Tetrahedron Vol. 49, No 44, pp 10017-10026, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

[1,5] Hydrogen Shift in Aza-*ortho*-xylylenes Generated from 3-Alkyl-2,1-benzisothiazoline 2,2-Dioxides.

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(*Received in UK* 23 *June* 1993; *accepted* 20 *August* 1993)

Abstract: Aza-*ortho*-xylylenes generated by the thermal extrusion of SO_2 from 3-alkyl-2,1-benzisothiazoline 2,2-dioxides **4** undergo [1,5] hydrogen shift leading to 2-aminostyrene derivatives **6**. In the case of 1,3-diallylbenzosultam **7** such transformation leads to *N*-allylaminophenyl-1,3-butadiene **9** which cyclizes to 5,6,6a,7,8,10a-hexahydrophenanthridine **10**. Cyclobutanospiro-3-benzosultams **11** after the extrusion of SO_2 and the [1,5] hydrogen shift form unstable phenylcyclobutenes, which undergo electrocyclic ring opening to 2-phenyl-1,3-butadienes **14**. 3-Chloromethyl-3-methylbenzosultams **17** transform into 1,3-dimethylindole derivatives **21**.

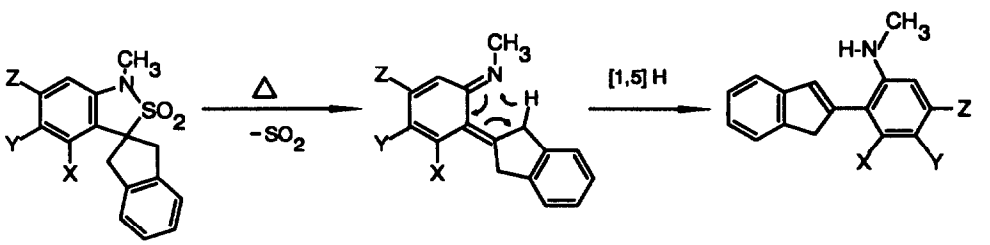
INTRODUCTION.

Aza-*ortho*-xylylenes are important active intermediates in the synthesis of heterocycles. For example, in the Diels-Alder they form 1,2,3,4-tetrahydroquinoline framework.[1] Recently we have reported that aza-*ortho*-xylylenes generated by the thermal extrusion of SO_2 from 2,1-benzisothiazoline 2,2-dioxides (benzosultams) enter the [4+2] cycloaddition reactions with electrophilic alkenes.[2,3] It was found, however that depending on the substituents present in the benzene ring of the starting 2,1-benzisothiazoline 2,2-dioxide, the ability of the generated aza-*ortho*-xylylene to enter this reaction is sometimes suppressed by the competing [1,5] hydrogen shift leading to the corresponding *N*-alkenylanilines.[3] This was observed particularly in the case of aza-*ortho*-xylylenes generated from 7-chloro- and 7-methyl-1-alkyl-2,1-benzisothiazoline 2,2-dioxides, in which the steric interaction of the substituents in the position 7 and that on the nitrogen atom forces the *Z* configuration. Such configuration facilitates the migration of the α-hydrogen from *N*-alkyl substituent to the exocyclic methylene group.

The [1,5] hydrogen shift in aza-*ortho*-xylylenes has been already reported. Storr *et al.*[4] have observed it in aza-*ortho*-xylylenes generated by flash vacuum thermolysis (FVT) of *ortho*-aminobenzyl alcohols. Such process has been observed also in the aza-*ortho*-xylylene generated by the photolysis of 1,3-dimethyl-2,1-benzisothiazoline 2,2-dioxide.[5] The [1,5] hydrogen shift in aza-*ortho*-xylylenes is considered rather as a side process without practical application and it seemed to be useless in organic synthesis.

In one of our previous papers[6] the synthesis of 2-arylindenes **3** from 2,1-benzisothiazolino-3-spiro-2'-indan 2,2-dioxides **1** was described. The key step of this transformation was the [1,5] hydrogen shift in aza-*ortho*-xylylene **2** generated by the thermal extrusion of SO_2 from **1** (**Scheme 1**).

SCHEME 1.



1 **2** **3**

X = H, NO_2; Y = H, F, CH_3, OCH_3; Z = H, NO_2.

In this paper the full account concerning our studies on the [1,5] hydrogen shift in aza-*ortho*-xylylenes generated from 3-alkyl-2,1-benzisothiazoline 2,2-dioxides **4** and some practical applications of this process in the organic synthesis is presented.

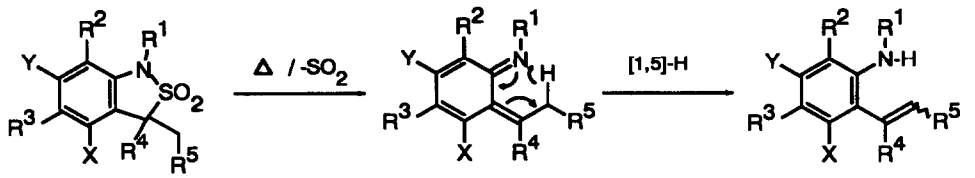
RESULTS AND DISCUSSION.

3-Alkyl and 3,3-dialkyl derivatives were obtained by the alkylation of 2,1-benzisothiazoline 2,2-dioxides with the corresponding alkyl bromides or iodides in the presence of solid potassium carbonate with catalytic amount of 18-crown-6 in dimethylformamide, analogously to the known procedures.[6,7] The starting 4-nitro- and 6-nitro derivatives of 2,1-benzisothiazoline 2,2-dioxide were easily obtained *via* the intramolecular vicarious nucleophilic substitution of hydrogen in *meta*-nitrochloromethanesulfonanilides[8] or *via* an intramolecular oxidative substitution of hydrogen in *meta*-nitromethanesulfonanilides.[9]

Thermolysis of 3-alkylbenzosultams **4** was carried out in boiling 1,2,4-trichlorobenzene at 215°C. The reaction of 1,3-dimethyl-4-nitrobenzosultam (**4a**) led to 6-nitro-2-vinyl-*N*-methylaniline (**6a**) in 75% yield, whereas 1,3,3-trimethyl-4-nitrobenzosultams **4b** and **4c** gave the corresponding 2-(2-propenyl)aniline derivatives **6b** and **6c**. Reactions of benzosultams **4d,e** (**Scheme 2**) proceeded similarly.

In the previous paper the succesful intramolecular Diels-Alder cyclizations of aza-*ortho*-xylylenes generated from 1-(4-pentenyl) and 1-(5-hexenyl)benzosultams were described.[3] One could expect that aza-*ortho*-xylylenes generated from benzosultams **4f,g**, which bear in the position 3 terminal alkenyl substituents, would react similarly giving condensed heterocycles. These reactions took however another course. Thus in the thermolysis of 5-chloro-1-methyl-3-(4-pentenyl)-4-nitrobenzosultam (**4f**) no intramolecular Diels-Alder reaction occured, and the only isolated product was 1-phenyl-1,4-pentadiene derivative **6f**. This might be the result of steric interaction between the nitro group and the alkyl chain forcing the *Z* configuration in which the [1,5] hydrogen shift is facilitated.

SCHEME 2.



4 **5** **6**

	R^1	R^2	R^3	R^4	R^5	X	Y	Yield (%)
a	CH_3	H	H	H	H	NO_2	H	75
b	CH_3	H	H	CH_3	H	NO_2	H	86
c	$CH_2C_6H_5$	H	CH_3	CH_3	H	NO_2	H	83
d	CH_3	H	CH_3	H	C_7H_{15}-*n*	NO_2	H	90
e	-$(CH_2)_3$-		H	H	H	NO_2	H	84
f	CH_3	H	Cl	H	-$(CH_2)_2$-CH=CH_2	NO_2	H	52
g	CH_3	H	H	H	-$(CH_2)_3$-CH=CH_2	H	NO_2	80
h	CH_3	H	CH_3		-CH_2-	NO_2	H	-
i	CH_3	H	H		-CH_2-	H	NO_2	-

To confirm this hypothesis, less stericaly demanding 3-(5-hexenyl)-6-nitro derivative **4g** was constructed. In this case also [1,5] hydrogen shift was a prevailing process and the only isolated product was 1,5-hexadiene derivative **6g**. These results are in contradiction to those obtained by Storr *et al.*[10] These authors have described the formation of 5,6,6a,7,8,9,10,10a-octahydrophenanthridine in the intramolecular Diels-Alder reaction of such substituted aza-*ortho*-xylylene generated from 3,1-benzoxazin-2-one derivative by FVT. Comparing the results obtained in these two processes one can conclude that such discrepancies in the reaction course are probably due to various geometries of the aza-*ortho*-xylylene generated by the thermal *retro*-Diels-Alder reaction (*E* configuration) and the thermal cheletropic extrusion of SO_2 from benzosultams (*Z* configuration).

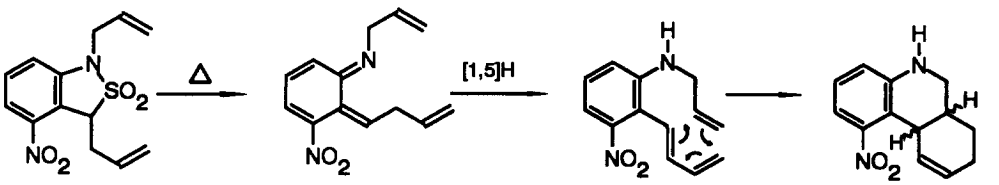
The facile formation of arylalkenes from benzosultams led to the expectation that 1-arylcyclopropenes could be synthesized from 3-spirocyclopropano-2,1-benzisothiazoline 2,2-dioxides **4h,i**. The attempts to execute such transformations were unsuccessful. In the standard conditions (215°C) no evolution of SO_2 was observed and even after prolonged heating (8 hr) these starting materials **4h,i** were recovered unchanged, whereas in higher temperature (245°C) only tars were formed. The reason for such stability of this system is unknown.

In this connection it is worthy of mention that electron impact (70 eV) mass spectra are good proof of the susceptibility of benzosultams to the extrusion of SO_2. Usually in the mass spectra of benzosultams the M-64 peaks corresponding to the loss of SO_2 from molecular ion are prevailing.[11] In the investigated

cyclopropanospiro-3-benzosultams **4h,i** such fragmentation for unknown reasons is disfavoured.

The [1,5] hydrogen shift in aza-*ortho*-xylylenes generated from 3-allyl derivatives should lead to 1-aryl-1,3-butadiene derivatives. Generation of this active diene was confirmed by the synthesis of the condensed heterocycle - 1-nitro-5,6,6a,7,8,10a-hexahydrophenanthridine **10** from 1,3-diallylbenzosultam **7**. The product **10** was obtained in 30% yield (**Scheme 3**).

SCHEME 3.

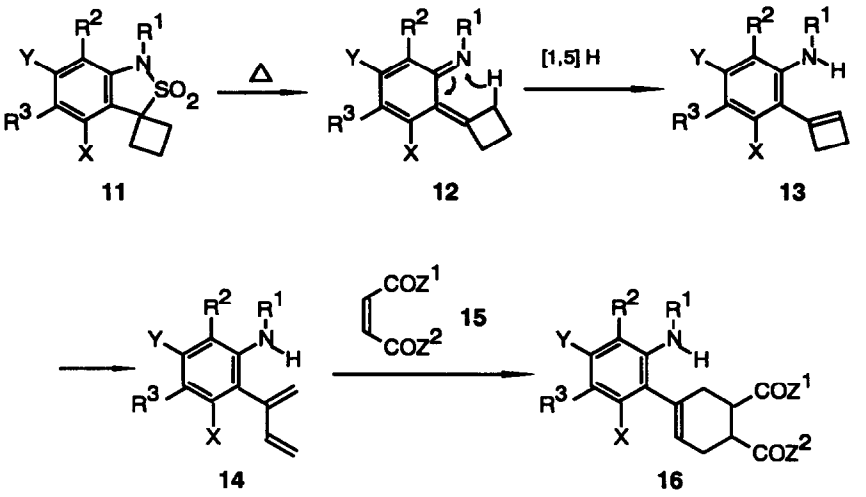


7 **8** **9** **10**

In this multi-step reaction sequence extrusion of SO_2 is followed by the [1,5] hydrogen shift leading to 1-(2-allylaminophenyl)-1,3-butadiene derivative **9** which then enters an intramolecular Diels-Alder reaction. The structure of the compound **10** was confirmed by means of mass and ^1H NMR spectra, however we were unable to determine the configuration on *C6a-C10a* bond.

Attempts to obtain 1-phenylcyclobutene derivatives **13** in the reaction of 3-spirocyclobutano-2,1-benzosultams **11** were only partly successful. Indeed, during the thermolysis of **11** evolution of SO_2 occured, but instead of the expected phenylcyclobutenes **13** the isomeric 2-phenyl-1,3-butadiene derivatives **14** were isolated. Thermal isomerisation of cyclobutenes to 1,3-butadienes is a well known process[12] and usually occurs at 100-200°C. The results obtained are proof that indeed extrusion of SO_2 from **11** gives cyclobutenyloxylylene **12** from which after the [1,5] hydrogen shift 1-phenylcyclobutene **13** is formed. 2-Phenyl-1,3-butadienes **14** generated by this way can be intercepted *in situ* by intermolecular Diels-Alder reactions with such dienophiles as *N*-phenylmaleinimide (**15a**) or dimethyl fumarate (**15b**) to give the expected 1-phenyl-cyclohexene-4,5-dicarboxylic acid derivatives **16** in high yield (**Scheme 4**). The reaction of 6-nitrobenzosultam **11** (R^1= CH_3, R^2=X=H, Y=NO_2) with **15a** led to one product **16b**. The reactions of 4-nitro derivatives **11** (X=NO_2) with **15a** and **15b** procedded similarly, but the products obtained **16a,c,d**, exist in two diastereoisomeric forms due to the hindered rotation of 2,6-disubstituted aryl group. The ^1H NMR spectra of these products showed two groups of signals corresponding to the protons of the nitroaryl substituent. Also in the case of dimethyl ester **16a** four signals corresponding to the methoxy groups were present. The integration shows that the ratio of these two diastereoisomers is 3:1. In the case of product **16d** all groups of signals are represented by broad peaks.

SCHEME 4.

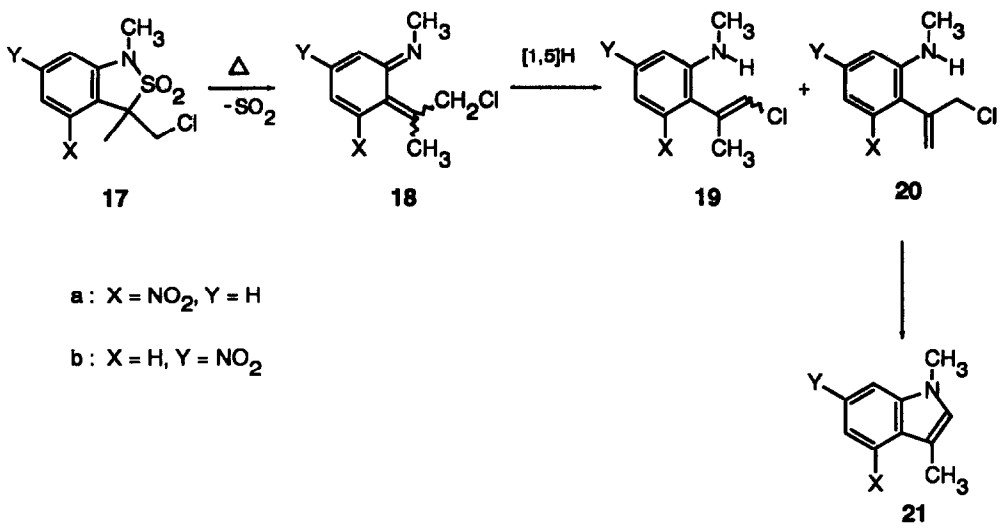


11 12 13 14 16

Product	R^1	R^2	R^3	X	Y	Z^1	Z^2	Yield (%)
14a	CH_3	H	H	NO_2	H	-	-	83
14b	CH_3	H	H	H	NO_2	-	-	75
14c	C_8H_{17}	H	CH_3	NO_2	H	-	-	75
16a	CH_3	H	H	NO_2	H	OCH_3	OCH_3	76
16b	CH_3	H	H	H	NO_2	>N-C_6H_5		82
16c	C_8H_{17}	H	CH_3	NO_2	H	>N-C_6H_5		87
16d	CH_3	Cl	H	NO_2	H	>N-C_6H_5		60

Interesting results were obtained in the thermolysis of 3-chloromethyl-3-methyl-2,1-benzisothiazoline derivatives (**17**). In these instances the extrusion of SO_2 leads to two isomeric aza-*ortho*-xylylenes **18**. The isomer *Z* (in respect to the C=N double bond and the CH_2Cl group) undergoing the [1,5] hydrogen shift gives 1-chloro-2-phenylpropene derivative **19**, whereas the second isomer (*E*) gives a 2-phenylallyl chloride derivative **20**. The derivative **20** in the reaction conditions undergoes an intramolecular alkylation of nitrogen leading, after a rearrangement, to 1,3-dimethyl-4- (or -6-)nitroindoles **21a** and **21b**. This a new approach to indole derivatives (**Scheme 5**).

SCHEME 5.



In summary, the presented results demonstrate that the [1,5] hydrogen shift in aza-*ortho*-xylylenes is a process of potential value in the synthesis of carbo- and heterocyclic systems.

EXPERIMENTAL.

Melting points are uncorrected. ^{1}H NMR spectra ($CDCl_3$ with TMS as an internal standard) were obtained on Varian Gemini (200 MHz) and Bruker AMX (500 MHz) instruments. Coupling constants *J* are expressed in Hertz. In the case of mixtures of diastereoisomers **16a,c,d** the signals corresponding to major and minor component are marked by ^{A} and ^{B}. Mass spectra (electron impact, 70 eV) were recorded with AMD 604 (AMD Intectra GmbH, Germany). Starting 3-alkyl-nitrobenzosultams were obtained from nitrobenzosultams[8,9] by alkylation with appropriate alkyl bromide or iodide analogously to procedures described earlier.[6,7]

Thermolysis of Benzosultams. General Procedure:

Benzosultam (1 mmol) was refluxed in 1,2,4-trichlorobenzene (2 mL). The progress of the reaction was followed by the TLC (hexane/ethyl acetate 4:1). When the starting material disappeared the reaction mixture was subjected to column chromatography (silica gel 230-400 mesh Merck 60, 2 x 20cm). The solvent was eluted with hexane/ethyl acetate 50:1, and then with hexane/ethyl acetate 5:1 the product was isolated. The following compounds were obtained:

***N*-Methyl-2-vinyl-3-nitroaniline (6a).** Yield 75%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.86 (d, 3H, *J*= 4.9); 4.50 (broad s, 1H); 5.43 (dd, 1H, *J*= 18.0, 1.6); 5.62 (dd, 1H, *J*= 11.4, 1.6); 6.68 (dd, 1H, *J*= 18.0, 11.4); 6.72, 7.13, 7.24 (ABX, 3H, *J*= 8.2, 8.0, 1.1). MS *m/z* (%): 178 (M^+, 100), 163 (13), 161 (13), 146 (20), 133 (23), 130 (29), 117 (4), 103 (18). Elemental analysis for $C_9H_{10}N_2O_2$ (178.17): calcd. C 60.67%, H 5.65%, N

15.72%; found C 60.70%, H 5.85%, N 15.69%.

***N*-Methyl-2-(2-propenyl)-3-nitroaniline (6b).** Yield 86%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.09 (dd, 3H, *J*= 1.6, 1.0); 2.86 (d, 3H, *J*= 5.0); 4.29 (broad s, 1H); 4.91 (dq, 1H, *J*= 1.6, 1.0); 5.33 (dq, 1H, *J*= 1.6, 1.6); 6.77, 7.16, 7.25 (ABX, 3H, *J*= 9.1, 7.7, 0.9). MS *m/z* (%): 192 (M^+, 100), 177 (30), 160 (39), 147 (37), 144 (28), 130 (74), 118 (24), 103 (17). Elemental analysis for $C_{10}H_{12}N_2O_2$ (192.19): calcd. C 62.49%, H 6.29%, N 14.57%; found C 62.47%, H 6.46%, N 14.70%.

***N*-Benzyl-2-(2-propenyl)-3-nitroaniline (6c).** Yield 83%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.07 (dd, 3H, *J*= 1.5, 1.0); 2.18 (s, 3H); 4.36 (broad s, 3H); 5.03 (m, 6 lines, 1H); 5.36 (m, 6 lines, 1H); 6.57 (d, 1H, *J*= 8.4); 6.98 (d, 1H, *J*= 8.4); 7.26- 7.40 (m, 5H). MS *m/z* (%): 282 (M^+, 27), 250 (4), 220 (3), 191 (100), 174 (45), 160 (8), 145 (57), 130 (5), 115 (6), 91 (75). Elemental analysis for $C_{17}H_{18}N_2O_2$ (282.34): calcd. C 72.32%, H 6.43%, N 9.92%; found C 72.19%, H 6.48%, N 9.70%.

***trans*-4,*N*-Dimethyl-3-nitro-2-[1-(1-nonenyl)]aniline (6d).** Yield 90%. Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.89 (t, 3H, *J*= 7.5); 1.25- 1.48 (m, 10H); 2.14- 2.20 (m, 2H); 2.17 (s, 3H); 2.84 (d, 3H, *J*= 5.0); 3.98 (broad s, 1H); 5.92 (dt, 1H, *J*= 16.1, 6.8); 6.05 (d, 1H, *J*= 16.1); 6.57 (d, 1H, *J*= 8.4); 7.02 (d, 1H, *J*= 8.4). MS *m/z* (%): 290 (M^+, 100), 275 (18), 273 (14), 260 (33), 245 (21), 205 (17), 177 (35), 175 (28). Elemental analysis for $C_{17}H_{26}N_2O_2$ (290.41): calcd. C 70.31%, H 9.02%, N 9.65%; found C 70.33%, H 9.14%, N 9.65%.

1,2,3,4-Tetrahydro-7-nitro-8-vinylquinoline (6e). Yield 84%. M.p. 34-35°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.82- 1.98 (m, 2H); 2.76- 2.86 (m, 2H); 3.29- 3.39 (m, 2H); 4.63 (broad s, 1H); 5.40 (dd, 1H, *J*= 18.0, 1.7); 5.59 (dd, 1H, *J*= 11.4, 1.7); 6.68 (dd, 1H, *J*= 18.0, 11.4); 6.94 (d, 1H, *J*= 8.2); 7.09 (d, 1H, *J*= 8.2). MS *m/z* (%): 204 (M^+, 100), 187 (18), 175 (13), 156 (25), 146 (59), 130 (37), 118 (23). Elemental analysis for $C_{11}H_{12}N_2O_2$ (204.2): calcd. C 64.70%, H 5.92%, N 13.72%; found C 64.44%, H 6.19%, N 13.80%.

4-Chloro-*N*-methyl-2-[1-(1,5-hexadienyl)]-3-nitroaniline (6f). Yield 52%. Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 2.18- 2.32 (m, 4H); 2.84 (d, 3H, *J*= 5.2); 4.20 (broad s, 1H); 5.03- 5.08 (m, 2H); 5.81- 5.85 (m, 1H); 5.95 (dt, 1H, *J*= 16.1, 6.2); 6.01 (d, 1H, *J*= 16.1); 6.55 (d, 1H, *J*= 8.9); 7.20 (d, 1H, *J*= 8.9). MS *m/z* (%): 266 (M^+, 100), 249 (39), 237 (28), 225 (32), 223 (37), 219 (33), 208 (53), 194 (50), 179 (73), 164 (32), 151 (23), 144 (43), 128 (24), 115 (44). Elemental analysis for $C_{13}H_{15}ClN_2O_2$ (266.73): calcd. C 58.54%, H 5.67%, N 10.50%; found C 58.59%, H 5.71%, N 10.55%.

2-[1-(1,6-Heptadienyl)]-*N*-methyl-5-nitroaniline (6g). Yield 74%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.50-1.70 (m, 2H); 2.05-2.40 (m, 4H); 2.93 (s, 3H); 4.10 (broad s, 1H); 4.93- 5.10 (m, 2H); 5.75- 5.95 (m, 1H); 6.17 (dt, 1H, *J*= 15.6, 6.4); 6.34 (d, 1H, *J*= 15.6); 7.25 (d, 1H, *J*= 8.4); 7.37 (d, 1H, *J*= 2.2); 7.53 (dd, 1H, *J*= 8.4, 2.2). MS *m/z* (%): 246 (M^+, 54), 231 (5), 217 (11), 203 (56), 189 (52), 177 (100), 165 (21), 159 (24), 144 (45), 131 (50), 117 (48). HRMS for $C_{14}H_{18}N_2O_2$ calcd. 246.1368, found 246.1369.

5,6,6a,7,8,10a-hexahydro-1-nitrophenanthridine (10). Yield 30%. M.p. 109-110°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.10 (dd, 1H, *J*= 11.1, 3.5); 3.37 (dd, 1H, *J*= 11.2, 11.1); 4.01- 4.05 (m, 1H); 4.20 (broad s, 1H); 5.60 (broad s, 2H); 6.65 (dd, 1H, *J*= 7.9, 1.3); 7.04 (dd, 1H, *J*= 8.4, 7.9); 7.09 (dd, 1H, *J*= 8.8, 1.3). MS *m/z* (%): 230 (M^+, 52), 213 (100), 196 (6), 183 (62), 167 (14), 154 (41), 143 (7), 129 (17), 115 (9). Elemental

analysis for $C_{13}H_{14}N_2O_2$ (230.25): calcd. C 67.81%, H 6.12%, N 12.17%; found C 67.39%, H 6.12%, N 12.12%.

2-[2-(1,3-Butadienyl)]-*N*-methyl-3-nitroaniline (14a). Yield 83%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.83 (s, 3H); 4.20 (broad d, 1H), 4.90 (d, 1H, *J*= 17.3); 5.13 (dd, 1H, *J*= 10.3, 0.7); 5.15 (d, 1H, *J*= 0.7); 5.57 (d, 1H, *J*= 0.7); 6.69 (dd, 1H, *J*= 17.3, 10.3); 6.80 (dd, 1H, *J*= 8.1, 1.1); 7.19 (dd, 1H, *J*= 8.0, 1.1); 7.32 (dd, *J*= 8.1, 8.0). MS *m/z* (%): 204 (M^+, 95); 187 (69), 175 (27), 172 (100), 159 (51), 157 (47), 143 (65), 130 (90), 115 (90), 103 (20), 91 (25), 77 (38). Elemental analysis for $C_{11}H_{12}N_2O_2$ (204.20): calcd. C 64.70%, H 5.92%, N 13.72%; found C 64.94%, H 6.00%, N 13.60%.

2-[2-(1,3-Butadienyl)]-*N*-methyl-5-nitroaniline (14b). Yield 75%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.87 (d, 3H, *J*= 4.8); 4.13 (broad s, 1H); 4.87 (d, 1H, *J*= 17.4); 5.18 (broad d, 1H, *J*= 10.4); 5.22 (dd, 1H, *J*= 1.4, 1.4); 5.53 (broad s, 1H); 6.55 (dd, 1H, *J*= 17.4, 10.4); 7.07 (d, 1H, *J*= 8.2); 7.40 (d, 1H, *J*= 2.2); 7.54 (d, 1H, *J*= 8.2, 2.2). MS *m/z* (%): 204 (M^+, 76), 189 (63), 176 (8), 172 (25), 157 (20), 143 (100), 130 (9), 128 (9), 115 (25). Elemental analysis for $C_{11}H_{12}N_2O_2$ (204.20): calcd. C 64.69%, H 5.92%, N 13.72%; found C 64.78%, H 5.89%, N 13.56%.

2-[2-(1,3-Butadienyl)]-4-methyl-3-nitro-*N*-octylaniline (14c). Yield 75%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 0.82- 0.94 (m, 3H); 1.20- 1.38 (m, 12H); 2.20 (s, 3H); 3.06 (dt, 2H, *J*= 6.7, 6.7); 3.74 (broad s, 1H); 4.98 (broad d, 1H, *J*= 17.3); 5.18 (broad d, 1H, *J*= 10.3); 5.23 (broad s, 1H); 5.56 (broad s, 1H); 6.50 (dd, 1H, *J*= 17.3, 10.4); 6.65 (d, 1H, *J*= 8.4); 7.09 (d, 1H, *J*= 8.4). MS *m/z* (%): 316 (M^+, 61), 299 (53), 284 911), 269 (7), 247 (5), 231 (12), 217 (12), 203 (58), 187 (100), 170 (34), 157 (42), 144 (18). Elemental analysis for $C_{19}H_{28}N_2O_4$ (316.40): calcd. C 72.12%, H 8.91%, N 8.85%; found C 72.15%, H 9.08%, N 8.76%.

1,3-Dimethyl-4-nitroindole (21a). Yield 20%. M.p. 99-100°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.39 (d, 3H, *J*= 1.0); 3.80 (s, 3H); 7.04 (broad s, 1H); 7.22 (dd, 1H, *J*= 8.2, 7.8); 7.54 (dd, 1H, *J*= 8.2, 0.9); 7.81 (dd, *J*= 7.8, 0.9). MS *m/z* (%): 190 (M^+, 44), 173 (52), 160 (4), 143 (100), 128 (8), 115 (12), 102 (7). Elemental analysis for $C_{10}H_{10}N_2O_2$ (190.18): calcd. C 63.15%, H 5.29%, N 14.73%; found C 63.02%, H 5.24%, N 14.83%.

As the second product **2-[2-(1-Chloropropenyl)]-*N*-methyl-3-nitroaniline (19a)** was isolated. Yield 40%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.13 (d, 3H, *J*= 1.5); 2.87 (s, 3H); 4.10 (broad s, 1H); 5.97 (q, 1H, *J*= 1.5); 6.80 (dd, 1H, *J*= 8.1, 1.1); 7.18 (dd, 1H, *J*= 8.0, 1.1); 7.31 (dd, 1H, *J*= 8.1, 8.0). MS *m/z* (%): 226 (M^+, 18), 191 (100), 174 (48), 161 (22), 144 (52), 130 (22), 117 (20), 103 (13). Elemental analysis for $C_{10}H_{11}ClN_2O_2$ (226.66): calcd. C 53.01%, H 4.89%, N 12.36%; found C 53.05%, H 4.84%, N 12.46%.

1,3-Dimethyl-6-nitroindole (21b). Yield 30%. M.p. 76-77°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.34 (d, 3H, *J*= 0.9); 3.84 (s, 3H); 7.12 (broad s, 1H); 7.58 (d, 1H, *J*= 8.7); 8.00 (dd, 1H, *J*= 8.7, 2.0); 8.27 (d, 1H, *J*= 2.0). MS *m/z* (%): 190 (M^+, 100), 174 (3), 160 (12), 143 (44), 132 (7), 128 (13), 115 (19). Elemental analysis for $C_{10}H_{10}N_2O_2$ (190.18): calcd. C 63.15%, H 5.29%, N 14.73%; found C 63.22%, H 5.17%, N 14.51%.

As the second product ***N*-Methyl-2-[2-(1-chloropropenyl)]-5-nitroaniline (19b)** was isolated. Yield 53%. M.p. 88-89°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.09 (d, 3H, *J*= 1.5); 2.91 (d, 3H, *J*= 5.2); 4.10 (broad s, 1H); 6.16 (q, 1H, *J*= 1.5); 7.06 (d, 1H, *J*= 8.2); 7.38 (d, 1H, *J*= 2.2); 7.53 (dd, 1H, *J*= 8.2, 2.2). MS *m/z* (%): 226 (M^+, 11), 191 (100), 174 (34), 160 (12), 145 (94), 130 (19), 115 (13), 103 (14). Elemental analysis for

$C_{10}H_{11}ClN_2O_2$ (226.73): calcd. C 53.01%, H 4.89%, N 12.36%; found C 53.11%, H 4.66%, N 12.50%.

Synthesis of Cyclohexene Derivatives (16). General Procedure.
Cyclobutanospirobenzosultam (**11**, 1 mmol) and dienophile (**15**, 1.2 mmol) were refluxed in 1,2,4-trichlorobenzene (2 mL) for 3 hr. After cooling the reaction mixture was subjected to column chromatography analogously to the former procedure. The following compounds were obtained:

***trans*-1-[2-(1-Methylamino-6-nitrophenyl)]cyclohexene-4,5-dicarboxylic Acid Dimethyl Ester (16a).** Yield 76%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.20- 2.70 (m, 4H); 2.85^B + 2.87^A (2 x s, 3H); 3.06- 3.19 (m, 2H); 3.36- 3.46 (m, 1H); 3.72^B, 3.73^B, 3.75^A, 3.79^A (4 x s, 6H); 4.25^B, 5.12^A (2 x broad s, 1H); 5.50- 5.63 (m, 1H); 6.71^A (dd, *J*= 8.1, 1.1) + 6.75^B (dd, *J*= 8.0, 1.2) (1H); 7.05^A (dd, *J*= 8.2, 1.1) + 7.11^B (dd, *J*= 8.1, 1.2) (1H); 7.22^A (dd, *J*= 8.2, 8.1) + 7.26^B (dd, *J*= 8.1, 8.0) (1H). MS *m/z* (%): 348 (M^+, 27), 331 (100), 316 (25), 299 (65), 289 (7), 271 (38), 253 (64), 239 (13), 229 (12), 223 (13), 211 (17), 195 (18), 182 (26), 167 (27). Elemental analysis for $C_{17}H_{20}N_2O_6$ (348.32): calcd. C 58.62% , H 5.78%, N 8.04%; found C 58.69%, H 5.96%, N 8.04%.

1-[2-(1-Methylamino-5-nitrophenyl)]cyclohexene-4,5-dicarboxylic Acid *N*-Phenylimide (16b). Yield 82%. M.p. 182-183°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.44- 2.72 (m, 2H); 2.85 (d, 3H, *J*= 4.4); 2.97 (ddd, 1H, *J*= 15.8, 6.9, 1.8); 3.06 (dd, 1H, *J*= 15.8, 1.8); 3.35- 3.58 (m, 2H); 4.35 (broad s, 1H); 6.20 (ddd, 1H, *J*= 6.7, 3.2, 3.2); 7.03 (d, 1H, *J*= 8.3); 7.20- 7.54 (m, 7H). MS *m/z* (%): 377 (M^+, 25), 360 (100), 347 (7), 330 (16), 229 (9), 203 (18), 189 (20), 173 (18), 157 (16), 143 (12). Elemental analysis for $C_{21}H_{19}N_3O_4$ (377.36): calcd. C 66.84%, H 5.07%, N 11.14%; found C 66.66%, H 4.90%, N 11.08%.

1-[2-(4-Methyl-3-nitro-1-octylaminophenyl)]cyclohexene-4,5-dicarboxylic Acid *N*-Phenylimide (16c). Yield 87%. Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 0.91- 0.96 (m, 3H); 1.12- 1.44 (m, 12H); 2.16^B, 2.18^A (2 x s, 3H); 2.50- 3.65 (m, 9H); 5.90- 6.05 (m, 1H); 6.59^A (d, *J*= 8.5), 6.62^B (d, *J*= 8.3) (1H); 7.04 (d, 1H, *J*= 8.5); 7.23-7.53 (m, 5H). MS *m/z* (%): 489 (M^+, 100), 472 (19), 457 (11), 390 (67), 372 (20), 356 (13), 344 (14), 330 (3), 297 (2), 225 (10). Elemental analysis for $C_{29}H_{35}N_3O_4$ (489.33): calcd. C 71.14%, H 7.20%, N 8.58%; found C 71.26%, H 7.28%, N 8.61%.

1-[2-(1-Methylamino-2-chloro-6-nitrophenyl)]cyclohexene-4,5-dicarboxylic Acid *N*-Phenylimide (16d). Yield 60%. M.p. 165-166°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 2.40- 3.00 (m, 6H); 3.23- 3.60 (m, 3H); 3.85 (broad s, 1H); 5.92 (dd, 1H, *J*= 5.1, 4.5); 7.14- 7.54 (m, 7H). MS *m/z* (%): 411 (M^+, 17), 394 (100), 379 (57), 366 (11), 359 (22), 348 (7), 331 (20), 257 (12), 247 (12), 229 (21), 217 (21), 204 (36), 193 (22), 181 (18), 167 (16), 152 (11), 128 (11). Elemental analysis for $C_{21}H_{18}ClN_3O_4$ (411.82): calcd. C 61.24% , H 4.40%, N 10.20%; found C 60.97%, H 4.19%, N 10.16%.

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