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Reactions of Aza-*ortho*-xylylenes Generated from 2,1-Benzisothiazoline 2,2-Dioxides.

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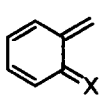
Abstract: Thermal extrusion of SO_2 from 2,1-benzisothiazoline 2,2-dioxides **2** leads to aza-*ortho*-xylylenes **3**, which depending on the substituents undergo various transformations. Aza-*ortho*-xylylenes substituted at the position 4, 5, and 6 gave Diels-Alder reactions with maleic acid derivatives **4** leading to *cis*-1,2,3,4-tetrahydroquinoline 2,3-dicarboxylic acid derivatives **5** in high yields. 7-Substituted derivatives underwent [1,5] hydrogen shift leading to *ortho*-toluidine derivatives **9** and **10**. Aza-*ortho*-xylylenes generated from *N*-(4-pentenyl) and *N*-(5-hexenyl) derivatives **11** gave products of intramolecular Diels-Alder reaction.

INTRODUCTION.

Cycloadditions [4+2] known as the Diels-Alder reactions are important tools used for the synthesis of six-membered carbo- and heterocyclic rings.[1,2] Amongst a wide variety of dienes entering this reaction, peculiar ones are *ortho*-xylylenes (**1a**) used as building blocks for the synthesis of condensed carbocyclic systems. There are a few methods used for generation of these reactive species, one of the most convenient consists of the thermal extrusion of SO_2 from 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides.[3]



1a X = CH_2
1b X = N-R

Contrary to *ortho*-xylylenes **1a**, their aza-analogues **1b**, which are potential building blocks for the synthesis of condensed heterocycles, focused much less attention.[4] There are a few methods enabling generation of these reactive species, for example, flash vacuum thermolysis (FVT) of *ortho*-aminobenzyl alcohols,[5,6] thermal ring-cleavage of 2-azidoindoles,[7] fluoride ion induced 1,4-elimination in *ortho*-(α-trimethylsilylalkyl)benzyltrimethylammonium halides,[8] or photochemical extrusion of SO_2 from 2,1-benzisothiazoline 2,2-dioxides[9] - the heteroanalogues of 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides.

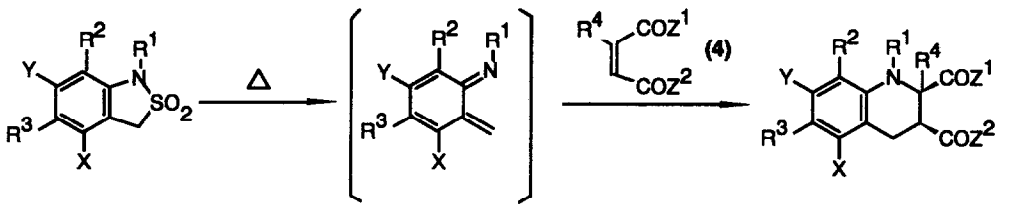
In our previous paper[10] the preliminary results of our studies on the cycloaddition of aza-*ortho*-xylylenes generated from nitro derivatives of 2,1-benzisothiazoline 2,2-dioxides (benzosultams) were presented. Now we would like to present the full account concerning cycloadditions and some other reactions of aza-*ortho*-xylylenes generated from benzosultams.

RESULTS AND DISCUSSION.

As precursors of aza-*ortho*-xylylenes we have used nitro derivatives of 2,1-benzisothiazoline 2,2-dioxides **2** which are easily accessible via vicarious nucleophilic substitution of hydrogen[11,12] or oxidative intramolecular substitution of hydrogen in *meta*-nitromethanesulfonanilides.[13]

Thus, when **2** are refluxed in 1,2,4-trichlorobenzene (b.p. 215°C) with an excess (1.5 mol) of maleic acid derivative **4**, such as dimethyl maleate, *N*-phenylmaleinimide and 2-methyl-*N*-phenylmaleinimide the 1,2,3,4-tetrahydroquinoline 2,3-dicarboxylic acid derivatives **5** are formed in high yields (**Scheme 1**).

SCHEME 1.



2 **3** **5**

	R^1	R^2	R^3	X	Y	R^4	Z^1	Z^2	Yield (%)
a	CH_3	H	H	NO_2	H	H	>N-C_6H_5		94
b	CH_3	H	H	NO_2	H	H	OCH_3	OCH_3	25
c	CH_3	H	H	NO_2	H	CH_3	>N-C_6H_5		63
d	CH_3	H	CH_3	NO_2	H	H	OCH_3	OCH_3	75
e	CH_3	H	CH_3	NO_2	H	H	>N-C_6H_5		80
f	$CH_2C_6H_5$	H	CH_3	NO_2	H	H	>N-C_6H_5		89
g	CH_3	H	CH_3	NO_2	H	CH_3	>N-C_6H_5		72
h	CH_3	H	Cl	NO_2	H	H	>N-C_6H_5		68
i	CH_3	H	F	NO_2	H	H	>N-C_6H_5		80
j	CH_3	F	H	NO_2	H	H	>N-C_6H_5		43[a)]
k	CH_3	H	CH_3	H	NO_2	H	>N-C_6H_5		63
l	CH_3	H	OCH_3	H	NO_2	H	OCH_3	OCH_3	75
m	CH_3	H	H	H	NO_2	CH_3	>N-C_6H_5		28
n	-$(CH_2)_3$-		H	NO_2	H	H	>N-C_6H_5		69
o	-$(CH_2)_3$-		H	NO_2	H	CH_3	>N-C_6H_5		57
p	-$(CH_2)_2$-O-		H	NO_2	H	H	>N-C_6H_5		82

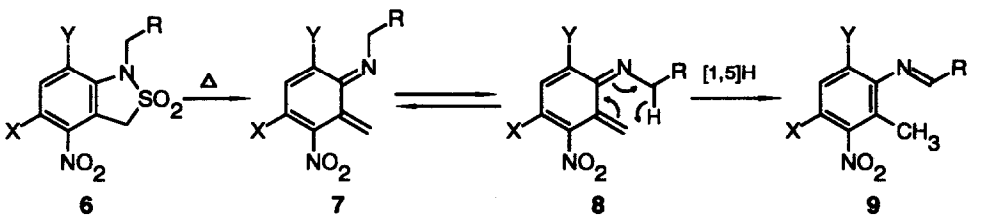
[a)] As additional product 6-fluoro-2-methyl-3-nitroaniline (**10**: X = H, Y = F; 15%) was isolated.

In the cycloaddition of aza-*ortho*-xylylenes with 2-methyl-*N*-phenylmaleinimide two isomeric cycloadducts might be formed, however the only isolated products were 2-methyl-1,2,3,4-tetrahydroquinoline derivatives. In

these instances the observed reaction course is in accord with the known *ortho-para* directing effect in the Diels-Alder cycloaddition.[14]

No expected cycloaddition products were obtained in the reactions of the benzosultams with other dienophiles: dimethyl fumarate, *N*-phenyl-2,3-dimethylmaleinimide, dimethyl acetylenedicarboxylate, *cis*- and *trans*-bis(phenylsulfonyl)ethylenes and terminal alkenes. Depending on the dienophile, different reaction courses were observed. The reactions of benzosultams with dimethyl acetylenedicarboxylate and also with *cis*- and *trans*-bis(phenylsulfonyl)ethylenes led to complex mixtures of products. The formation of cycloadducts in these instances can not be excluded, but probably these products decomposed under the reaction conditions. The reactions with less reactive dienophiles: dimethyl fumarate, 2,3-dimethyl-*N*-phenylmaleinimide and 1-hexadecene took another course. In these instances the dienophile was intact and the products of the transformation of the intermediate aza-*ortho*-xylylenes were isolated. For example, in the attempted reaction of **2e** with dimethyl fumarate, the major component of the reaction mixture was 2,6-dimethyl-3-nitroaniline (**10a**). Its formation was the result of a [1,5] hydrogen shift in the intermediate aza-*ortho*-xylylene, followed by a hydrolysis of the intermediate methyleneimine (**Scheme 2**). Such [1,5] hydrogen shift has been observed earlier in aza-*ortho*-xylylenes generated by means of FVT from *ortho*-aminobenzyl alcohol derivatives.[5] In the similar reaction of the *N*-benzyl derivatives **6c,d**, the Schiff bases **9c,d** were more stable and could be isolated and identified.

SCHEME 2.



6-10	X	Y	R
a	H	CH_3	H
b	H	Cl	H
c	H	CH_3	C_6H_5
d	CH_3	H	C_6H_5

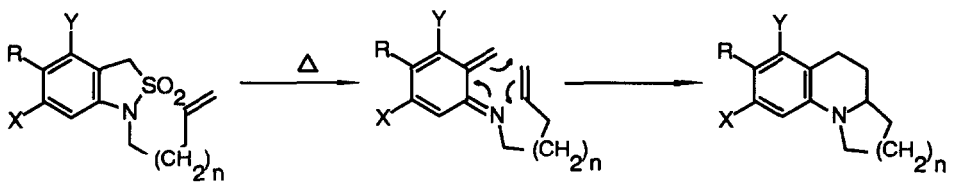
Also in the attempted reactions of 1,7-dimethyl-4-nitrobenzosultam (**6a**) and 7-chloro-1-methyl-4-nitrobenzosultam (**6b**) with *N*-phenylmaleinimide no cycloaddition products were formed, instead *ortho*-toluidine derivatives **10a** and **10b** were isolated. In the reaction of 1-benzyl-7-methyl-4-nitrobenzosultam (**6c**) with *N*-phenylmaleinimide the reaction course was similar and stable *N*-benzylidene-2,6-dimethyl-3-nitroaniline (**9c**) was obtained. It is worthy of mention that the isomeric 5-methyl derivative **2f** formed the corresponding cycloadduct **5f** in high yield, but gave however, the Schiff base **9d** when heated in the absence of dienophile.

From this observation one can conclude that the primarily formed aza-*ortho*-xylylene has the *E* configuration, and the formation of Schiff base is the result of the *E*/*Z* isomerisation, followed by the [1,5] hydrogen shift. The question arises, how the substituents in the benzosultam influence the reaction course. From the results obtained one can see that, there is practically no influence of substituents (Cl, F, CH_3, OCH_3, NO_2) in the positions 4, 5, and 6. In these instances the expected cycloaddition products were formed in good yields. On the other hand this reaction seems to be sensitive to a substituent in the position 7. When this position is occupied by a substituent such as a methyl group or chlorine atom, a steric interaction of these substituents with that on the exocyclic C=N bond forces the *Z* configuration **8** enabling [1,5] hydrogen shift leading to isomeric Schiff bases **9**. To confirm the hypothesis of the steric interaction of substituents at the positions 1 and 7 we constructed the derivative **2j** in which the position 7 was occupied by a small fluorine atom. In this case the steric interactions were diminished and both of these processes- cycloaddition to *N*-phenylmaleinimide leading to 1,2,3,4-tetrahydroquinoline derivative **5j** (43%) and [1,5] hydrogen shift leading, after hydrolysis, to 6-fluoro-2-methyl-3-nitroaniline (**10**, X = H, Y = F, 15%)- took place.

Additional support for this hypothesis came from the reactions of aza-*ortho*-xylylenes generated from tricyclic sultams **2n,o,p**. Thermolysis of these compounds produce aza-*ortho*-xylylenes with *E*-configuration fixed by the additional ring, therefore the [1,5] hydrogen shift was hindered and the expected cycloadducts **5n,o,p** were formed in good yields.

Contrary to unsuccesful intermolecular cycloadditions of aza-*ortho*-xylylenes to alkenes the intramolecular reactions of N-(4-pentenyl)- and N-(5-hexenyl)- derivatives **11** lead to the expected hexahydropyrrolo[1,2-*a*]quinoline (**13**, n=1) and hexahydro-1*H*-benzo[*c*]quinolizine (**13**, n=2) derivatives in good yields (**Scheme 3**).

SCHEME 3.



11 **12** **13**

11,12,13	R	X	Y	n
a	H	H	NO_2	1
b	H	NO_2	H	1
c	Cl	H	NO_2	1
d	H	H	NO_2	2
e	Cl	H	NO_2	2

This reaction requires the *E* configuration on the imine double bond and this is the configuration of the primarily formed aza-*ortho*-xylylene **12**. From these results can be drawn the conclusion that the isomerisation

under these conditions proceeds at a low rate. This is in contrast with described earlier reactions of *N*-(5-hexenyl)- and *N*(4-pentenyl)azaxylylenes generated by FVT of the corresponding *ortho*-aminobenzyl alcohols,[5] in which such isomerisation and consecutive [1,5] hydrogen shift was predominant leading to the Schiff bases. The above mentioned side reaction, being a result of *E/Z* isomerisation followed by [1,5] hydrogen shift, are secondary processes, occuring when the rate of cycloaddition is diminished.

The present study shows that cycloaddition [4+2] of aza-*ortho*-xylylenes generated *via* thermal extrusion of SO_2 from 2,1-benzisothiazoline 2,2-dioxide derivatives is valuable method of synthesis of 1,2,3,4-tetrahydroquinoline derivatives.

EXPERIMENTAL.

Melting points are uncorrected. ^{1}H NMR spectra were obtained on Bruker AMX (500 MHz) and Varian Gemini (200 MHz) instruments with TMS as internal standard. Coupling constants *J* are given in Hz. Mass spectra (electron impact, 70 eV) were obtained on AMD 604 (AMD Intectra GmbH, Germany) instrument. Starting benzosultams were obtained analogously to described in the literature.[12,13]

General Procedure:

The mixture of **1** (1 mmol) and maleic acid derivative **3** (1.5 mmol) in 1,2,4-trichlorobenzene (2 mL) is refluxed until the starting material **1** disappeared (TLC control: silica gel, hexane/ethyl acetate 4:1). Then the reaction mixture was subjected to column chromatography (silica gel 60, 200-300 mesh, 2 x 20 cm). Elution of trichlorobenzene was performed with n-hexane/ethyl acetate (50:1), and then with n-hexane/ethyl acetate (2:1) the product was isolated and recrystallized. The following products were obtained:

***cis*-3a,4,9,9a-Tetrahydro-4-methyl-8-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5a).** Yield 94%. M.p. 178-179°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 3.02, 3.67, 3.72, 4.35 (AMNX,[15] 1H, *J*= 15.3, 9.3, 6.1, 4.1); 3.28 (s, 3H); 6.98-7.07 (m, 3H); 7.28-7.45 (m, 5H). MS *m/z* (%): 337 (M^+, 57), 320 (8), 307 (11), 292 (5), 216 (8), 190 (17), 173 (65), 159 (13), 143 (100). Elemental analysis for $C_{18}H_{15}N_3O_4$ (337.33): calcd. C 64.09%, H 4.48%, N 12.46%; found. C 64.28%, H 4.44%, N 12.45%.

***cis*-1,2,3,4-Tetrahydro-1-methyl-5-nitroquinoline-2,3-dicarboxylic Acid Dimethyl Ester (5b).** Yield 25%. M.p. 90-92°C (from MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.05-3.11 (m, 1H); 3.09 (s, 3H); 3.19 - 3.26 (m, 2H); 3.69 (s, 3H); 3.80 (s, 3H); 4.50 (d, 1H, *J*= 4.2); 6.87, 7.23, 7.24 (ABX, 3H, *J*= 8.4, 8.0, 2.2). MS *m/z* (%): 308 (M^+, 13), 291 (2), 278 (3), 249 (100), 228 (7), 219 (10), 217 (12), 203 (6), 189 (9), 173 (27), 159 (8), 143 (32), 117 (7). Elemental analysis for $C_{14}H_{16}N_2O_6$ (308.26): calcd. C 54.55%, H 5.23%, N 9.09%; found C 54.88%, H 5.09%, N 9.40%.

***cis*-3a,4,9,9a-Tetrahydro-3a,4-dimethyl-2-phenyl-8-nitro-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5c).** Yield 63%. M.p. 211-212°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.81 (s, 3H); 3.04 (dd, 1H, *J*= 15.5, 5.2); 3.10 (s, 3H); 3.31 (dd, 1H, *J*= 5.2, 4.0); 3.79 (dd, 1H, *J*= 15.5, 4.0); 6.96-7.08 (m, 3H); 7.29-7.45 (m, 5H). MS *m/z* (%): 351 (M^+, 55), 336 (12), 321 (10), 306 (5), 230 (14), 202 (23), 187 (99), 173 (12), 157 (100), 143 (11).Elemental analysis for $C_{19}H_{17}N_3O_4$ (351.34): calcd. C 64.95%, H 4.87%, N 11.96%; found C

64.70%, H 4.65%, N 11.54%.

***cis*-1,2,3,4-Tetrahydro-1,6-dimethyl-5-nitro-2,3-quinolinedicarboxylic Acid Dimethyl Ester (5d).** Yield 75%. M.p. 111-113°C (from MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 2.18 (s, 3H); 2.86, 3.00, 3.10, 4.46 (AMNX,[15] 4H, *J*= 17.1, 13.1, 6.2, 4.1); 3.06 (s, 3H); 3.66 (s, 3H); 3.77 (s, 3H); 6.65 (d, 1H, *J*= 8.5); 7.03 (d, 1H, *J*= 8.5). MS *m/z* (%): 322 (M^+, 15), 305 (0.4), 292 (0.6), 276 (0.5), 263 (100), 246 (4), 231 (4), 217 (6), 203 (3), 187 (17), 171 (6). Elemental analysis for $C_{15}H_{18}N_2O_6$ (322.32): calcd. C 55.90%, H 5.63%, N 8.69%; found C 55.93%, H 5.46%, N 8.59%.

***cis*-3a,4,9,9a-Tetrahydro-4,7-dimethyl-8-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5e).** Yield 80%. M.p. 213°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.23 (s, 3H); 2.85 (dd, 1H, *J*= 14.9, 6.4); 3.13 (dd, 1H, *J*= 14.9, 4.0); 3.24 (s, 3H); 3.64 (ddd, 1H, *J*= 9.4, 6.4, 4.0); 4.30 (d, 1H, *J*= 9.4); 6.82 (d, 1H, *J*= 8.4); 7.01-7.08 (m, 2H); 7.12 (d, 1H, *J*= 8.4); 7.30- 7.48 (m, 3H). MS *m/z* (%): 351 (M^+, 100), 334 (18), 321 (4), 306 (7), 231 (7), 202 (14), 187 (66), 174 (10), 157 (57), 142 (15). Elemental analysis for $C_{19}H_{17}N_3O_4$ (351.34): calcd. C 64.95%, H 4.87%, N 11.96%; found C 64.61%, H 4.84%, N 11.41%.

***cis*-3a,4,9,9a-Tetrahydro-7-methyl-8-nitro-2-phenyl-4-(phenylmethyl)-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5f).** Yield 89%. M.p. 183-184°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.24 (s, 3H); 2.88 (dd, 1H, *J*= 14.7, 6.7); 3.23 (dd, 1H, *J*= 14.7, 2.8); 3.64 (ddd, *J*= 9.6, 6.7, 2.8); 4.31 (d, 1H, *J*= 9.6); 4.78 (s, 2H); 6.90 (d, 1H, *J*= 8.3); 6.97-7.04 (m, 2H); 7.09 (d, 1H, *J*= 8.3); 7.29-7.49 (m, 8H). MS *m/z* (%): 427 (M^+, 46), 410 (4), 397 (7), 392 (8), 381 (3), 263 (12), 237 (20), 142 (8), 91 (100). Elemental analysis for $C_{25}H_{21}N_3O_4$ (427.46): calcd. C 70.25%, H 4.95%, N 9.83%; found C 70.42%, H 4.96%, N 9.89%.

***cis*-3a,4,9,9a-Tetrahydro-3a,4,7-trimethyl-6-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5g).** Yield 72%. M.p. 240-242°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.77 (s, 3H); 2.24 (s, 3H); 3.07 (s, 3H); 2.86, 3.20, 3.27 (ABX, 3H, *J*= 14.9, 4.9, 3.9); 6.82 (d, 1H, *J*= 8.4); 6.99-7.06 (m, 2H); 7.11 (d, 1H, *J*= 8.4); 7.30-7.44 (m, 3H). MS *m/z* (%): 365 (M^+, 66), 350 (12), 335 (4), 320 (3), 273 (2), 245 (4), 216 (23), 201 (100), 187 (14), 171 (72), 156 (23). Elemental analysis for $C_{20}H_{19}N_3O_4$ (365.36): calcd. C 65.74%, H 5.24%, N 11.50%; found C 65.85%, H 4.99%, N 11.53%.

***cis*-7-Chloro-3a,4,9,9a-tetrahydro-4-methyl-8-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5h).** Yield 68%. M.p. 194-195°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.84 (dd, 1H, *J*= 14.7, 6.4); 3.11 (dd, 1H, *J*= 14.7, 4.2);3.26 (s, 3H); 3.66 (ddd, 1H, *J*= 9.5, 6.4, 4.2); 4.34 (d, 1H, *J*= 9.5); 6.84 (d, 1H, *J*= 8.7); 7.05-7.13 (m, 2H); 7.29-7.50 (m, 4H). MS *m/z* (%): 371 (M^+, 70), 354 (5), 341 (11), 326 (4), 251 (4), 222 (12), 207 (57), 194 (13), 177 (100), 142 (41). Elemental analysis for $C_{18}H_{14}ClN_3O_4$ (371.78): calcd. C 58.15%, H 3.80%, N 11.30%; found C 58.09%, H 3.78%, N 11.06%.

***cis*-7-Fluoro-3a,4,9,9a-tetrahydro-4-methyl-8-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5i).** Yield 80%. M.p. 173-174°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.90 (dd, 1H, *J*= 15.2, 6.4); 3.26 (s, 3H); 3.30 (dd, 1H, *J*= 15.2, 3.9); 3.70 (ddd, 1H, *J*= 9.6, 6.4, 3.9); 4.33 (d, 1H, *J*= 9.6); 6.89 (dd, 1H, *J*= 9.0, 4.2); 7.02- 7.08 (m, 2H); 7.15 (d, 1H, *J*= 9.0); 7.33- 7.46 (m, 3H). MS *m/z* (%): 355 (M^+, 59), 338 (4), 325 (7), 310 (4), 235 (4), 207 (8), 191 (52), 177 (12), 161 (100), 146 (8). Elemental analysis for $C_{18}H_{14}FN_3O_4$ (355.31): calcd. C 60.84%, H 3.96%, N 11.83%; found C 60.61%, H 3.83%, N 11.85%.

***cis*-5-Fluoro-3a,4,9,9a-tetrahydro-4-methyl-8-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5j).** Yield 43%. M.p. 185-187°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.84 (dd, 1H, *J*= 15.2, 6.0); 3.50 (d, 3H, *J*= 7.5, N-CH_3); 3.80 (ddd, 1H, *J*=9.6, 6.0, 2.8); 4.00 (ddd, 1H, *J*= 15.4, 2.8, 2.0); 4.28 (d, 1H, *J*= 9.6); 6.97-7.16 (m, 3H); 7.31-7.44 (m, 3H); 7.45 (dd, 1H, *J*= 9.1, 4.2). MS *m/z* (%): 355 (M^+, 43), 338 (7), 325 (20), 306 (5), 208 (10), 191 (57), 177 (23), 161 (100). Elemental analysis for $C_{18}H_{14}FN_3O_4$ (355.31): calcd. C 60.84%, H 3.96%, N 11.83%; found C 61.27%, H 3.74%, N 11.67%.

As a by-product **6-fluoro-2-methyl-3-nitroaniline (10, X = H, Y = F)** was formed. Yield 15%. M.p. 62-63°C (from *n*-hexane). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.33 (s, 3H); 3.95 (broad s, 2H); 6.95 (dd, 1H, *J*= 9.4, 9.0); 7.26 (dd, 1H, *J*= 9.0, 4.90). MS *m/z* (%): 170 (M^+, 98), 153 (100), 125 (23), 105 (15), 98 (56), 77 (50). Elemental analysis for $C_7H_7FN_2O_2$ (170.14): calcd. C 49.42%; H 4.15%; N 16.46%; found C 49.18%, H 4.29%, N 16.22%.

***cis*-3a,4,9,9a-Tetrahydro-4,7-dimethyl-6-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5k).** Yield 63%. M.p. 198-199°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.50 (s, 3H, CH_3); 2.97 (dd, 1H, *J*= 14.6, 6.5); 3.22 (dd, 1H, *J*= 14.6, 3.7); 3.26 (s, 3H); 3.70 (ddd, 1H, *J*= 3.7, 6.5, 9.3); 4.33 (d, 1H, *J*= 9.3); 6.98-7.10 (m, 3H); 7.31-7.50 (m, 4H). MS *m/z* (%): 351 (M^+, 91), 334 (23), 321 (15), 306 (15), 279 (3), 258 (3), 31 (4), 203 (100), 187 (11), 173 (18), 157 (42). Elemental analysis for $C_{19}H_{17}N_3O_4$ (351.36): calcd. C 64.95%, H 4.88%, N 11.96%; found C 65.07%, H 4.87%, N 11.82.

***cis*-1,2,3,4-Tetrahydro-6-methoxy-1-methyl-7-nitroquinoline-2,3-dicarboxylic Acid Dimethyl Ester (5l).** Yield 75%. M.p. 187-188°C (from MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.03 (s, 3H); 3.03, 3.16, 3.19, 4.45 (AMNX,[15] 4H, *J*= 16.6, 13.2, 5.5, 4.2); 3.66 (s, 3H); 3.80 (s, 3H); 3.88 (s, 3H); 6.80 (s, 1H); 7.16 (s, 1H). MS *m/z* (%): 338 (M^+, 15), 322 (1), 308 (5), 293 (3), 279 (100), 263 (3), 249 (11), 232 (9), 219 (20), 204 (5), 189 (4), 172 (7). Elemental analysis for $C_{15}H_{18}N_2O_7$ (338.31): calcd. C 53.25%, H 5.36%, N 8.28%; found C 52.97%, H 5.15%, N 8.02%.

3a,4,9,9a-Tetrahydro-3a,4-dimethyl-6-nitro-2-phenyl-1*H*-pyrrolo[3,4-*b*]quinoline-1,3(2*H*)-dione (5m). Yield 28%. M.p. 163-164°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.82 (s, 3H); 2.97, 3.34, 3.36 (ABX, 3H, *J*= 13.5, 6.2, 3.7); 3.14 (s, 3H); 6.96-7.02 (m, 2H); 7.26 (d, 1H, *J*= 8.2); 7.32-7.44 (m, 3H); 7.63 (d, 1H, *J*= 2.2); 7.73 (dd, 1H, *J*=8.0, 2.2). MS *m/z* (%): 351 (M^+, 97), 336 (16), 321 (8), 259 (13), 203 (100), 189 (81), 173 (13), 164 (21), 157 (47), 143 (26), 115 (12). Elemental analysis for $C_{19}H_{17}N_3O_4$ (351.34): calcd. C 64.95%, H 4.87%, N 11.96%; found C 64.71%, H 4.75%, N 11.74%.

2,3,7a,10a-Tetrahydro-6-nitro-9-phenyl-1*H*-benzo[*ij*]pyrrolo[3,4-*c*]quinolizine-8,10(7*H*,9*H*)-dione (5n). Yield 69%. M.p. 201-202°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.90-2.20 (m, 2H); 2.83 (t, 2H, *J*= 6.2); 3.25-3.37 (m, 2H); 3.40-3.58 (m, 2H); 4.17 (ddd, 1H, *J*=8.9, 7.6, 3.9); 4.29 (d, 1H, *J*= 8.9); 7.00 (d, 1H, *J*= 8.4); 7.14-7.50 (m, 6H). MS *m/z* (%): 363 (M^+, 11), 346 (2), 333 (8), 260 (100), 245 (20), 199 (11), 185 (8), 169 (13). Elemental analysis for $C_{20}H_{17}N_{34}$ (363.29): calcd. C 66.11%, H 4.72%, N 11.57%; found C 66.16%, H 4.79%, N 11.02%.

2,3,7a,10a-Tetrahydro-10a-methyl-6-nitro-9-phenyl-1*H*-benzo[*ij*]pyrrolo[3,4-*c*]quinolizine-8,10(7*H*,9*H*)-dione (5o). Yield 57%. M.p. 184-186°C (from EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.77 (s, 3H); 1.70-1.98 (m, 2H); 2.72- 2.82 (m, 2H); 2.94 (dd, 1H, *J*= 16.0, 5.2); 3.29 (dd, 1H, *J*= 5.2, 3.7); 3.35-3.50 (m, 2H); 3.81 (dd,

1H, *J*= 16.0, 3.7); 3.79-3.84 (m, 2H); 6.95 (d, 1H, *J*= 8.3); 7.08-7.11 (m, 2H); 7.27 (d, 1H, *J*= 8.3, 1H); 7.32-7.47 (m, 3H). MS *m/z* (%): 377 (M^+, 100), 360 (10), 344 (13), 314 (7), 228 (11), 213 (71), 197 (13), 173 (11). Elemental analysis for $C_{21}H_{19}N_3O_4$ (377.37): calcd. C 66.83%, H 5.07%, N 11.14%; found C 66.70%, H 4.69%, N 10.50%.

2,3,7a,10a-Tetrahydro-3-oxa-6-nitro-9-phenyl-1*H*-benzo[*ij*]pyrrolo[3,4-*c*]quinolizine-8,10(7*H*,9*H*)-dione (5p). Yield 82%. M.p. 160-161°C (from EtOH). ^1H NMR (200 MHz, $CDCl_3$): δ= 3.24-3.73 (m, 4H); 4.08-4.39 (m, 3H); 4.28 (d, 1H, *J*= 10.4); 6.83 (d, 1H, *J*= 9.0); 7.17-7.24 (m, 2H), 7.38-7.52 (m, 3H); 7.50 (d, 1H, *J*= 9.0). MS *m/z* (%): 365 (M^+, 60), 347 (24), 335 (15), 320 (7), 229 (4), 216 (4), 201 (60), 187 (9), 171 (100), 115 (14). Elemental analysis for $C_{19}H_{15}N_3O_5$ (365.33): calcd. C 62.24%, H 4.14%, N 11.51%; found C 62.36%, H 4.06%, N 11.56%.

***N*-Benzylidene-2,6-dimethyl-3-nitroaniline (9c).** Yield 48%. M.p. 79-80°C (from *n*-hexane). ^1H NMR (200 MHz, $CDCl_3$): δ= 2.19 (s, 3H); 2.30 (s, 3H); 7.17 (d, 1H, *J*= 8.4); 7.45-7.65 (m, 4H); 7.90-7.98 (m, 2H); 8.20 (s, 1H). MS *m/z* (%): 254 (M^+, 100), 237 (66), 220 (6), 207 (48), 193 (18), 177 (46), 160 (9), 131 (12). Elemental analysis for $C_{15}H_{14}N_2O_2$ (254.29): calcd. C 70.85%, H 5.55%, N 11.02%; found C 70.62%, H 5.31%, N 10.82%.

***N*-Benzylidene-2,4-dimethyl-3-nitroaniline (9d).** Yield 51%. M.p. 82-83°C (from *n*-hexane). ^1H NMR (200 MHz, $CDCl_3$): δ= 2.24 (s, 3H); 2.27 (s, 3H); 6.94 (d, 1H, *J*= 8.1); 7.06 (d, 1H, *J*= 8.1); 7.42-7.62 (m, 3H); 7.84-7.94 (m, 2H); 8.34 (s, 1H). MS *m/z* (%): 254 (M^+, 100), 237 (42), 220 (8), 207 (31), 193 (13), 177 (52), 160 (11), 131 (22). Elemental analysis for $C_{15}H_{14}N_2O_2$ (254.29): calcd. C 70.85%, H 5.55%, N 11.02%; found C 70.53%, H 5.26%, N 10.74%.

6-Chloro-2-methyl-3-nitroaniline (10a). Yield 56%. M.p 74-76°C (from *n*-hexane). ^1H NMR (200 MHz, $CDCl_3$): δ=2.31 (s, 3H); 4.36 (broad s, 2H); 7.15 (d, 1H, *J*= 8.7); 7.24 (d, 1H, *J*= 8.7). MS *m/z* (%): 186 (M^+, 80), 169 (58), 156 (4), 141 (23), 134 (19), 114 (46), 104 (43), 77 (100). Elemental analysis for $C_7H_7ClN_2O_2$ (186.60): calcd. C 45.06%, H 3.78%, N 15.01%; found C 45.24%, H 3.60%, N 14.81%.

2,6-Dimethyl-3-nitroaniline (10b). Yield 42%. M.p. 75-76°C (from *n*-hexane). ^1H NMR (200 MHz, $CDCl_3$): δ= 2.23 (s, 3H); 2.30 (s, 3H); 4.85 (broad s, 2H); 7.01 (d, 1H, *J*= 8.3); 7.17 (d, 1H, *J*= 8.3). MS *m/z* (%): 166 (M^+, 100), 149 (66), 121 (44), 118 (27), 104 (38), 94 (78), 91 (66), 77 (75). Elemental analysis for $C_8H_{10}N_2O_2$ (166.16): calcd. C 57.82%, H 6.06%, N 16.85; found C 57.99%, 6.18%, N 16.70%.

General Procedure for Intramolecular Cycloaddition:

N-(4-Pentenyl)- or *N*-(5-hexenyl)benzosultam **11** (100 mg) in 1,2,4-trichlorobenzene (1.5 mL) was refluxed until the starting material disappeared (usually 1 to 2 hr). The reaction was monitored by TLC (silica gel, hexane/ethyl acetate 4:1). Then the product was isolated as in the former procedure. The following products were obtained:

1,2,3,3a,4,5-Hexahydro-6-nitropyrrolo[1,2-*a*]quinoline (13a). Yield 44%. M.p. 92-93°C (from n-hexane). ^1H NMR (500 MHz, $CDCl_3$): δ= 1.25-1.35 (m, 1H); 1.50 (dddd, 1H, *J*= 12.1, 12.1, 10.3, 7.4); 1.90-2.01 (m, 1H); 2.10 (ddd, 1H, *J*= 12.8, 7.4, 7.3); 2.16-2.26 (m, 2H); 2.83-3.01 (m, 2H); 3.23 (ddd, 1H, *J*= 9.5, 9.5, 7.4); 3.38

(ddd, 1H, 9.1, 9.1, 1.7); 3.45 (dddd, 1H, *J*= 10.8, 10.8, 5.1, 3.0); 6.55 (d,1H, *J*= 8.1); 7.03 (dd, 1H, *J*= 8.0, 1.0); 7.12 (dd, 1H, *J*= 8.1, 8.0). MS *m/z* (%): 218 (M^+, 87), 217 (31), 201 (72), 187 (14), 171 (100), 165 (28), 159 (80), 143 (30). Elemental analysis for $C_{12}H_{14}N_2O_2$ (218.24): calcd. C 66.04%, H 6.46%, N 12.84%; found C 65.82%, H 6.43%, N 12.76%.

1,2,3,3a,4,5-Hexahydro-7-chloro-6-nitropyrrolo[1,2-*a*]quinoline (13b). Yield 72%. M.p. 173-174°C (from n-hexane). ^1H NMR (500 MHz, $CDCl_3$): δ= 1.33 (dddd, 1H, *J*= 12.9, 12.8, 11.2, 4.9); 1.49 (dddd, 1H, *J*= 12.1, 12.1, 10.5, 7.3); 1.95 (ddddd, 1H, *J*= 12.6, 12.1, 9.6, 9.1, 6.8); 2.10 (ddddd, 1H, *J*= 12.6, 7.5, 7.3, 1.8, 1.1); 2.182 (dddd, 1H, *J*= 12.1, 6.8, 5.1, 1.1); 2.190 (dddd, 1H, *J*= 12.8, 5.2, 3.1, 2.4); 2.64 (ddd, 1H, *J*= 16.7, 4.9, 2.4); 2.72 (ddd, 1H, *J*= 16.7, 12.9, 5.2); 3.18 (ddd, 1H, *J*= 9.6, 9.3, 7.5); 3.34 (ddd, 1H, *J*= 9.3, 9.1, 1.8); 3.40 (dddd, 1H, *J*= 11.2, 10.5, 5.1, 3.1); 6.35 (d, 1H, *J*= 8.8); 7.09 (d, 1H, *J*= 8.8). MS *m/z* (%): 252 (M^+, 100), 251 (35), 235 (52), 221 (16), 205 (95), 193 (79), 177 (18), 170 (37), 142 (18), 128 (14), 115 (26). Elemental analysis for $C_{12}H_{13}ClN_2O_2$ (252.77): calcd. C 57.01%, H 5.18%, N 11.08%; found C 57.18%, H 5.10%, N 11.14%.

1,2,3,3a,4,5-Hexahydro-8-nitropyrrolo[1,2-*a*]quinoline (13c). Yield 80%. M.p. 142-143°C (from n-hexane). ^1H NMR (500 MHz, C_6D_6): δ= 0.77-0.98 (m, 2H); 1.20-1.37 (m, 2H); 1.41-1.48 (m, 2H); 1.51 (dddd, 1H, *J*= 6.0, 6.0, 4.4, 3.1); 2.28 (broad d, 1H, *J*= 3.2); 2.29 (ddd, 1H, *J*= 17.4, 4.8, 1.0); 2.55 (ddd, 1H, *J*= 9.5, 9.5, 7.4); 2.68 (ddd, 1H, *J*= 9.1, 9.1, 1.7); 2.77 (dddd, 1H, *J*= 10.8, 10.8, 5.1, 3.1); 6.60 (d, 1H, *J*= 8.1); 7.30 (d, 1H, *J*= 2.2); 7.46 (dd, 1H, *J*= 8.1, 2.2). MS *m/z* (%): 218 (M^+, 67), 217 (100), 190 (13), 171 (30), 162 (6), 144 (10), 130 (7), 115 (7), 94 (24). Elemental analysis for $C_{12}H_{14}N_2O_2$ (218.24): calcd. C 66.04%, H 6.46%, N 12.84%; found C 66.04%, H 6.62%, N 12.77%.

2,3,4,4a,5,6-Hexahydro-7-nitro-1*H*-benzo[*c*]quinolizine (13d). Yield 82%. M.p. 54-55°C (from n-hexane). ^1H NMR (500 MHz, C_6D_6): δ= 0.85-1.50 (m, 8H); 2.24 (ddd, 1H, *J*= 12.5, 12.4, 3.2); 2.35 (dddd, 1H, *J*=12.6, 8.2, 4.0, 2.5); 2.57 (ddd, 1H, *J*= 16.8, 5.4, 5.4); 2.68 (ddd, 1H, *J*= 16.8, 10.1, 5.4); 3.38 (broad d, 1H, *J*= 12.6); 6.47 (dd, 1H, *J*= 8.4, 1.0); 6.71 (dd, 1H, *J*= 8.4, 8.0); 6.97 (dd, 1H, *J*= 8.0, 1.0). MS *m/z* (%): 232 (M^+, 94), 215 (100), 202 (9), 191 (7), 185 (67), 173 (49), 159 (20), 156 (18), 129 (22). Elemental analysis for $C_{13}H_{16}N_2O_2$ (232.26): calcd. C 67.22%, H 6.94%, N 12.06%; found C 66.91%, H 6.99%, N 12.29%.

2,3,4,4a,5,6-Hexahydro-8-chloro-7-nitro-1*H*-benzo[*c*]quinolizine (13e). Yield 56%. M.p. 123-124°C (from n-hexane). ^1H NMR (500 MHz, C_6D_6): δ= 0.81-1.00 (m ,2H); 1.02- 1.35 (m, 4H); 1.37-1.43 (m, 2H); 2.10 (ddd, 1H, *J*= 12.5, 12.5, 3.0); 2.20 (dddd, *J*= 8.5, 8.4, 3.7, 2.7); 2.29 (d, 1H, *J*= 5.8); 2.31 (dd, 1H, *J*= 5.4, 2.3); 3.20 (broad d, 1H, *J*= 12.5); 6.10 (d, 1H, *J*= 9.1); 6.77 (d, 1H, *J*= 9.1). MS *m/z* (%): 266 (M^+, 100), 249 (57), 236 (11), 219 (50), 207 (27), 193 (14), 184 (10). Elemental analysis for $C_{13}H_{15}ClN_2O_2$ (266.80): calcd. C 58.52%, H 5.66%, N 10.50%; found C 58.51%, H 5.60%, N 10.53%.

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