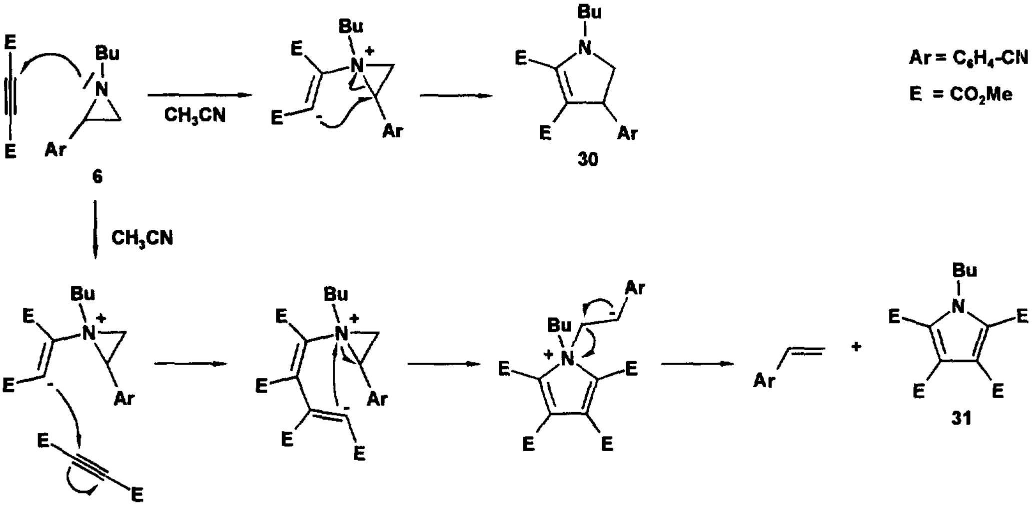


Scheme 10. Winterfeldt-Dillinger reaction[11]

The key step of the mechanism is the nucleophilic attack of the lone pair at the nitrogen to the acetylenic compound. This step is also involved during the formation of azetidines from azabicyclobutanes and

DMAD.[12] Guimanini proposed an analogeous mechanism concerning the reaction of *N*-benzylaziridine with aryne.[13] The cycloaddition of 1,2-disubstituted aziridines to heterocumulenes by organoantimony halides is explained with a nucleophilic attack of the lone electron pair at the nitrogen atom of the aziridine to the heterocumulene.[14]

In order to increase the yields of the dihydropyrrole, we synthesized aziridine **6**. The electron-withdrawing cyano group should facilitate the second step of the mechanism, the intramolecular nucleophilic substitution. Interestingly, we obtained the corresponding dihydropyrrole **30** only as side product in yields of 4 %. As main product the pyrrole **31** is formed in yields of 7 %. The rationalization of the formation of the main product is given by an insertion step (Scheme 11). First the lone pair attacks the acetylenic compound. Then an insertion of another acetylenic unit takes place followed by an intramolecular substitution of the aziridine. The negative charge is located at the carbon center with the electron-withdrawing aryl substituent. Finally the pyrrole **31** is formed under elemination of *p*-cyanostyrole, which could be identified by gas chromatography.



Scheme 11. Reaction of aziridine **6** with DMAD in acetonitrile

In conclusion, we have shown that the formation of products during the [3+2] cycloaddition of aziridines depends on the reaction conditions. Direct photolysis generates the azomethine ylide. With reactive dipolarophiles, this intermediate reacts in a stereospecific conversion. Under PET conditions the corresponding radical cation is formed. Contrasting the azomethine ylide, the radical cation undergoes isomerization. In addition we have presented a new formal [3+2] cycloaddition of aziridines to DMAD under mild conditions (r.t.) which occurs under C-N bond cleavage of the aziridine ring instead of the normal C-C bond cleavage. Changing the solvent from acetonitrile to more protic solvents, such as methanol, we observed the formation of an 1:1:1 addition product consisting of the aziridine, the dipolarophile and the solvent. The products are highly substituted enamines which may be simply functionalized at least in the case of the hydroxy substituted species. The use of activated acetylene derivatives seems to be important for this conversions because 1,2-diphenyl acetylene or cyclooctyne do not undergo any reaction. Further investigations are in progress.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 P, Bruker AM 300, Bruker WM 300 or Bruker AM 360 spectrometer using CDCL$_3$ as solvent and TMS as internal standard. IR spectra were conducted on a Perkin-Elmer 298 or a FTIR Perkin-Elmer 1600 spectrometer. UV spectra were run on a Shimadzu UV-2100 spectrophotometer. GC-MS spectra were performed on a Varian MAT CH 7A with GC Varian 1400, Finnigan MAT 8230 with GC Varian 3400 or a Varian Saturn 2 spectrometer. Elemental analyses were carried out by the Analytische Abteilung, Organisch-Chemisches Institut, Universität Münster, Germany. Column chromatography was executed using Merck silica gel or ICN aluminium oxide. Solvents were dried using standard procedures. The irradiations were performed in a Rayonet photoreactor (Southern New England) fitted with 253.7 nm or 419.0 nm lamps using quartz or pyrex tubes of ca. 12 mL volume.

Due to the conformational flexibility of nitrogen-containing five-membered heterocycles, it is difficult to base structural conclusions on *J* values alone.[15] Important for the assignment is the anisotropic effect of the phenyl group. A ring substituent is shielded by *cis-vic*-phenyl, but deshilded by *trans-vic*-phenyl groups.[15,16]

1-Butyl-2-phenylaziridine (1)

Starting with commercial available 2-phenyloxirane the corresponding β-amino alcohol is prepared according to the procedure of Chapman and Triggle in yields of 44 %.[17] The formation of 1-butyl-2-phenylaziridine (**1**) occurred as described by Okada et al. in yields of 56 %.[18]

(E)-1-Butyl-2,3-diphenylaziridine (2)

Using *trans*-stilbene as starting material, epoxidation with MCPBA formed the corresponding *(E)*-1,2-diphenyloxirane in yields of 84 %. Following the procedure of Deyrup and Moyer[19], the epoxide is opened to the β-amino alcohol[20] in yields of 88 %. The cyclization as described above formed *(E)*-1-butyl-2,3-diphenylaziridine (**2**) as a colorless liquid in yields of 58 %, b.p. 103°C/0.1 Torr. **^{1}H NMR** (CDCl$_3$): δ = 0.79 (t, *J* = 7.3 Hz, 3 H, 4'-H), 1.26 (sex, *J* = 7.3 Hz, 2 H, 3'-H), 1.49 (quint, *J* = 7.3 Hz, 2 H, 2'-H), 2.07 (dt, *J* = 7.3, 11.9 Hz, 1 H, 1'-H$_a$), 2.46 (dt, *J* = 7.3, 11.9 Hz, 1 H, 1'-H$_b$), 2.99 (br, 1 H, 1/2-H), 3.23 (br, 1 H, 2/1-H), 7.20-7.41 (m, 10 H, H$_{arom.}$). **^{13}C NMR** (CDCl$_3$): δ = 13.90 (C-4'), 20.42 (C-3'), 32.10 (C-2'), 45.59 (C-1/2), 50.41 (C-2/1), 52.32 (C-1'), 126.41, 126.62, 127.49, 128.12, 128.57, 129.88 (CH$_{arom.}$), 134.27 (C-1''/1'''), 140.24 (C-1''/1'''). **IR** (KBr): $\tilde{\nu}$ = 2956 cm^{-1}, 2929, 1602, 1496, 1449, 1029, 751, 698. **UV** (CH$_3$CN): λ_{max} (lg ε): 230 nm (4.07), 265 (2.99). **GC-MS** *m/z* (%): 252 (12) [M^+ + H], 251 (69) [M^+], 250 (58) [M^+ - H], 208 (92) [M^+ - C$_3$H$_7$], 194 (100, [M^+ - C$_4$H$_9$], 174 (21), 165 (31), 130 (13), 116 (31), 104 (20), 91 (66), 77 (19), 65 (21), 57 (20), 41 (35). C$_{18}$H$_{21}$N (251.4): calcd. C 86.01, H 8.42, N 5.57; found C 85.48, H 8.49, N 5.53.

3 and **4** were prepared by reported procedures.[21]

1-(*p*-Cyanophenyl)-2-phenylaziridine (5)

Starting with 4-benzylideneamino-benzonitrile,[22] aziridine **5** is synthesized following the procedure of Franzen and Driesen[21] as a yellow oil in yields of 26 %. **^{1}H NMR** (CDCl$_3$): δ = 2.50 (dd, *J* = 1.0, 3.4 Hz, 1 H, 3-H$_a$), 2.54 (dd, *J* = 1.0, 6.4 Hz, 1 H, 3-H$_b$), 3.19 (dd, *J* = 3.4, 6.4 Hz, 1 H, 2-H), 7.08 (dm, *J* = 8.6 Hz, 2 H, 2''-H), 7.25-7.40 (m, 5 H, $H_{arom.}$), 7.53 (dm, J = 8.6 Hz, 2 H, 3''-H). **^{13}C NMR** ($CDCl_3$): δ = 37.71 (C-3), 41.76 (C-2), 105.46 (C-4'), 119.27 ($\underline{C}$N), 121.15 (2'-C), 126.05 (C-4''), 127.76 (C-3''), 128.61 (C-2''), 133.29 (C-3'), 138.08 (C-1''), 158.49 (C-1'). **IR** (kap.): $\tilde{\nu}$ = 2222 cm^{-1}, 1603, 1500, 1464, 1418, 1394, 1319, 1281, 1177, 1151, 988, 842, 759, 699, 558. **UV** (CH_3CN) λ_{max} (lg ε): 213 nm (4.09), 266 (4.25). **GC-MS** *m/z* (%): 220 (53) [M^+], 219 (100) [M^+ - H], 129 (76), 116 (18), 102 (44), 92 (20), 91 (26), 77 (8). CI (*Iso*butane): *m/z* (%): 221 (100, MH^+). $C_{15}H_{12}N_2$ (220.3): calcd. C 81.79, H 5.49, N 12.72; found C 81.57, H 5.49, N 12.63.

1-Butyl-2-(*p*-cyanophenyl)aziridine (6)

3.96 g (40 mmol) 1-azidobutane[23] were added to 5 g (38.8 mmol) *p*-cyanostyrole dissolved in 100 mL cyclohexane. After refluxing for 14 d the solvent was removed and the crude product was separated on silica gel with 10% ethyl acetate/cyclohexane. The aziridine **6** was obtained as pale yellow oil in yields of 17 %. **^{1}H NMR** ($CDCl_3$): δ = 0.92 (t, J = 7.3 Hz, 3 H, 4'-H), 1.41 (m, 2 H, 3'-H), 1.58 (m, 2 H, 2'-H), 1.75 (dd, J = 0.9, 6.6 Hz, 1 H, 3-H_a), 1.86 (dd, J = 0.9, 3.2 Hz, 1 H, 3-H_b), 2.33 (dd, J = 3.1, 6.5 Hz, 1 H, 2-H), 2.36 (dt, J = 7.0, 11.6 Hz, 1 H, 1'-H_a), 2.49 (ddd, J = 7.0, 7.1, 11.5 Hz, 1 H, 1'-H_b), 7.32 (d, J = 8.4 Hz, 2 H, 2''-H), 7.54 (d, J = 8.4 Hz, 2 H, 3''-H). **^{13}C NMR** ($CDCl_3$): δ = 14.06 (C-4'), 20.55 (C-3'), 31.88 (C-2'), 38.81 (C-3), 40.65 (C-2), 61.21 (C-1'), 110.37 (C-4''), 119.04 ($\underline{C}$N), 126.88 (C-2''), 132.06 (C-3''), 146.55 (C-1''). **IR** (kap.): $\tilde{\nu}$ = 2957 cm^{-1}, 2937, 2869, 2227, 1610, 1506, 1208, 1077, 850, 562. **GC-MS** *m/z* (%): 200 (12) [M^+], 199 (42) [M^+ - H], 157 (100) [M^+ - C_3H_7], 143 (42) [M^+ - C_4H_9], 129 (8) [M^+ - NC_4H_9], 116 (64), 98 (48), 89 (18), 41 (26). $C_{13}H_{16}N_2$ (200.3): calcd. C 77.96, H 8.05, N 13.99; found C 77.52, H 8.21, N 13.45.

PET conversion of aziridine 1 with DMAD [9a]

1.192 g (8.4 mmol) DMAD and 37 mg (0.16 mmol) DCA were added to 490 mg (2.8 mmol) aziridine **1** dissolved in 140 mL acetonitrile . The argon-saturated solution was irradiated for 3.5 h at λ = 419 nm. The solvent was removed and the products were separated by HPLC with 10 % ethyl acetate/cyclohexane. We obtained **7**, **8**, **9** and **10** in yields of 2 %, 10 %, 9 % and 4 %.

Dimethyl 1-butyl-2-phenyl-2,5-dihydro-1H-pyrrole-3,4-dicarboxylate (7). **^{1}H NMR** ($CDCl_3$): δ = 0.77 (t, J = 7.4 Hz, 3 H, 4'-H), 1.10-1.45 (m, 4 H, 2',3'-H), 2.50 (m, 2 H, 1'-H), 3.52 (s, 3 H, $CO_2C\underline{H}_3$), 3.75 (s, 3 H, $CO_2C\underline{H}_3$), 3.78 (dd, J = 5.7, 14.6 Hz, 1 H, 5-H_a), 4.22 (dd, J = 5.7, 14.6 Hz, 1 H, 5-H_b), 4.79 (dd, J = 5.7, 5.8 Hz, 1 H, 2-H), 7.23-7.40 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.83 (C-4'), 19.53 (C-3'), 32.84 (C-2'), 47.21 (C-1'), 51.44 ($CO_2\underline{C}H_3$), 52.08 ($CO_2\underline{C}H_3$), 52.63 (C-5'), 76.32 (C-2), 126.36, 128.29, 130.33 ($\underline{C}H_{arom.}$), 132.86 (C-4/3), 136.91 (C-3/4), 139.78 ($C_{arom.}$), 164.28 ($\underline{C}$=O), 165.72 ($\underline{C}$=O). **IR** (kap.): $\tilde{\nu}$ = 3020 cm^{-1}, 2940, 1720, 1570, 1440, 1370, 1270, 1235, 1200, 1170, 1145, 1095, 1060, 700. **GC-MS** *m/z* (%): 317 (10) [M^+], 286 (10) [M^+ - OCH_3], 274 (100) [M^+ - C_3H_7], 258 (8) [M^+ - CO_2CH_3], 226 (10), 208 (15), 91 (11), 42 (12). $C_{18}H_{23}NO_4$ (317.4).

Dimethyl 1-butyl-2-phenyl-1H-pyrrole-3,4-dicarboxylate (8). **^{1}H NMR** ($CDCl_3$): δ = 0.71 (t, J = 7.4 Hz, 3 H, 4'-H), 1.09 (sex, J = 7.4 Hz, 2 H, 3'-H), 1.48 (quint, J = 7.4 Hz, 2 H, 2'-H), 3.56 (s, 3 H, $CO_2C\underline{H}_3$), 3.67 (t, J = 7.4 Hz, 2 H, 1'-H), 3.74 (s, 3 H, $CO_2C\underline{H}_3$), 7.16-7.36 (m, 5 H, $H_{arom.}$), 7.33 (s, 1 H, 5-H). **^{13}C NMR** ($CDCl_3$): δ = 13.33 (C-4'), 19.46 (C-3'), 32.79 (C-2'), 47.17 (C-1'), 51.30 ($CO_2\underline{C}H_3$), 51.52

($CO_2\underline{C}H_3$), 114.46 (C-4/3), 115.21 (C-3/4), 126.27 (C-5), 128.18, 128.62, 130.31 ($\underline{C}H_{arom.}$), 136.75, 138.94 ($C_{arom.}$), 164.12 ($\underline{C}$=O), 165.52 ($\underline{C}$=O). **IR** (kap.): $\tilde{\nu}$ = 2940 cm^{-1}, 1710, 1570, 1520, 1480, 1430, 1375, 1280, 1230, 1200, 1165, 1150, 1060, 755, 700. **GC-MS** *m/z* (%): 315 (100) [M^+], 284 (80) [M^+ - OCH_3], 272 (71) [M^+ - C_3H_7], 254 (8) [M^+ - CO_2CH_3], 240 (37), 228 (19), 214 (27), 196 (21), 182 (19), 169 (12), 115 (11), 41 (26). $C_{18}H_{21}NO_4$ (315.4).

Dimethyl 1-butyl-4-phenyl-4,5-dihydro-1H-pyrrole-2,3-dicarboxylate (9). **^{1}H NMR** ($CDCl_3$): δ = 0.87 (t, J = 7.3 Hz, 3 H, 4'-H), 1.10-1.52 (m, 4 H, 2',3'-H), 3.00 (tq, J = 7.0, 13.8 Hz, 2 H, 1'-H), 3.40 (dd, J = 5.5, 10.5 Hz, 1 H, 4-H), 3.48 (s, 3 H, $CO_2C\underline{H}_3$), 3.88 (dd, J = 10.5, 11.7 Hz, 1 H, 5-H_a), 3.92 (s, 3 H, $CO_2C\underline{H}_3$), 4.22 (dd, J = 5.5, 11.7 Hz, 1 H, 5-H_b), 7.14-7.30 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.56 (C-4'), 19.71 (C-3'), 29.91 (C-2'), 45.58 (C-4), 48.01 (C-5), 50.54 ($CO_2\underline{C}H_3$), 52.84 ($CO_2\underline{C}H_3$), 60.52 (C-1'), 103.15 (C-3), 126.62, 127.00, 128.52 ($\underline{C}H_{arom.}$), 144.52 ($C_{arom.}$), 153.99 (C-2), 163.97 ($\underline{C}$=O), 165.15 ($\underline{C}$=O). **IR** (kap.): $\tilde{\nu}$ = 2940 cm^{-1}, 2850, 1720, 1700, 1500, 1440, 1430, 1370, 1255, 1195, 1120, 1085, 695. **GC-MS** *m/z* (%): 317 (40) [M^+], 286 (19) [M^+ - OCH_3], 274 (100) [M^+ -C_3H_7], 258 (12) [M^+ - CO_2CH_3], 226 (12), 115 (13), 91 (12), 45 (14). $C_{18}H_{23}NO_4$ (317.4).

Dimethyl 1-butyl-4-phenyl-1H-pyrrole-2,3-dicarboxylate (10). **^{1}H NMR** ($CDCl_3$): δ = 0.92 (t, J = 7.4 Hz, 3 H, 4'-H), 1.34 (sex, J = 7.4 Hz, 2 H, 3'-H), 1.75 (tquint, J = 2.4, 7.4 Hz, 2 H, 2'-H), 3.80 (s, 3 H, $CO_2C\underline{H}_3$), 3.82 (s, 3 H, $CO_2C\underline{H}_3$), 4.27 (t, J = 7.4 Hz, 2 H, 1'-H), 6.89 (s, 1 H, 5-H), 7.21-7.40 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.65 (C-4'), 19.83 (C-3'), 33.48 (C-2'), 49.38 (C-1'), 51.76 ($CO_2\underline{C}H_3$), 52.37 ($CO_2\underline{C}H_3$), 121.93 (C-3), 123.41 (C-4), 125.50 (C-5), 126.82, 127.26, 128.57 ($\underline{C}H_{arom.}$), 133.40, 142.09 ($C_{arom.}$), 160.58 ($\underline{C}$=O), 167.49 ($\underline{C}$=O). **IR** (kap.): $\tilde{\nu}$ = 2940 cm^{-1}, 1735, 1680, 1580, 1485, 1430, 1340, 1300, 1270, 1210, 1185, 1130, 1090, 695. **GC-MS** *m/z* (%): 315 (82) [M^+], 284 (42) [M^+ - OCH_3], 273 (24) [M^+ + H - C_3H_7], 256 (100) [M^+ - CO_2CH_3], 240 (21), 224 (70), 214 (25), 196 (28), 182 (13), 169 (17), 140 (25), 115 (12), 41 (29). $C_{18}H_{21}NO_4$ (315.4).

PET conversion of aziridine 1 with dimethyl fumarate

1.728 g (12 mmol) dimethyl fumarate and 54 mg (0.24 mmol) DCA were added to 700 mg (4 mmol) aziridine 1 dissolved in 200 mL acetonitrile. The argon-saturated solution was irradiated for 60 h at λ = 419 nm. The solvent was removed and the products were separated by HPLC with 5% ethyl acetate/cyclohexane. We obtained **11** and **12** in yields of 4 % each as yellow oils.

(2S,3S*,4S*)-Dimethyl 1-butyl-2-phenylpyrrolidine-3,4-dicarboxylate (11).*[16] **^{1}H NMR** ($CDCl_3$): δ = 0.78 (t, J = 7.2 Hz, 3 H, 4'-H), 1.10-1.70 (m, 4 H, 2',3'-H), 1.95 (ddd, J = 4.7, 6.9, 11.7 Hz, 1 H, 1'-H_a), 2.37 (dt, J = 7.8, 11.7 Hz, 1 H, 1'-H_b), 2.55 (dd, J = 8.8, 9.0 Hz, 1 H, 5-H_a), 3.35 (m, 2 H), 3.58 (m, 1 H), 3.59 (s, 3 H, $CO_2C\underline{H}_3$), 3.70 (m, 1 H), 3.72 (s, 3 H, $CO_2C\underline{H}_3$), 7.20-7.35 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.88 (C-4'), 20.70 (C-3'), 30.26 (C-2'), 44.94 (C-4), 52.00 ($CO_2\underline{C}H_3$), 52.32 ($CO_2\underline{C}H_3$), 52.74 (C-1'), 54.86 (C-3), 55.13 (C-5), 73.43 (C-2), 127.71, 127.95, 128.39 ($\underline{C}H_{arom.}$), 140.90 ($C_{arom.}$), 173.43 ($\underline{C}$=O), 174.07 ($\underline{C}$=O). **IR** (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 2900, 1725, 1650, 1425, 1285, 1240, 1200, 1160. **GC-MS** *m/z* (%): 318 (1) [M^+ - H], 288 (9) [M^+ - OCH_3], 276 (100) [M^+ - C_3H_7], 262 (12) [M^+ - C_4H_9], 244 (14), 91 (11), 42 (12). $C_{18}H_{25}NO_4$ (319.4).

(2S,3R*,4R*)-Dimethyl 1-butyl-2-phenylpyrrolidine-3,4-dicarboxylate (12).*[16] **^{1}H NMR** ($CDCl_3$): δ = 0.78 (t, J = 7.2 Hz, 3 H, 4'-H), 1.10-1.70 (m, 4 H, 2',3'-H), 2.05 (ddd, J = 4.4, 8.3, 12.1 Hz, 1 H, 1'-H_a), 2.37

(dd, J = 8.2, 10.0 Hz, 1 H, 5-H_a), 2.47 (dt, J = 8.3, 11.9 Hz, 1 H, 1'-H_b), 3.04 (s, 3 H, $CO_2C\underline{H}_3$), 3.53 (dd, J = 7.5, 10.2 Hz, 1 H, 3-H), 3.63 (m, 1 H, 5-H_b/4-H), 3.68 (s, 3 H, $CO_2C\underline{H}_3$), 3.71 (dd, J = 7.5, 10.0 Hz, 1 H, 5-H_b/4-H), 3.76 (d, J = 10.2 Hz, 1 H, 2-H), 7.18-7.27 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.71 (C-4'), 20.18 (C-3'), 29.49 (C-2'), 43.78 (C-4), 50.86, 51.90 ($CO_2\underline{C}H_3$), 52.98 (C-1'), 53.17 (C-3), 54.82 (C-5), 71.11 (C-2), 127.23, 127.74, 128.18 ($\underline{C}H_{arom.}$), 136.77 ($C_{arom.}$), 173.87 ($\underline{C}$=O), 174.20 ($\underline{C}$=O). **IR** (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2895, 1720, 1240, 1115, 1080, 1000, 780. **GC-MS** m/z (%): 318 (2) [M^+ - H], 288 (8) [M^+ - OCH_3], 276 (100) [M^+ - C_3H_7], 262 (15) [M^+ - C_4H_9], 244 (15), 91 (12), 42 (12). $C_{18}H_{25}NO_4$ (319.4).

PET conversion of aziridine 1 with dimethyl maleate

1.728 g (12 mmol) dimethyl maleate and 54 mg (0.24 mmol) DCA were added to 700 mg (4 mmol) aziridine **1** dissolved in 200 mL acetonitrile . The argon-saturated solution was irradiated for 48 h at λ = 419 nm. The solvent was removed and the products were purified by HPLC with 15% ethyl acetate/cyclohexane. We obtained **13** and **14** in yields of 5 % and 1 % as yellow oils. We could not completely separate the two isomers.

(2S,3S*,4R*)-Dimethyl 1-butyl-2-phenylpyrrolidine-3,4-dicarboxylate (13).*[16] **^{1}H NMR** ($CDCl_3$): δ = 0.78 (t, J = 7.2 Hz, 3 H, 4'-H), 1.10-1.42 (m, 4 H, 2',3'-H), 2.11 (ddd, J = 5.2, 7.4, 12.4 Hz, 1 H, 1'-H_a), 2.46 (dt, J = 8.0, 12.4 Hz, 1 H, 1'-H_b), 2.70 (t, J = 9.3 Hz, 1 H, 5-H_a), 3.08 (dd, J = 8.1, 10.5 Hz, 1 H, 3-H), 3.40 (ddd, J = 7.6, 9.3, 10.5 Hz, 1 H, 4-H), 3.53 (dd, J = 7.6, 9.0 Hz, 1 H, 5-H_b), 3.59 (s, 3 H, $CO_2C\underline{H}_3$), 3.64 (s, 3 H, $CO_2C\underline{H}_3$), 3.69 (d, J = 8.1 Hz, 1 H, 2-H), 7.18-7.38 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.85 (C-4'), 20.35 (C-3'), 30.40 (C-2'), 44.58 (C-4), 51.76, 51.86 ($CO_2\underline{C}H_3$), 53.24 (C-1'), 54.56 (C-3), 55.00 (C-5), 71.98 (C-2), 127.65, 128.09, 128.42 ($\underline{C}H_{arom.}$), 141.50 ($C_{arom.}$), 172.60 ($\underline{C}$=O), 172.70 ($\underline{C}$=O). **IR** (KBr): mixture of the two isomers **13** and **14**: $\tilde{\nu}$ = 2940 cm^{-1}, 2850, 1730, 1455, 1440, 1430, 1350, 1315, 1260, 1200, 1165, 1025, 755, 600. **GC-MS** m/z (%): 318 (3) [M^+ - H], 288 (10) [M^+ - OCH_3], 276 (100) [M^+ - C_3H_7], 262 (10) [M^+ - C_4H_9], 244 (12), 91 (12), 40 (34). $C_{18}H_{25}NO_4$ (319.4).

(2S,3R*,4S*)-Dimethyl 1-butyl-2-phenylpyrrolidine-3,4-dicarboxylate (14).*[16] **^{1}H NMR** ($CDCl_3$): δ = 0.82 (t, J = 7.1 Hz, 3 H, 4'-H), 1.10-1.52 (m, 4 H, 2',3'-H), 2.06 (ddd, J = 4.1, 8.3, 11.7 Hz, 1 H, 1'-H_a), 2.52 (dt, J = 7.9, 11.7 Hz, 1 H, 1'-H_b), 2.75 (t, J = 9.5 Hz, 1 H, 5-H_a), 3.16 (s, 3 H, $CO_2C\underline{H}_3$), 3.29 (ddd, J = 6.3, 7.6, 10.1 Hz, 1 H, 4-H), 3.40 (dd, J = 6.0, 7.6 Hz, 1 H, 3-H), 3.62 (s, 3 H, $CO_2C\underline{H}_3$), 3.89 (d, J = 6.4 Hz, 1 H, 2-H), 3.92 (dd, J = 6.7, 9.5 Hz, 1 H, 5-H_b), 7.18-7.38 (m, 5 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 14.02 (C-4'), 28.88 (C-3'), 30.87 (C-2'), 43.98 (C-4), 51.02 (2 $CO_2\underline{C}H_3$), 52.64 (C-1'), 53.51 (C-3), 53.98 (C-5), 72.28 (C-2), 127.65, 128.09, 128.42 ($\underline{C}H_{arom.}$), 138.88 ($C_{arom.}$), 171.19 ($\underline{C}$=O), 172.36 ($\underline{C}$=O). **GC-MS** m/z (%): 320 (10) [M^+ + H], 319 (1) [M^+], 318 (4) [M^+ - H], 288 (8) [M^+ -OCH_3], 276 (100) [M^+ - C_3H_7], 262 (16) [M^+ - C_4H_9], 42 (15). $C_{18}H_{25}NO_4$ (319.4).

Direct photolysis of aziridine 2

100 mg (0.4 mmol) aziridine **2** dissolved in 20 mL argon-saturated cyclohexane were irradiated for 3 h at λ = 253.7 nm. The solvent was removed and the products were separated by HPLC with 5% ethyl acetate/cyclohexane. We obtained *(Z)*-1-butyl-2,3-diphenylaziridine (**15**)[6] in yields of 49 % and aziridine **2** in yields of 20 %.

PET conversion of aziridine 2 with DMAD

852 mg (6 mmol) DMAD and 25 mg (0.12 mmol) DCA were added to 502 mg (2 mmol) aziridine **2** dissolved in 70 mL acetonitrile. The argon-saturated solution was irradiated for 5 h at $\lambda = 419$ nm. The solvent was removed and the products were separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained **16**, **17** and **18** in yields of 5 %, 31 % and 18 %. **16** and **17** were pale yellow oils whereas **18** was a colorless solid.

(4S,5S*)-Dimethyl 1-butyl-4,5-diphenyl-4,5-dihydro-1H-pyrrole-2,3-dicarboxylate (16).* ^{1}**H NMR** ($CDCl_3$): δ = 0.81 (t, J = 7.1 Hz, 3 H, 4'-H), 1.10-1.27 (m, 2 H, 3'-H), 1.29-1.48 (m, 2 H, 2'-H), 2.88 (dt, J = 7.0, 14.5 Hz, 1 H, 1'-H_a), 3.08 (dt, J = 7.7, 14.4 Hz, 1 H, 1'-H_b), 3.49 (s, 3 H, $CO_2C\underline{H}_3$), 4.01 (s, 3 H, $CO_2C\underline{H}_3$), 4.09 (d, J = 5.8 Hz, 1 H, 4-H), 4.52 (d, J = 5.8 Hz, 1 H, 5-H), 7.18-7.43 (m, 10 H, $H_{arom.}$). ^{13}**C NMR** ($CDCl_3$): δ = 13.56 (C-4'), 19.75 (C-3'), 29.99 (C-2'), 45.82 (C-1'), 50.68 ($CO_2\underline{C}H_3$), 53.00 ($CO_2\underline{C}H_3$), 56.37 (C-5), 75.49 (C-8), 99.91 (C-2), 126.39, 126.81, 127.12, 128.20, 128.70, 129.06 ($\underline{C}H_{arom.}$), 140.81, 144.36 ($C_{arom.}$), 153.84 (C-3), 163.96 ($\underline{C}$=O), 165.36 ($\underline{C}$=O). **IR** (kap.): $\tilde{\nu}$ = 2955 cm^{-1}, 1747, 1682, 1592, 1435, 1101, 1031. **GC-MS** *m/z* (%): 394 (21) [M^+ + H], 393 (56) [M^+], 362 (18) [M^+ -OCH_3], 350 (100) [M^+ - C_3H_7], 334 (12), 318 (11), 302 (18), 290 (12), (16). $C_{24}H_{27}NO_4$ (393.5).

(2R,5R*)-Dimethyl 1-butyl-2,5-diphenyl-2,5-dihydro-1H-pyrrole-3,4-dicarboxylate (17).*[6] ^{1}**H NMR** ($CDCl_3$): δ = 0.62 (t, J = 7.0 Hz, 3 H, 4'-H), 0.90-1.30 (m, 4 H, 2',3'-H), 2.27 (m, 2 H, 1'-H), 3.60 (s, 6 H, $CO_2C\underline{H}_3$), 5.35 (s, 2 H, 2,5-H), 7.20-7.40 (m, 10 H, $H_{arom.}$). ^{13}**C NMR** ($CDCl_3$): δ = 13.71 (C-4'), 19.92 (C-3'), 30.49 (C-2'), 45.90 (C-1'), 51.98 ($CO_2\underline{C}H_3$), 66.94 (C-2,5), 128.02, 128.36, 128.40 ($\underline{C}H_{arom.}$), 138.73, 140.27 ($C_{arom.}$), 163.84 ($\underline{C}$=O). **IR** (kap.): $\tilde{\nu}$ = 2953 cm^{-1}, 1724, 1484, 1453, 1436, 1276, 1225, 1200, 1169, 1101, 733, 701. **GC-MS** *m/z* (%): 393 (8) [M^+], 362 (5) [M^+ - OCH_3], 350 (100) [M^+ -C_3H_7], 316 (16), 284 (16), 91 (11). CI (*Iso*butane) *m/z* (%): 394 (100) [MH^+]. $C_{24}H_{27}NO_4$ (393.5): calcd. C 73.26, H 6.92, N 3.56; found C 73.04, H 7.07, N 3.88.

Dimethyl 1-butyl-2,5-diphenyl-1H-pyrrole-dicarboxylate (18).[6,24] ^{1}**H NMR** ($CDCl_3$): δ = 0.49 (t, J = 7.4 Hz, 3 H, 4'-H), 0.83 (sex, J = 7.3 Hz, 2 H, 3'-H), 1.16 (m, 2 H, 2'-H), 3.65 (s, 6 H, $CO_2C\underline{H}_3$), 3.67 (m, 2 H, 1'-H), 7.40-7.49 (m, 10 H, $H_{arom.}$). ^{13}**C NMR** ($CDCl_3$): δ = 13.06 (C-4'), 19.30 (C-3'), 32.36 (C-2'), 44.68 (C-1'), 51.43 ($CO_2\underline{C}H_3$), 114.45 (C-3,4), 128.17, 128.60, 130.51 ($\underline{C}H_{arom.}$), 131.08 (C-2,5), 136.52 ($C_{arom.}$), 165.33 ($\underline{C}$=O). **IR** (KBr): $\tilde{\nu}$ = 1731 cm^{-1}, 1709, 1482, 1438, 1255, 1197, 1168, 1058, 772, 702. **GC-MS** *m/z* (%): 391 (100) [M^+], 360 (26) [M^+ - OCH_3], 348 (10) [M^+ - C_3H_7], 316 (19), 304 (13), 290 (31), 271 (13), 258 (11). $C_{24}H_{25}NO_4$ (391.5): calcd. C 73.64, H 6.44, N 3.58; found C 73.94, H 6.50, N 3.82.

The X-ray crystallographic data of **18** are also available.

Direct photolysis of aziridine 2 with DMAD

170 mg (1.2 mmol) DMAD were added to 100 mg (0.4 mmol) aziridine **2** dissolved in 20 mL acetonitrile. The argon-saturated solution was irradiated for 24 h at $\lambda = 253.7$ nm. The solvent was removed and the products were separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained **16**, **17** and **18** in yields of 5 %, 8 % and 21 %.

Direct photolysis of aziridine 2 with acrylonitrile

65 mg (1.2 mmol) acrylonitrile were added to 100 mg (0.4 mmol) aziridine **2** dissolved in 20 mL acetonitrile. The argon-saturated solution was irradiated for 24 h at $\lambda = 253.7$ nm. The solvent was removed

and the products were separated by HPLC with 5% ethyl acetate/cyclohexane. We obtained **19** and **20** in yields of 40 % and 18 %.

(2S,3R*,5S*)-1-Butyl-3-cyano-2,5-diphenylpyrrolidine (**19**).* **^{1}H NMR** ($CDCl_3$): δ = 0.71 (t, *J* = 7.2 Hz, 3 H, 4'-H), 1.00-1.40 (m, 4 H, 2',3'-H), 2.26 (ddd, *J* = 3.6, 8.9, 12.5 Hz, 1 H, 4-H_a), 2.37 (m, 2 H, 1'-H), 2.84 (ddd, *J* = 9.3, 9.5, 13.2 Hz, 1 H, 4-H_b), 3.61 (ddd, *J* = 7.3, 9.0, 9.5 Hz, 1 H, 3-H), 4.48 (dd, *J* = 3.6, 9.2 Hz, 1 H, 5-H), 4.65 (d, *J* = 7.2 Hz, 1 H, 2-H), 7.25-7.50 (m, 10 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.78 (C-4'), 20.20 (C-3'), 30.43 (C-2'), 33.56 (C-3), 37.69 (C-4), 47.00 (C-1'), 64.93 (C-5), 67.40 (C-2), 119.66 ($\underline{C}$N), 127.13, 127.34, 128.19, 128.37, 128.48, 128.53 ($\underline{C}H_{arom.}$), 138.25, 143.67 ($C_{arom.}$). **IR** (kap.): $\tilde{\nu}$ = 2956 cm^{-1}, 2861, 2242, 1454, 754, 702. **GC-MS** *m/z* (%): 304 (1) [M^+], 303 (2) [M^+ - H], 261 (100) [M^+ - C_3H_7], 227 (3) [M^+ - C_6H_5], 91 (19). $C_{21}H_{24}N_2$ (304.4).

(2S,3S*,5S*)-1-Butyl-3-cyano-2,5-diphenylpyrrolidine (**20**).* **^{1}H NMR** ($CDCl_3$): δ = 0.72 (t, *J* = 7.3 Hz, 3 H, 4'-H), 1.00-1.40 (m, 4 H, 2',3'-H), 2.09 (m, 1 H, 1'-H_a), 2.22 (dt, *J* = 8.0, 12.5 Hz, 1 H, 1'-H_b), 2.28 (ddd, *J* = 5.3, 6.1, 13.3 Hz, 1 H, 4-H_a), 2.92 (ddd, *J* = 8.1, 9.9, 13.2 Hz, 1 H, 4-H_b), 3.04 (ddd, *J* = 5.7, 5.9, 9.9 Hz, 1 H, 3-H), 4.41 (dd, *J* = 5.4, 8.2 Hz, 1 H, 5-H), 4.54 (d, *J* = 5.7 Hz, 1 H, 2-H), 7.25-7.55 (m, 10 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.83 (C-4'), 20.04 (C-3'), 29.93 (C-2'), 36.07 (C-3), 37.55 (C-4), 45.75 (C-1'), 64.87 (C-5), 69.70 (C-2), 121.82 ($\underline{C}$N), 127.54, 127.62, 128.12, 128.17, 128.53, 128.76 ($\underline{C}H_{arom.}$), 139.69, 142.12 ($C_{arom.}$). **IR** (kap.): $\tilde{\nu}$ = 2956 cm^{-1}, 2861, 2240, 1493, 1454, 755, 701. **GC-MS** *m/z* (%): 303 (3) [M^+ - H], 261 (100) [M^+ - C_3H_7], 227 (4) [M^+ - C_6H_5]. $C_{21}H_{24}N_2$ (304.4).

PET conversion of aziridine 2 with acrylonitrile

636 mg (12 mmol) acrylonitrile were added to 1 g (4 mmol) aziridine **2** dissolved in 140 mL acetonitrile. The argon-saturated solution was irradiated for 4 h at λ = 419 nm. The solvent was removed and the products were separated by HPLC with 7% ethyl acetate/cyclohexane. We obtained **19**, **20**, **21** and **22** in yields of 29 %, 17 %, 4 % and 4 %. All compounds were pale yellow oils.

(2R,3S*,5S*)-1-Butyl-3-cyano-2,5-diphenylpyrrolidine (**21**).* **^{1}H NMR** ($CDCl_3$): δ = 0.59 (t, *J* = 7.1 Hz, 3 H, 4'-H), 0.80-1.70 (m, 4 H, 2',3'-H), 2.16 (ddd, *J* = 6.6, 8.1, 13.1 Hz, 1 H, 4-H_a), 2.46 (t, *J* = 8.1 Hz, 2 H, 1'-H), 2.62 (ddd, *J* = 7.6, 8.5, 13.1 Hz, 1 H, 4-H_b), 3.31 (ddd, *J* = 6.5, 7.6, 8.5 Hz, 1 H, 3-H), 3.80 (t, *J* = 7.8 Hz, 1 H, 5-H), 4.02 (d, *J* = 7.7, 1 H, 2-H), 7.20-7.62 (m, 10 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.65 (C-4'), 20.36 (C-3'), 27.85 (C-2'), 35.29 (C-3), 38.75 (C-4), 51.38 (C-1'), 67.44 (C-5), 69.24 (C-2), 120.16 ($\underline{C}$N), 127.60, 127.65, 128.17, 128.38, 128.44, 128.58 ($\underline{C}H_{arom.}$), 139.23, 142.80 ($C_{arom.}$). **IR** (kap.): $\tilde{\nu}$ = 2959 cm^{-1}, 2223, 1637, 1449, 700. **GC-MS** *m/z* (%): 303 (3) [M^+ - H], 302 (12), 261 (13) [M^+ - C_3H_7], 189 (13), 105 (100), 91 (12), 77 (43), 51 (13). $C_{21}H_{24}N_2$ (304.4).

(2R,3R*,5S*)-1-Butyl-3-cyano-2,5-diphenylpyrrolidine (**22**).* **^{1}H NMR** ($CDCl_3$): δ = 0.61 (t, *J* = 7.1 Hz, 3 H, 4'-H), 0.92-1.13 (m, 4 H, 2',3'-H), 2.17 (ddd, *J* = 7.5, 9.6, 13.0 Hz, 1 H, 4-H_a), 2.46 (dd, *J* = 6.9, 9.5 Hz, 2 H, 1'-H), 2.52 (ddd, *J* = 6.7, 8.2, 13.0 Hz, 1 H, 4-H_b), 2.92 (ddd, *J* = 6.7, 8.1, 9.6 Hz, 1 H, 3-H), 3.99 (d, *J* = 8.1 Hz, 1 H, 2-H), 4.01 (dd, *J* = 7.4, 8.1 Hz, 1 H, 5-H), 7.26-7.58 (m, 10 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 13.66 (C-4'), 20.37 (C-3'), 27.85 (C-2'), 36.56 (C-3), 38.34 (C-4), 51.18 (C-1'), 66.82 (C-5), 72.22 (C-2), 121.09 ($\underline{C}$N), 127.17, 127.22, 127.56, 128.33, 128.60, 128.84 ($\underline{C}H_{arom.}$), 140.68, 143.27 ($C_{arom.}$). **IR** (kap.): $\tilde{\nu}$ = 3029 cm^{-1}, 2956, 2861, 2241, 1493, 1453, 1170, 753, 701. **GC-MS** *m/z* (%): 261 (100) [M^+ - C_3H_7], 227 (3) [M^+ - C_6H_5], 205 (12), 154 (10), 91 (18). $C_{21}H_{24}N_2$ (304.4).

Thermal reaction of aziridine 1 with DMAD in acetonitrile

1.278 mg (12 mmol) DMAD were added to 525 mg (3 mmol) aziridine **1** dissolved in 200 mL acetonitrile. After 2 d the solvent was removed and separation occurred by HPLC with 15% ethyl acetate/cyclohexane. We obtained **9** in yields of 13 %.

Thermal reaction of aziridine 2 with DMAD in acetonitrile

85 mg (0.6 mmol) DMAD were added to 250 mg (0.2 mmol) aziridine **2** dissolved in 10 mL acetonitrile. After several days the solvent was removed and the products separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained **16** in yields of 13 %.

General procedures of the thermal transformations in methanol

In 54 mL absolute methanol 1 mmol of the aziridine was treated with 3 mmol of the dipolarophile and stirred at room temperature for several hours. After complete conversion (GC monitored) the solvent was removed by distillation under reduced pressure and the crude product is purified on silica gel. In the case of 1-aryl substituted aziridines neutral aluminium oxide is used due to decomposition on silica gel.

Dimethyl 2-[butyl-(2'-methoxy-2'-phenylethyl)amino]maleate (25a). The conversion of aziridine **1** with DMAD in methanol afforded **25a** as a yellow oil in 70 % yield. ^{1}**H NMR** (CDCl$_3$): δ = 0.86 (t, J = 7.3 Hz, 3 H, 4''-H), 1.22 (sex, J = 7.3 Hz, 2 H, 3''-H), 1.50 (quint, J = 7.7 Hz, 2 H, 2''-H), 2.95 (dt, J = 7.5, 14.6 Hz, 1 H, 1''-H$_a$), 3.14 (dd, J = 3.8, 15.0 Hz, 1 H, 1'-H$_a$), 3.19 (s, 3 H, CH-OC$\underline{H}_3$), 3.23 (dt, J = 7.5, 14.6 Hz, 1 H, 1''-H$_b$), 3.30 (dd, J = 8.3, 15.0 Hz, 1 H, 1'-H$_b$), 3.62 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.88 (s, 3 H, CO$_2$C$\underline{H}_3$), 4.43 (dd, J = 3.8, 8.3 Hz, 1 H, 2'-H), 4.64 (s, 1 H, 3-H), 7.24-7.38 (m, 5 H, H$_{\text{arom.}}$). ^{13}**C NMR** (CDCl$_3$): δ = 13.63 (C-4''), 19.86 (C-3''), 28.71 (C-2''), 50.59 (CO$_2$$\underline{C}H_3$), 52.18 (C-1'/1''), 52.71 (CO$_2$$\underline{C}H_3$), 56.83 (CH-O$\underline{C}H_3$), 57.29 (C-1''/1'), 82.12 (C-3/2'), 84.22 (C-2'/3), 126.34 (2 $\underline{C}$H$_{\text{arom.}}$), 128.17 ($\underline{C}$H$_{\text{arom.}}$), 128.64 (2 $\underline{C}$H$_{\text{arom.}}$), 139.15 (C$_{\text{arom.}}$), 154.15 (C-2), 165.97 (C-4), 168.10 (C-1). **IR** (kap.): $\tilde{\nu}$ = 2940 cm^{-1}, 2860, 1730, 1690, 1565, 1435, 1420, 1360, 1250, 1150, 1100, 1040, 1020, 700. **GC-MS** *m/z* (%): 350 (1) [M^+ + H], 349 (2) [M^+], 318 (7) [M^+ - OCH$_3$], 290 (2) [M^+ - CO$_2$CH$_3$], 258 (2) [M^+ - 91], 228 (100) [M^+ - PhCHOCH$_3$], 186 (52), 140 (14), 121 (12) [PhCHOCH$_3^+$], 112 (13), 91 (10), 77 (12). $C_{19}H_{27}NO_5$ (349.4).

(E)-Methyl 3-[butyl-(2'-methoxy-2'-phenylethyl)amino]acrylate (25b). The conversion of aziridine **1** with methyl propiolate in methanol afforded **25b** as a yellow oil in 95 % yield. ^{1}**H NMR** (CDCl$_3$): δ = 0.80 (t, J = 7.4 Hz, 3 H, 4''-H), 1.17 (sex, J = 7.6 Hz, 2 H, 3''-H), 1.40 (quint, J = 7.6 Hz, 2 H, 2''-H), 2.90 (dt, J = 7.4, 14.1 Hz, 1 H, 1''-H$_a$), 3.05 (m, 2 H, 1'-H$_a$, 1''-H$_b$), 3.10 (s, 3 H, CH-OC$\underline{H}_3$), 3.25 (dd, J = 8.2, 14.4 Hz, 1 H, 1'-H$_b$), 3.55 (s, 3 H, CO$_2$C$\underline{H}_3$), 4.25 (br, 1 H, 2'-H), 4.50 (d, J = 13.1 Hz, 1 H, 2-H), 7.16-7.30 (m, 5 H, H$_{\text{arom.}}$), 7.35 (d, J = 13.1 Hz, 1 H, 3-H). ^{13}**C NMR** (CDCl$_3$): δ = 14.35 (C-4''), 19.84 (C-3''), 29.58 (C-2''), 50.34 (CO$_2$$\underline{C}H_3$), 51.25 (C-1'/1''), 56.81 (CH-O$\underline{C}$H$_3$), 57.50 (C-1'/1''), 82.78 (C-2'), 83.86 (C-2), 126.49 (2 $\underline{C}$H$_{\text{arom.}}$), 128.16 ($\underline{C}$H$_{\text{arom.}}$), 128.62 (2 $\underline{C}$H$_{\text{arom.}}$), 139.12 (C$_{\text{arom.}}$), 151.95 (C-3), 170.07 (C-1). **IR** (kap.): $\tilde{\nu}$ = 2920 cm^{-1}, 2860, 2810, 1680, 1600, 1450, 1415, 1350, 1240, 1180, 1140, 1100, 1045, 1015, 780, 750, 700. **GC-MS** *m/z* (%): 292 (2) [M^+ + H], 260 (12) [M^+-OCH$_3$], 248 (1) [M^+ - C$_3$H$_7$], 170 (88) [M^+ - PhCHOCH$_3$], 128 (100), 121 (16) [PhCHOCH$_3^+$], 91 (11), 82 (19), 77 (12), 41 (13). $C_{17}H_{25}NO_3$ (291.4).

Dimethyl 2-[butyl-(2'-methoxy-1',2'-diphenylethyl)amino]maleate (25c). The conversion of aziridine **2** with DMAD in methanol afforded **25c** as a yellow oil in 78 % yield. ^{1}**H NMR** (CDCl$_3$): δ = 0.60 (m, 1 H, 2''-H$_a$), 0.71 (t, J = 7.3 Hz, 3 H, 4''-H), 1.00 (m, 2 H, 3''-H), 1.40 (m, 1 H, 2''-H$_b$), 3.03 (ddd, J = 4.6, 10.8, 14.7 Hz, 1 H, 1''-H$_a$), 3.21 (ddd, J = 5.0, 10.9, 14.6 Hz, 1 H, 1''-H$_b$), 3.31 (s, 3 H, CH-OC$\underline{H}_3$), 3.59 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.86 (s, 3 H, CO$_2$C$\underline{H}_3$), 4.51 (s, 1 H, 3-H), 4.56 (d, J = 6.5 Hz, 1 H, 1'-H), 4.87 (d, J = 6.5 Hz, 1 H, 2'-H), 7.20-7.60 (m, 10 H, H$_{\text{arom.}}$). ^{13}**C NMR** (CDCl$_3$): δ = 13.48 (C-4''), 20.09 (C-3''), 27.40 (C-2''), 47.07 (C-1''), 50.68 (CO$_2\underline{C}$H$_3$), 52.77 (CO$_2\underline{C}$H$_3$), 57.25 (CH-O$\underline{C}$H$_3$), 68.25 (C-1'), 84.71 (C-3/2'), 85.56 (C-2'/3), 127.25, 127.96, 128.09, 128.23, 128.28, 129.74 ($\underline{C}$H$_{\text{arom.}}$), 135.9, 137.89 (C$_{\text{arom.}}$), 153.39 (C-2), 166.30 (C-4), 168.02 (C-1). **IR** (kap.): $\tilde{\nu}$ = 2949 cm^{-1}, 2869, 1736, 1697, 1567,1437, 1420, 1374, 1151, 1104, 1046, 795, 761, 701. **GC-MS** *m/z* (%): 394 (5) [M^+-OCH$_3$], 304 (100) [M^+ - PhCHOCH$_3$], 156 (12), 142 (12), 121 (44), 105 (10), 91 (16), 77 (18), 57 (48), 41 (13). $C_{25}H_{31}NO_5$ (425.5).

(E)-Methyl 3-[butyl-(2'-methoxy-1',2'-diphenylethyl)amino]acrylate (25d). The conversion of aziridine **2** with methyl propiolate in methanol afforded **25d** as a pale yellow oil in 83 % yield. ^{1}**H NMR** (CDCl$_3$): δ = 0.74 (t, J = 7.2 Hz, 3 H, 4''-H), 1.00 (m, 3 H, 3''-H, 2''-H$_a$), 1.24 (m, 1 H, 2''-H$_b$), 2.63 (m, 1 H, 1''-H$_a$), 2.78 (m, 1 H, 1''-H$_b$), 3.20 (s, 3 H, CH-OC$\underline{H}_3$), 3.63 (s, 3 H, CO$_2$C$\underline{H}_3$), 4.34 (d, J = 8.7 Hz, 1 H, 1'-H), 4.43 (d, J = 13.1 Hz, 1 H, 2-H), 4.72 (d, J = 8.3 Hz, 1 H, 2'-H), 7.20-7.35 (m, 10 H, H$_{\text{arom.}}$), 7.56 (d, J = 13.1 Hz, 1 H, 3-H). ^{13}**C NMR** (CDCl$_3$): δ = 13.59 (C-4''), 19.04 (C-3''), 28.19 (C-2''), 49.61 (C-1''), 50.39 (CO$_2\underline{C}$H$_3$), 56.68 (CH-O$\underline{C}$H$_3$), 72.43 (1'), 83.60 (C-2'/2), 84.57 (C-2/2'), 127.55, 127.97, 128.40 ($\underline{C}$H$_{\text{arom.}}$), 137.47, 138.56 (C$_{\text{arom.}}$), 150.01 (C-3), 170.04 (C-1). **IR** (kap.): $\tilde{\nu}$ = 2956 cm^{-1}, 2949, 1693, 1606, 1454, 1422, 1360, 1241, 1147, 1098, 790, 701. **GC-MS** *m/z* (%): 336 (8) [M^+-OCH$_3$], 246 (100) [M^+ - PhCHOCH$_3$], 163 (25), 131 (33), 121 (38) [PhCHOCH$_3^+$], 91 (15), 77 (19), 57 (23), 41 (12). $C_{23}H_{29}NO_3$ (367.5).

Dimethyl 2-[(2'-methoxy-2'-phenylethyl)phenylamino]maleate (25e). The conversion of aziridine **3** with DMAD in methanol afforded **25e** as a yellow oil in 81 % yield. As a side product **26a** was isolated in yields of 10 %. ^{1}**H NMR** (CDCl$_3$): δ = 3.19 (s, 3 H, OC$\underline{H}_3$), 3.60 (m, 1 H, 1'-H$_a$), 3.65 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.67 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.78 (dd, J = 8.7, 14.8 Hz, 1 H, 1'-H$_b$), 4.43 (dd, J = 3.8, 8.7 Hz, 1 H, 2'-H), 4.89 (s, 1 H, 3-H), 7.14-7.36 (m, 10 H, H$_{\text{arom.}}$). ^{13}**C NMR** (CDCl$_3$): δ = 50.84 (CO$_2\underline{C}$H$_3$), 52.48 (CO$_2\underline{C}$H$_3$), 56.81 (CH-O$\underline{C}$H$_3$), 59.89 (C-1'), 80.86 (C-2'), 88.82 (C-3), 126.69 (C-2''), 127.46 (C-4''), 127.84 (C-2'''), 128.29 (C-4'''), 128.67 (C-3'''), 129.21 (C-3''), 138.95 (C-1'''), 143.67 (C-1''), 154.26 (C-2), 165.29 (C-4/1), 167.78 (C-1/4). **IR** (kap.): $\tilde{\nu}$ = 2950 cm^{-1}, 1731, 1714, 1596, 1574, 1494, 1453, 1435, 1258, 1173, 1106, 1023, 755, 700. **GC-MS** *m/z* (%): 338 (1) [M^+ - OCH$_3$], 248 (100) [M^+ - PhCHOCH$_3$], 144 (31), 121 (13) [PhCHOCH$_3^+$], 91 (18), 77 (43), 51 (14). CI (NH$_3$) *m/z* (%): 370 (100) [MH$^+$]. $C_{21}H_{23}NO_5$ (369.4).

(2-Methoxy-2-phenylethyl)phenylamine (26a).[25] ^{1}**H NMR** (CDCl$_3$): δ = 1.59 (br, 1 H, NH), 3.28 (s, 3 H, OC$\underline{H}_3$), 3.30 (m, 2 H, 1-H), 4.40 (dd, J = 4.8, 7.9 Hz, 1 H, 2-H), 6.65 (dd, J = 1.0, 8.6 Hz, 2 H, 3'-H), 6.73 (tt, J = 1.0, 7.4 Hz, 1 H, 4'-H), 7.18 (dd, J = 7.4, 8.6 Hz, 2 H, 2'-H), 7.33-7.42 (m, 5 H, H$_{\text{arom.}}$). ^{13}**C NMR** (CDCl$_3$): δ = 50.75 (C-1), 56.84 (O$\underline{C}$H$_3$), 82.22 (C-2), 113.34 (C-2'), 117.69 (C-4'), 126.73 (C-2''), 128.06 (C-4''), 128.58 (C-3''), 129.23 (C-3'), 139.87 (C-1''), 148.02 (C-1'). **IR** (kap.): $\tilde{\nu}$ = 1603 cm^{-1}, 1504, 1454, 1317, 1249, 1106, 750, 701. **GC-MS** *m/z* (%): 227 (2) [M^+], 121 (12) [PhCHOCH$_3^+$], 106 (100) [M^+ - PhCHOCH$_3$], 91 (13), 77 (39), 51 (16). CI (NH$_3$) *m/z* (%): 228 (100) [MH$^+$]. $C_{15}H_{17}NO$ (227.3).

(E)-Methyl 3-[(2'-methoxy-2'-phenylethyl)phenylamino]acrylate (25f). The conversion of aziridine **3** with methyl propiolate in methanol afforded **25f** as a yellow oil in 64 % yield. As a side product **26a** was isolated in yields of 7 %. **^{1}H NMR** (CDCl$_3$): δ = 3.21 (s, 3 H, CH-OC$\underline{H}_3$), 3.69 (dd, J = 4.2, 14.8 Hz, 1 H, 1'-H$_a$), 3.72 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.87 (dd, J = 8.8, 14.9 Hz, 1 H, 1'-H$_b$), 4.52 (dd, J = 3.9, 8.8 Hz, 1 H, 2'-H), 4.97 (d, J = 13.3 Hz, 1 H, 2-H), 7.13-7.37 (m, 10 H, H$_{\text{arom.}}$), 7.85 (d, J = 13.3 Hz, 1 H, 3-H). **^{13}C NMR** (CDCl$_3$): δ = 50.72 (CO$_2\underline{C}$H$_3$), 57.06 (CH-O$\underline{C}$H$_3$), 58.08 (C-1'), 80.02 (C-2'), 89.94 (C-2), 122.53, 125.05, 126.63, 128.30, 128.72, 129.33 ($\underline{C}$H$_{\text{arom.}}$), 139.09, 146.03 (C$_{\text{arom.}}$), 149.12 (C-3), 169.59 (C-1). **IR** (kap.): $\tilde{\nu}$ = 2985 cm^{-1}, 2928, 1694, 1614, 1585, 1495, 1454, 1435, 1343, 1262, 1156, 1107, 1023, 979, 801, 756, 700. **GC-MS** *m/z* (%): 280 (5) [M^+ - OCH$_3$], 190 (100) [M^+ - PhCHOCH$_3$], 177 (22), 158 (23), 130 (12), 121 (23) [PhCHOCH$_3^+$], 104 (22), 91 (23), 77 (58), 45 (42). CI (NH$_3$) *m/z* (%): 312 (100) [MH$^+$]. C$_{19}$H$_{21}$NO$_3$ (311.4).

Dimethyl 2-[(p-methoxyphenyl)-(2'-methoxy-2'-phenylethyl)amino]maleate (25g). The conversion of aziridine **4** with DMAD in methanol afforded **25g** as a yellow oil in 85 % yield. As a side product **26b** was isolated in yields of 10 %. **^{1}H NMR** (CDCl$_3$): δ = 3.19 (s, 3 H, CH-OC$\underline{H}_3$), 3.55 (dd, J = 3.8, 14.7 Hz, 1 H, 1'-H$_a$), 3.64 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.68 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.73 (dd, J = 8.8, 14.7 Hz, 1 H, 1'-H$_b$), 3.81 (s, 3 H, Ar-OC$\underline{H}_3$), 4.43 (dd, J = 3.8, 8.8 Hz, 1 H, 2'-H), 4.83 (s, 1 H, 3-H), 6.84 (d, J = 9.1 Hz, 2 H, 3''-H), 7.08 (d, J = 9.1 Hz, 2 H, 2''-H), 7.23-7.38 (m, 5 H, 2''',3''',4'''-H). **^{13}C NMR** (CDCl$_3$): δ = 50.85 (CO$_2\underline{C}$H$_3$), 52.57 (CO$_2\underline{C}$H$_3$), 55.39 (Ar-O$\underline{C}$H$_3$), 56.79 (CH-O$\underline{C}$H$_3$), 59.97 (C-1'), 80.73 (C-2'), 87.47 (C-3), 114.31 (C-3''), 126.70 (C-2''), 128.30 (C-4'''), 128.68 (C-2'''), 129.33 (C-3'''), 136.14 (C-1''), 138.90 (C-1'''), 154.82 (C-2), 158.70 (C-4''), 165.43 (C-4/1), 167.96 (C-1/4). **IR** (kap.): $\tilde{\nu}$ = 1745 cm^{-1}, 1698, 1574, 1510, 1249, 1149. **GC-MS** *m/z* (%): 278 (100) [M^+ - PhCHOCH$_3$], 248 (14), 174 (47), 146 (14), 121 (26) [PhCHOCH$_3^+$], 104 (23), 77 (31), 63 (16). CI (NH$_3$) *m/z* (%): 400 (100) [MH$^+$]. C$_{22}$H$_{25}$NO$_6$ (399.4).

(p-Methoxyphenyl)-(2-methoxy-2-phenylethyl)amine (26b). **^{1}H NMR** (CDCl$_3$): δ = 3.20 (m, 2 H, 1-H), 3.27 (s, 3 H, CH-OC$\underline{H}_3$), 3.75 (s, 3 H, Ar-OC$\underline{H}_3$), 4.38 (dd, J = 5.4, 7.5 Hz, 1 H, 2-H), 6.63 (d, J = 9.1 Hz, 2 H, 3'-H), 6.78 (d, J = 9.1 Hz, 2 H, 2'-H), 7.25-7.41 (m, 5 H, 2'',3'',4''-H). **^{13}C NMR** (CDCl$_3$): δ = 51.95 (C-1), 55.79 (O$\underline{C}$H$_3$), 56.88 (O$\underline{C}$H$_3$), 82.20 (C-2), 114.85 (C-2'), 114.93 (C-3'), 126.77 (C-4''), 128.07 (C-2''), 128.60 (C-3''), 139.96 (C-1'), 142.21 (C-1''), 152.44 (C-4'). **IR** (kap.): $\tilde{\nu}$ = 1513 cm^{-1}, 1454, 1235, 1180, 1109, 1037, 821, 702. **GC-MS** *m/z* (%): 258 (2) [M^+ + H], 257 (8) [M^+], 136 (100) [M^+ - PhCHOCH$_3$], 121 (12) [PhCHOCH$_3^+$]. CI (NH$_3$) *m/z* (%): 258 (100) [MH$^+$]. C$_{16}$H$_{19}$NO$_2$ (257.3).

(E)-Methyl 3-[(p-methoxyphenyl)-(2'-methoxy-2'-phenylethyl)amino]acrylate (25h). The conversion of aziridine **4** with methyl propiolate in methanol afforded **25h** as a yellow oil in 80 % yield. As a side product **26b** was isolated in yields of 8 %. **^{1}H NMR** (CDCl$_3$): δ = 3.21 (s, 3 H, CH-OC$\underline{H}_3$), 3.62 (dd, J = 4.0, 14.6 Hz, 1 H, 1'-H$_a$), 3.68 (s, 3 H, CO$_2$C$\underline{H}_3$), 3.78 (dd, J = 8.6, 14.4 Hz, 1 H, 1'-H$_b$), 3.81 (s, 3 H, Ar-OC$\underline{H}_3$), 4.45 (br, d, J = 4.9 Hz, 1 H, 2'-H), 4.81 (br, d, J = 12.3 Hz, 1 H, 3-H), 6.86 (d, J = 9.1 Hz, 2 H, 3''-H), 7.11 (d, J = 9.1 Hz, 2 H, 2''-H), 7.26-7.39 (m, 5 H, 2''',3''',4'''-H), 7.74 (d, J = 13.2 Hz, 1 H, 2-H). **^{13}C NMR** (CDCl$_3$): δ = 50.68 (CO$_2\underline{C}$H$_3$), 55.50 (2 O$\underline{C}$H$_3$), 57.02 (C-1'), 80.17 (C-2'), 88.37 (C-2), 114.71 (C-3''), 126.72 (C-2''), 126.77 (C-1''), 128.32 (C-4'''), 128.75 (C-2''',3'''), 139.06 (C-1'''), 150.53 (C-3), 157.51 (C-4''), 169.85 (C-1). **IR** (kap.): $\tilde{\nu}$ = 3031 cm^{-1}, 2932, 1682, 1614, 1514, 1441, 1107. **GC-MS** *m/z* (%): 341 (1) [M^+], 310 (5) [M^+ - OCH$_3$], 220 (100) [M^+ - PhCHOCH$_3$], 190 (18), 134 (23), 121 (17) [PhCHOCH$_3^+$], 91 (16), 77 (28), 45 (30). CI (NH$_3$) *m/z* (%): 342 (100) [MH$^+$]. C$_{20}$H$_{23}$NO$_4$ (341.4).

Dimethyl 2-[(p-cyanophenyl)-(2'-methoxy-2'-phenylethyl)amino]maleate (25i). The conversion of aziridine **5** with DMAD in methanol afforded **25i** as a yellow oil in 42 % yield. As a side product **26c** was isolated in yields of 18 %. **^{1}H NMR** ($CDCl_3$): δ = 3.03 (s, 3 H, $OC\underline{H}_3$), 3.61 (s, 3 H, $OC\underline{H}_3$), 3.72 (s, 3 H, $OC\underline{H}_3$), 3.74 (dd, *J* = 4.5, 7.5 Hz, 2 H, 1'-H), 4.39 (dd, *J* = 4.2, 7.3 Hz, 1 H, 2'-H), 6.71 (d, *J* = 9.0 Hz, 2 H, 2''-H), 6.74 (s, 1 H, 3-H), 7.29-7.33 (m, 5 H, $H_{arom.}$), 7.42 (d, *J* = 9.0 Hz, 2 H, 3''-H). **^{13}C NMR** ($CDCl_3$): δ = 52.02, 53.13 ($CO_2\underline{C}H_3$), 56.50 ($O\underline{C}H_3$), 59.23 (C-1'), 82.49 (C-2'), 101.83 (C-4''), 114.89 (C-3), 119.30 ($\underline{C}N$), 122.03, 126.54, 128.44, 128.84, 133.44 ($\underline{C}H_{arom.}$), 138.74 (C-1'''), 144.61 (C-1''), 150.40 (C-2), 164.01 (C-4/1), 164.60 (C-1/4). **IR** (kap.): $\tilde{\nu}$ = 2951 cm^{-1}, 2218, 1732, 1603, 1513, 1435, 1392, 1336, 1258, 1174, 1105, 1054, 1022, 825, 784, 760, 733, 703. **GC-MS** *m/z* (%): 394 (3) [M^+], 363 (3) [M^+ - OCH_3], 273 (100) [M^+ - Ph-CH-OCH_3], 169 (13), 121 (53) [Ph-CH-OCH_3^+], 77 (12). $C_{22}H_{22}N_2O_5$ (394.4).

(p-Cyanophenyl)-(2-methoxy-2-phenylethyl)amine (26c). **^{1}H NMR** ($CDCl_3$): δ = 3.28 (s, 3 H, $OC\underline{H}_3$), 3.32 (dd, *J* = 4.5, 7.7 Hz, 2 H, 1-H), 4.37 (dd, *J* = 5.1, 7.5 Hz, 1 H, 2-H), 6.56 (dm, *J* = 8.9 Hz, 2 H, 2'-H), 7.30-7.45 (m, 7 H, $H_{arom.}$). **^{13}C NMR** ($CDCl_3$): δ = 49.62 (C-1), 56.89 ($O\underline{C}H_3$), 81.82 (C-2), 98.88 ($\underline{C}N$), 112.48 (C-2'), 120.44 (C-4'), 126.68 (C-2''), 128.44 (C-4''), 128.77 (C-3''), 133.67 (C-3'), 138.96 (C-1''), 151.13 (C-1'). **IR** (kap.): $\tilde{\nu}$ = 3372 cm^{-1}, 2932, 2211, 1606, 1525, 1454, 1338, 1173, 1110, 824, 763, 702, 545. **GC-MS** *m/z* (%): 252 (7) [M^+], 131 (29), 121 (100) [Ph-CH-OCH_3^+], 77 (13). CI (*Iso*butane) *m/z* (%): 253 (100) [MH^+]. $C_{16}H_{16}N_2O$ (252.3).

(E)-Methyl 3-[(p-cyanophenyl)-(2'-methoxy-2'-phenylethyl)amino]acrylate (25k). On the conversion of aziridine **5** with methyl propiolate in methanol **25i** was afforded only as a side product. It was identified by the GC-MS spectrum. As main product **26c** was detected. **GC-MS** *m/z* (%): 336 (4) [M^+], 305 (4) [M^+ - OCH_3], 215 (40), 121 (100) [$PhCHOCH_3^+$], 91 (9), 77 (13). CI (*Iso*butane) *m/z* (%): 337 (100) [MH^+]. $C_{20}H_{20}N_2O_3$ (336.4).

(E)-Methyl 3-[butyl-(2'-hydroxy-2'-phenylethyl)amino]acrylate (25l). 2.016 g (24 mmol) methyl propiolate and 90 mL water were added to 1.4 g (8 mmol) aziridine **1** dissolved in 90 mL acetonitrile. After 5 d the organic layer was extracted with pentane and dried over magnesium sulfate. The solvent was removed and the product was purified on silica gel with 20% ethyl acetate/cyclohexane. **25l** was afforded in yields of 18 % as a yellow oil. **^{1}H NMR** ($CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3 H, 4''-H), 1.26 (sex., *J* = 7.3 Hz, 2 H, 3''-H), 1.51 (m, 2 H, 2''-H), 2.55 (br, 1 H, OH), 3.03 (m, 1 H, 1''-H_a), 3.18 (m, 1 H, 1''-H_b), 3.28 (dd, *J* = 4.5, 14.3 Hz, 1 H, 1'-H_a), 3.35 (dd, *J* = 8.0, 14.4 Hz, 1 H, 1'-H_b), 3.65 (s, 3 H, $CO_2C\underline{H}_3$), 4.64 (d, *J* = 13.2 Hz, 1 H, 2-H), 4.93 (br, 1 H, 2'-H), 7.28-7.38 (m, 5 H, $H_{arom.}$), 7.48 (d, *J* = 13.2 Hz, 1 H, 3-H). **^{13}C NMR** ($CDCl_3$): δ = 13.71 (C-4''), 19.96 (C-3''), 29.53 (C-2''), 50.44 ($CO_2\underline{C}H_3$), 52.75 (C-1'/1''), 59.45 (C-1''/1'), 71.84 (C-2/2'), 84.21 (C-2'/2), 125.82 (2 $\underline{C}H_{arom.}$), 128.02 ($\underline{C}H_{arom.}$), 128.58 (2 $\underline{C}H_{arom.}$), 141.70 ($C_{arom.}$), 152.15 (C-3), 170.20 (C-1). **IR** (kap.): $\tilde{\nu}$ = 3408 cm^{-1}, 2956, 2872, 1672, 1614, 1423, 1360, 1257, 1152, 1113, 1060, 788, 701. **GC-MS** *m/z* (%): 246 (12) [M^+ -OCH_3], 204 (15), 176 (11), 170 (68) [M^+ - PhCHOH], 158 (21), 128 (100), 105 (48), 98 (38), 91 (11), 82 (47), 77 (76), 70 (10), 51 (32), 41 (28). $C_{16}H_{23}NO_3$ (277.4).

(E)-Methyl 3-[butyl-(1',2'-diphenyl-2'-hydroxyethyl)amino]acrylate (25m). 2.016 g (24 mmol) methyl propiolate were added to 2 g (8 mmol) aziridine **2** dissolved in a mixture of 90 mL acetonitrile and 10 mL water. After 4 d the solvent was removed and the product was purified on silica gel with 50% diethyl ether/pentane. **25m** was isolated in yields of 29 % as a yellow oil. **^{1}H NMR** ($CDCl_3$): δ = 0.74 (t, *J* = 7.6 Hz,

3 H, 4'-H), 0.94-1.10 (m, 2 H, 3'-H), 1.15-1.35 (m, 2 H, 2'-H), 2.25 (br, s, 1 H, $O\underline{H}$), 2.60-2.90 (m, 2 H, 1'-H), 3.62 (s, 3 H, $CO_2C\underline{H}_3$), 4.34 (d, *J* = 8.5 Hz, 1 H, 1''-H), 4.45 (d, *J* = 13.1 Hz, 1 H, 2-H), 5.27 (d, *J* = 8.5 Hz, 1 H, 2''-H), 7.29-7.40 (m, 10 H, $H_{arom.}$), 7.67 (d, *J* = 13.0 Hz, 1 H, 3-H). ^{13}**C NMR** ($CDCl_3$): δ = 13.62 (C-4'), 19.99 (C-3'), 27.94 (C-2'), 49.71 (C-1'), 50.47 ($CO_2\underline{C}H_3$), 73.16 (C-2''), 74.13 (C-2), 84.39 (C-1''), 126.78, 128.30, 128.33, 128.47, 128,52, 128.73 ($\underline{C}H_{arom.}$), 137.01, 141.07 ($C_{arom.}$), 149.80 (C-3), 170.19 (C-1). **IR** (kap.): $\tilde{\nu}$ = 3406 cm^{-1}, 2956, 2236, 1682, 1614, 1496, 1454, 1360, 1250, 1151, 1096, 791, 756, 701, 606. **GC-MS** *m/z* (%): 335 (6) [M^+ - H_2O], 280 (16), 247 (78) [M^+-PhCHO], 246 (33) [M^{+} - PhCHOH], 204 (33), 188 (21), 174 (100) [M^+ - Ph - OH - CH=$CHCO_2CH_3$], 158 (16), 132 (32), 117 (22), 106 (49) [$PhCHO^+$], 91 (72), 77 (59). CI (*Iso*butane) *m/z* (%): 354 (100) [MH^+]. $C_{22}H_{27}NO_3$ (353.5).

Thermal conversion of aziridine 6 with DMAD in acetonitrile

852 mg (6 mmol) DMAD were added to 200 mg (1 mmol) aziridine **6** dissolved in 50 mL acetonitrile. After 24 h refluxing the solvent was removed and the products were separated by HPLC with 25 % ethyl acetate/cyclohexane. **30** and **31** were isolated in yields of 4 % and 7 % as yellow oils.

Dimethyl 1-butyl-4-(p-cyanophenyl)-4,5-dihydro-1H-pyrrole-2,3-dicarboxylate (30). ^{1}**H NMR** ($CDCl_3$) δ = 0.84 (t, *J* = 7.3 Hz, 3 H, 4'-H), 1.15 (sex, *J* = 7.3 Hz, 2 H, 3'-H), 1.30-1.43 (m, 2 H, 2'-H), 2.50 (ddd, *J* = 5.7, 9.7, 15.1 Hz, 1 H, 1'-H_a), 2.94 (ddd, *J* = 5.7, 9.8, 15.1 Hz, 1 H, 1'-H_b), 3.58 (dd, *J* = 8.6, 15.1 Hz, 1 H, 5-H_a), 3.66 (s, 3 H, $CO_2C\underline{H}_3$), 3.86 (dd, *J* = 6.1, 15.1 Hz, 1 H, 5-H_b), 4.66 (s, 3 H, $CO_2C\underline{H}_3$), 5.17 (dd, *J* = 6.1, 8.6 Hz, 1 H, 4-H), 7.56 (dm, *J* = 8.4 Hz, 2 H, 2''-H), 7.66 (dm, *J* = 8.4 Hz, 2 H, 3''-H). ^{13}**C NMR** ($CDCl_3$): δ = 13.64 (C-4'), 19.79 (C-3'), 26.88 (C-2'), 51.06 ($CO_2\underline{C}H_3$), 52.33 (C-5), 53.18 ($CO_2\underline{C}H_3$), 58.19 (C-1'), 86.59 (C-4), 109.56 (C-4''), 112.85 ($\underline{C}N$), 118.09 (C-3), 128.80 (C-2''), 132.66 (C-3''), 144.01 (C-1''), 153.18 (C-2), 165.64, 167.69 ($\underline{C}O_2CH_3$). **IR** (KBr, CH_2Cl_2): $\tilde{\nu}$ = 2229 cm^{-1}, 1741, 1697, 1577, 1438, 1417, 1254, 1150. **GC-MS** *m/z* (%): 342 (31) [M^+], 311 (15) [M^+ - OCH_3], 299 (100) [M^+ - C_3H_7], 283 (12) [M^+ - CO_2CH_3], 140 (13). CI (*Iso*butane) *m/z* (%): 343 (100) [MH^+]. $C_{19}H_{22}N_2O_4$ (342.4).

Teteramethyl 1-butyl-1H-pyrrole-2,3,4,5-tetracarboxylate (31). ^{1}**H NMR** ($CDCl_3$): δ = 0.92 (t, *J* = 7.4 Hz, 3 H, 4'-H), 1.23-1.43 (m, 2 H, 3'-H), 1.63-1.79 (m, 2 H, 2'-H), 3.86 (s, 6 H, $CO_2C\underline{H}_3$), 3.89 (s, 6 H, $CO_2C\underline{H}_3$), 4.39 (m, 2 H, 1'-H). ^{13}**C NMR** ($CDCl_3$): δ = 17.53 (C-4'), 19.74 (C-3'), 33.46 (C-2'), 47.63 (C-1'), 52.40, 52.65 ($CO_2\underline{C}H_3$), 119.76 (C-3), 133.11 (C-2), 160.60, 163.84 ($\underline{C}O_2CH_3$). **IR** (kap.): $\tilde{\nu}$ = 2956 cm^{-1}, 1724, 1507, 1456, 1314, 1242, 1120. **GC-MS** *m/z* (%): 355 (17) [M^+], 324 (36) [M^+ - OCH_3], 313 (17), 296 (63) [M^+ - CO_2CH_3], 254 (55), 236 (100) [M^+ + H -2 x CO_2CH_3], 206 (30), 178 (19), 93 (10). CI (*Iso*butane) *m/z* (%): 356 (100) [MH^+]. $C_{16}H_{21}NO_8$ (355.3).

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