Molecules **1996**, *1*, 51 – 56

Transformations of Cumulated Aza-*ortho*-xylylenes Generated from 3-Arylmethylene-2,1-benzisothiazoline 2,2-Dioxides.

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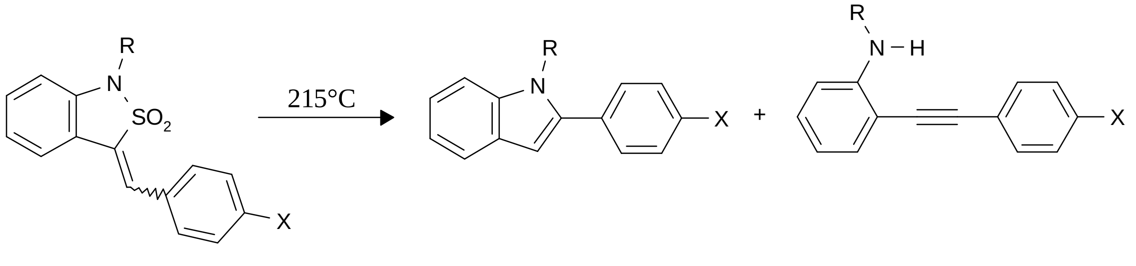
Received: 10 July 1996 / Accepted: 7 August 1996 / Published: 24 September 1996

Abstract

Thermal extrusion (215°C) of SO_2 from 3-arylmethylene-2,1-benzisothiazoline 2,2-dioxides **4** leads to cumulated aza-*ortho*-xylylenes. These reactive intermediates transform into 2-arylindoles **5** and *ortho*-alkylaminodiphenylacetylenes **6**. The formation of 2-arylindoles is the result of electrocyclisation followed by [1,2]-hydrogen shift. Diarylacetylenes **6** are a result of the [1,5]-hydrogen shift in the intermediate aza-*ortho*-xylylene.

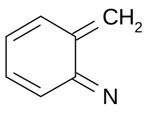


4 **5** **6**

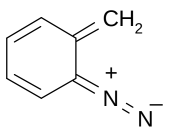
Keywords: 6-methylene-2,4-cyclohexadiene-1-imine derivatives, 1-alkyl-3-arylmethylene-2,1-benzisothiazoline 2,2-dioxides, electrocyclisation, indoles, diphenylacetylenes.

Aza-*ortho*-xylylenes (6-methylene-2,4-cyclohexadiene-1-imines, **1a**), active 1-azadienes, are still much less known and less used in organic synthesis than their carbon analogues. [1] This is mostly due to the lack of convenient methods for the generation of these reactive species. In recent years we have developed a method for generating these reactive intermediates by thermal extrusion of SO_2 from 2,1-benzisothiazoline 2,2-dioxide derivatives. Aza-*ortho*-xylylenes can enter a [4+2] cycloaddition reaction leading to 1,2,3,4-tetrahydroquinoline derivatives, [2] or can undergo other processes, particularly a [1,5]-hydrogen shift leading to *ortho*-vinylaniline derivatives. [3]

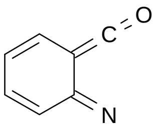
Cumulated xylylenes are much rarer than normal xylenes. A few examples of such species reported in the literature include: 1-methylene-6-diazo-2,4-cyclohexadiene (**1b**), [4,5] 1-keto-2,4-cyclohexadiene-6-imine (**1c**), [6,7] 1,6-diketo-2,4-cyclohexadiene (**1d**), [8] and 1,6-diallenyl-2,4-cyclohexadiene (**1e**). [9]



1a



1b



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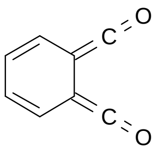

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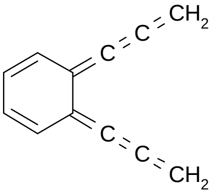
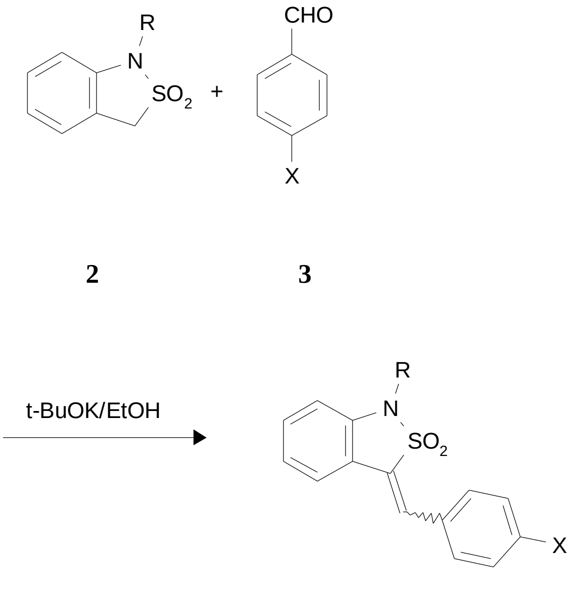


1e

The unusual structure of cumulated xylylenes attracted the attention of theoretical chemists and some of them have also found application in organic synthesis. Compound **1b** was generated by a photochemical ring opening of indazoles [4] or by potassium *tert*-butoxide-mediated 1,5-elimination of *tert*-butanethiol from *tert* -butyl (2-methylphenyl)azosulfide. [5] Iminoketenes, *e.g.* **1c**, were formed from anthranilic acid derivatives [6] or by ring opening in benzazetinones, [7] and were used as intermediates for the synthesis of condensed heterocycles. Compound **1d** was generated by laser flash photolysis of 1,2-benzocyclobutanedione. [8] "Extended" *ortho*-xylylene **1e**, which was reported recently, underwent electrocyclisation to 3,4-benzocycloocten-1,5-diyne. [9]

Our continuing interest in the reactions of aza-*ortho*-xylylenes prompted us to study the reactions of the cumulated aza-*ortho*-xylylenes generated by the thermal extrusion of SO_2 from 3-arylmethylene-2,1-benzisothiazoline 2,2-dioxides. Some 3-arylmethylene-2,1-benzisothiazoline 2,2-dioxides were obtained earlier by Skorcz and Suh [10] by the Knoevenagel condensation of benzosultams **2** with aromatic aldehydes **3** in the presence of potassium hydroxide in boiling ethanol (scheme 1). We synthesized these starting materials **4** by modification of this approach using a base prepared from potassium *tert*-butoxide in ethanol at room temperature. In this reaction a mixture of both *E* and *Z* isomers was formed, from which the major component was isolated by crystallization. Determination of the stereochemistry of the isolated isomer by spectral means proved impossible. However, this question was not crucial for further studies, since structural analysis of the *E* and *Z* isomers showed that the same aza-*ortho*-xylylene should be formed from both of them.



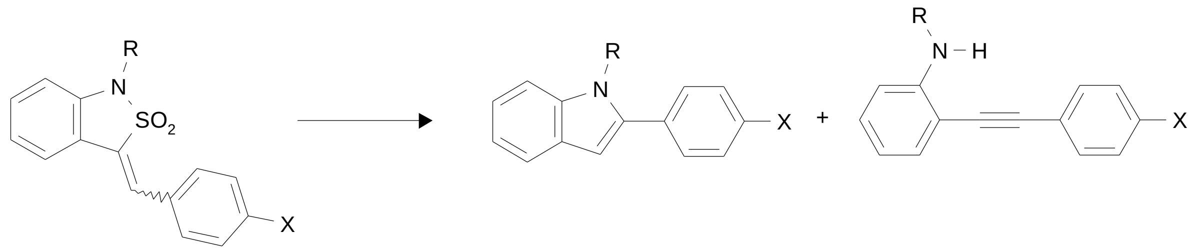
2 **3**

4

Scheme 1.

In our earlier work we found that aza-*ortho*-xylylenes generated by thermal extrusion of SO_2 from 2,1-benzisothiazoline 2,2-dioxides **2** undergoes [4+2] cycloaddition leading to 1,2,3,4-tetrahydroquinoline derivatives [2] or a [1,5]-hydrogen shift leading to Schiff bases and 2-vinylanilines. [3]

We attempted the reaction of aza-*ortho*-xylylenes generated from 3-arylmethylenebenzosultams **4** with *N*-phenylmaleimide (NPMI). During a reaction of 1-methyl-3-(phenylmethylene)-2,1-benzisothiazoline 2,2-dioxide (**4a**) with NPMI performed in boiling 1,2,4-trichlorobenzene (215 °C) a complex mixture of products was formed. Analysis of the crude reaction mixture by GC-MS has revealed that no [4+2] cycloaddition products were formed, and two major peaks, corresponding to compounds formed by the loss of SO_2 from the starting arylmethylene-benzosultam, were observed. The reaction was repeated without the dienophile and, under these conditions, led to a less complex mixture from which the two isomeric products were separated by preparative TLC. These major products were identified as 1-methyl-2-phenylindole (**5a**) and 2-methylaminodiphenylacetylene (**6a**) on the basis of ^{1}H-NMR and mass spectra. The product **5a** also showed properties identical to the independently synthesised standard.



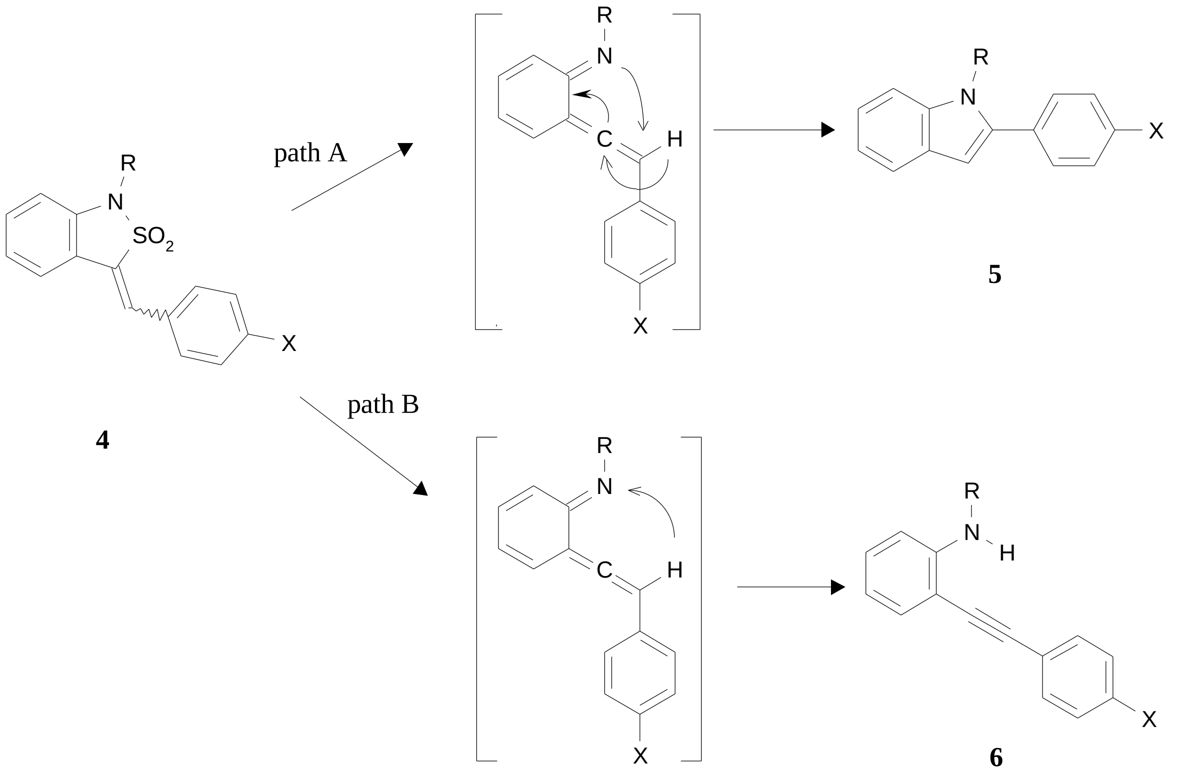
4 **5** **6**

	R	X	**5** (%)	**6** (%)
a	CH_3	H	40	16
b	C_2H_5	CH_3	30	18
c	C_2H_5	Cl	34	10
d	C_2H_5	OCH_3	42	traces
e	C_2H_5	NO_2	47	19

Scheme 2.

Reactions of other benzosultams **4b-e** proceeded similarly (Scheme 2).

A plausible mechanism for the formation of 1-alkyl-2-arylindole **5** from cumulated aza-*ortho*-xylylene could involve electrocyclization followed by the [1,2]-hydrogen shift (Scheme 3, path A). The formation of 2-alkylaminodiphenylacetylene could be a result of the [1,5]-hydrogen shift (path B)). The extrusion of SO_2 from 3-arylmethylene benzosultams **4** proceeded much slower than from 3-alkyl- or 3,3-dialkyl derivatives. Usually it took 4 to 24 h until the starting material completely disappeared. The reasons for this difference in reactivity are unclear. One could speculate that the ease of the extrusion of SO_2 from substituted 2,1-benzisothiazoline 2,2-dioxides depends on the hybridization of the C-3 carbon atom. The concerted cheletropic extrusion reaction of SO_2 requires sp^3-hybridization at the reacting center. In all compounds investigated during this study this atom was sp^2-hybridized. A similar problem with the ease of cheletropic extrusion of SO_2 was reported earlier by Skatebøl, [11] who investigated the reversibility of the additon of SO_2 to vinylallene and found that the formed 2-methylene-2,5-dihydrothiophene 1,1-

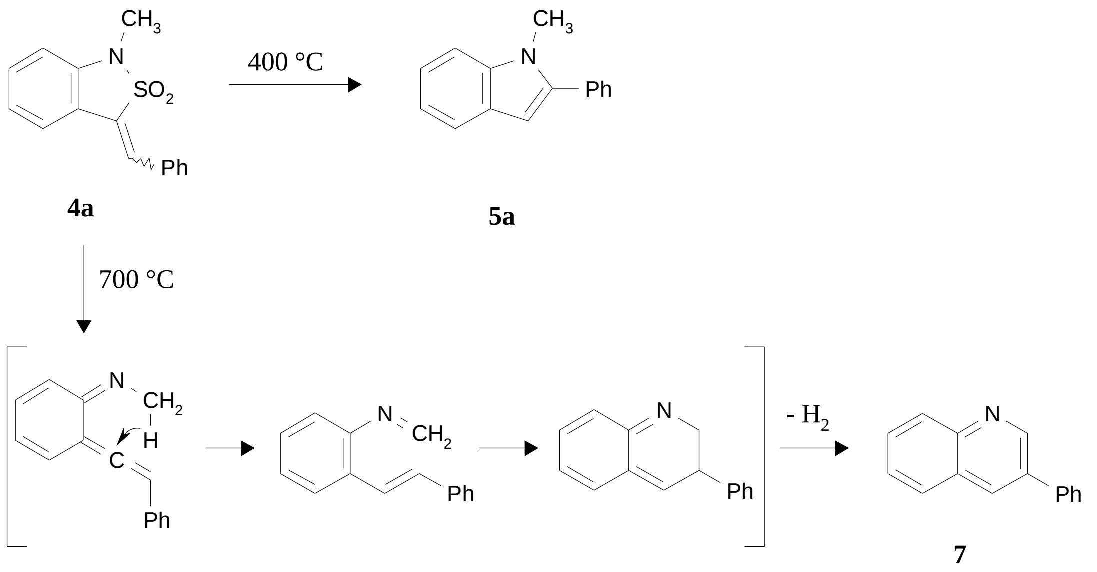


4

5

6

Scheme 3.



Scheme 4.

dioxides are much more thermally stable than 2,5-dihydrothiophene 1,1-dioxides. Some support for this hypothesis can also be drawn from our earlier observations. We observed a high thermal stability of 3,3-spirocyclopropano-2,1-benzisothiazoline 2,2-dioxides. [3] In that case, the reluctance to undergo SO_2 extrusion might have been caused by the strain of the cyclopropane ring, leading to a perturbation of the sp^3-hybridization of the C-3 carbon atom.

Some insight into the stability of the 3-arylmethylenebenzosultams and into transformations of cumulated xylylenes generated from them was obtained from the studies of the pyrolysis of 1-methyl-3-phenylmethylene-2,1-benzisothiazoline 2,2-dioxide (**4a**). Employing a pyrolytic oven attached directly to the inlet of a gas chromatograph equipped with a quadrupole mass selective detector (GC-MS), we screened the products formed from this sultam using a broader range of temperatures (400-800 °C). At 400 °C the extrusion of SO_2 proceeded to a minor extent, and 1-methyl-2-phenylindole (**5a**) was determined as the major product (>80%) (Scheme 4). At 500 °C the extrusion of SO_2 ran to completion and **5a** was also the major product (>85%) amongst the volatile ones. In this instance the acetylene **6a** was observed as a minor component (<5%). The small amount of **6a** obtained might have been the result of its thermal instability at higher temperatures. To prove this we injected pure 2-methylaminodiphenylacetylene (**6a**) into the oven at 500 °C. This compound was intact and no cyclization product, *i.e.* indole **5a**, was observed. Among the products of the pyrolysis of phenylmethylenebenzosultam **4a** performed at higher temperatures (600-700 °C) a second major product was detected in addition to 1-methyl-2-phenylindole. On the basis of the mass spectrum the structure of 3-phenylquinoline (**7**) was assigned to this compound. The formation of 3-phenylquinoline was probably a result of multistep transformations of the aza-*ortho*-xylylene, the [1,5]-hydrogen shift leading to an imine, which then underwent an electrocyclization leading to dihydroquinoline, and finally aromatized by losing the hydrogen molecule (Scheme 4). At 800 °C indole, 1-methylindole, 2-phenylindole and quinoline were determined amongst other products, probably resulting from the pyrolysis of the original products **5a** and **6a**. We have found that both **5a** and **6a** underwent pyrolysis under this conditions.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian Gemini (200 MHz) instrument in $CDCl_3$ solution with tetramethylsilane as an internal standard (coupling constants J expressed in Hz). Mass spectra (electron impact, 70 eV) were obtained on an AMD 604 (AMD Intectra GmbH, Germany) instrument. IR spectra were recorded on a Perkin Elmer 1670 FT-IR instrument. Benzosultams were obtained from the corresponding *ortho*-chloro-*N*-alkyl methanesulfonanilides following the procedure described by Bunnett. [12] Other starting materials were commercial. Preparative TLC was performed using 2 mm silica gel plates (Merck 60 F_{254}) with hexane-ethyl acetate (5:1) as an eluent. Pyrolysis was performed using a SGE pyrolytic oven attached directly to the injector of a Hewlett-Packard GC/MS system containing a HP 5890 Series II gas chromatograph coupled directly to a MSD 5972A quadrupole mass-sensitive detector. The injector temperature was set to 350 °C. A HP-5 capillary column (30 m length, 0.25 ID) was used. Analyses were run using the temperature program: 200 °C-5 min; 10°C/min; 300 °C-10 min.

Synthesis of 3-Arylmethylene-2,1-benzisothiazoline 2,2-Dioxides (General Procedure).

To a solution of benzosultam (1 mmol) and aromatic aldehyde (1.5 mmol) in absolute ethanol (10 mL) potassium *tert*-butoxide (50 mg) was added in one portion. The reaction mixture was kept at room temperature for 24 h (the reaction with 4-nitrobenzaldehyde was completed in 1 h). Then the solvent was evaporated and the residue dissolved in dichloromethane (30 mL), washed with diluted (5%) HCl, and dried over $MgSO_4$. After evaporation of the solvent the product was crystallized from ethanol. In each instance one isomer was isolated. The following compounds were obtained:

1-Methyl-3-phenylmethylene-2,1-benzisothiazoline 2,2-Dioxide (4a)

Mp: 118-119°C. ^{1}H-NMR: δ= 3.19 (s, 3H); 6.70 (d, *J*= 7.9, 1H); 7.02 (ddd, *J*= 7.7, 7.7, 1.0, 1H); 7.35 (ddd, *J*= 7.7, 7.7, 1.2, 1H); 7.41-7.54 (m, 5H), 7.86-7.93 (m, 2H). MS *m/z* (%): 271 (M^+, 85), 207 (21), 206 (100), 204 (7), 178 (8), 165 (10), 130 (13). Elemental analysis for $C_{15}H_{13}NO_2S$ (271.2): calcd. C 66.40%, H 4.83%, N 5.15%; found C 66.36%, H 4.84%, N 5.09%.

1-Ethyl-3-(4-methylphenyl)methylene-2,1-benzisothiazoline 2,2-Dioxide (4b)

Mp: 77-78 °C. ^{1}H-NMR: δ= 1.41 (t, *J*= 7.5, 3H); 2.40 (s, 3H); 3.74 (q, *J*= 7.5, 2H); 6.69 (br. d, *J*= 8.1, 1H); 6.97 (ddd, *J*= 7.8, 7.8, 1.0, 1H); 7.21- 7.28 (m, 2H); 7.32 (dd, *J*= 7.7, 1.3, 1H); 7.37 (s, 1H); 7.47 (dd, *J*= 7.7, 1.3, 1H); 7.65-7.83 (m, 2H). MS *m/z* (%): 299 (M^+, 63); 235 (5), 234 (20), 220 (100), 204 (18), 190 (7), 178 (13), 165 (4), 152 (4), 144 (7), 128 (8), 115 (6).Elemental analysis for $C_{17}H_{17}NO_2S$ (299.2): calcd. C 68.20%, H 5.72%, N 4.68%; found C 68.14%, H 5.83%, N 4.70%.

1-Ethyl-3-(4-chlorophenyl)methylene-2,1-benzisothiazoline 2,2-Dioxide (4c)

Mp: 114-115 °C. ^{1}H-NMR: δ= 1.40 (t, *J*= 7.1, 3H); 2.39 (s, 3H); 3.75 (q, *J*= 7.1, 2H); 6.69 (d, *J*= 8.1, 1H); 6.97 (ddd, *J*= 7.6, 7.6, 1.0, 1H); 7.20-7.34 (m, 3H); 7.36 (s, 1H); 7.47 (dd, *J*= 7.6, 1.2, 1H), 7.74-7.83 (m, 2H). MS *m/z* (%): 319 (M^+, 92), 304 (4), 240 (100), 204 (37), 190 (13), 178 (13), 153 (8), 144 (9), 128 (9) .Elemental analysis for $C_{16}H_{14}ClNO_2S$ (319.7): calcd. C 60.09%, H 4.41%, N 4.38%; found C 59.87%, H 4.44%, N 4.37%.

1-Ethyl-3-(4-methoxyphenyl)methylene-2,1-benzisothiazoline 2,2-Dioxide (4d)

Unseparable mixture of *E* and *Z* isomers. ^{1}H-NMR (major isomer ~85%): δ= 1.41 (t, *J*= 7.2, 3H); 3.75 (q, *J*= 7.2, 2H); 3.85 (s, 3H); 6.69 (d, *J*= 8.1, 1H); 6.92-7.01 (m, 3H); 7.28 (dd, *J*= 7.9, 1.2, 1H); 7.33 (s, 1H); 7.46 (dd, *J*= 7.7, 1.2, 1H); 7.83-7.92 (m, 2H). MS *m/z* (%): 315 (M^+, 68), 286 (3), 251 (6), 250 (18), 236 (100), 221 (23), 204 (7), 193 (20), 178 (7), 165 (11), 152 (10), 144 (8). Elemental analysis for $C_{17}H_{17}NO_3S$ (315.3): calcd. C 64.76%, H 5.43%, N 4.44%; found 64.70%, H 5.38%, N 4.54%.

1-Ethyl-3-(4-nitrophenyl)methylene-2,1-benzisothiazoline 2,2-Dioxide (4e)

Mp: 203-204 °C. ^{1}H-NMR: δ= 1.42 (t, *J*=7.2, 3H); 3.76 (q, *J*= 7.2, 2H); 6.75 (d, *J*= 8.1, 1H); 7.03 (ddd, *J*= 7.7, 7.7, 1.0, 1H); 7.41 (ddd, *J*= 7.7, 7.7, 1.2, 1H); 7.40 (s, 1H); 7.54 (dd, *J*= 7.7, 1.2, 1H); 7.99-8.07 (m, 2H); 8.25-8.33 (m, 2H). MS *m/z* (%): 330 (M^+, 100), 315 (4), 300 (9), 266 (3), 251 (75), 221 (17), 219 (15), 205 (83), 204 (47), 190 (15), 176 (10), 163 (12) .Elemental analysis for $C_{16}H_{14}N_2O_4S$ (330.3): calcd. C 58.17%, H 4.27%, N 8.47%; found C 57.96%, H 4.20%, N 8.49%.

Thermolysis of 3-Arylmethylenebenzosultams 4

A solution of benzosultam **4** (1 mmol) in 1,2,4-tetrachlorobenzene (2 mL) was refluxed for 12-48 h. The progress of the reaction was followed by TLC (Silicagel Merck F_{254}-hexane/ethyl acetate 4:1). When the starting material disappeared the reaction mixture was cooled and subjected to column chromatography. Trichlorobenzene was eluted with hexane, and then the mixture of products was eluted with hexane/ethyl acetate 4:1. The products were then separated by preparative TLC on silicagel 2 mm- hexane/ethyl acetate 4:1. The following compounds were obtained:

1-Methyl-2-phenylindole (5a)

Mp: 97-98 °C. Lit. [13] mp: 101 °C. ^{1}H-NMR: δ= 3.76 (s, 3H); 6.57 (d, *J*= 0.8, 1H); 7.10-7.30 (m, 3H); 7.34-7.56 (m, 5H); 7.64 (br. d, *J*= 7.6, 1H). MS *m/z* (%): 207 (M^+, 100), 206 (52), 191 (5), 179 (12), 165 (12), 152 (4). HRMS for $C_{15}H_{13}N$ calcd. 207.1048 found 207.1067.

1-Ethyl-2-(4-methylphenyl)indole (5b)

Mp: 43-44 °C. Lit [14] mp: 48 °C. ^{1}H-NMR: δ= 1.40 (t, *J*= 7.1, 3H); 2.39 (s, 3H); 3.75 (q, *J*= 7.1, 2H); 6.69 (d, *J*= 8.1, 1H); 6.97 (ddd, *J*= 7.6, 7.6, 1.0, 1H); 7.22 (s, 1H); . MS *m/z* (%): 235 (M^+, 100), 220 (60), 205 (24), 204 (17), 178 (5).HRMS for $C_{17}H_{17}N$ calcd. 235.1361, found 235.1362.

1-Ethyl-(4-chlorophenyl)indole (5c)

Mp: 85-86 °C. Lit. [15] mp. 86-87 °C. ^{1}H-NMR: δ= 1.31 (t, *J*= 7.1, 3H); 4.17 (q, *J*= 7.1, 1, 2H); 6.51 (d, *J*= 0.8, 1H); 7.09-7.29 (m, 2H); 7.35-7.46 (m, 5H); 7.63 (ddd, *J*= 8.4, 1.3, 0.8, 1H). MS *m/z* (%): 255 (M$^+$, 63), 240 (21), 205 (100), 190 (7), 176 (8), 154 (4), 130 (3), 128 (3). HRMS for $C_{16}H_{14}ClN$ calcd. 255.0815; found 255.0815.

1-Ethyl-2-(4-methoxyphenyl)indole (5d)

Mp: 94-96°C. ^{1}H-NMR: δ= 1.31 (t, *J*= 7.1, 3H); 3.87 (s, 3H); 4.17 (q, *J*= 7.1, 2H); 6.47 (d, *J*= 0.8, 1H); 6.95-7.04 (m, 2H); 7.07-7.23 (m, 2H); 7.35-7.48 (m, 3H); 7.62 (br. d, *J*= 7.5, 1H). MS *m/z* (%): 251 (M$^+$, 100), 236 (87), 221 (18), 205 (15), 193 (13), 178 (7), 165 (4), 152 (4), 126 (5). HRMS for $C_{17}H_{17}NO$ calcd. 251.1310; found 251.1309.

1-Ethyl-2-(4-nitrophenyl)indole (5e)

Mp: 107-108 °C. ^{1}H-NMR: δ= 1.35 (t, *J*= 7.2, 3H); 4.24 (q, *J*= 7.2, 2H); 6.67 (d, *J*= 0.8, 1H); 7.17 (ddd, *J*= 8.0, 7.0, 1.2, 1H); 7.32 (dd, *J*= 7.0, 1.2, 1H); 7.44 (dd, *J*= 8.2, 1.2, 1H); 7.60-7.72 (m, 3H); 8.30-8.38 (m, 2H). MS *m/z* (%): 266 (M$^+$, 100), 251 (39), 236 (7), 220 (12), 205 (75), 204 (63), 191 (12), 176 (8), 163 (5).HRMS for $C_{16}H_{14}N_2O_2$ calcd.266.1055, found 266.1058.

2-Methylaminodiphenylacetylene (6a)

Mp: 71-73 °C. ^{1}H-NMR: δ= 2.93 (s, 3H); 4.69 (br. s, 1H); 6.56-6.72 (m, 2H); 7.20-7.29 (m, 2H); 7.31-7.41 (m, 3H); 7.49-7.56 (m, 2H). MS *m/z* (%): 207 (M$^+$, 84), 206 (100), 204 (20), 190 (4), 178 (17), 165 (8), 149 (5), 130 (32), 128 (18). HRMS for $C_{15}H_{13}N$ calcd. 207.1048, found 207.1045.

2-Ethylamino-4’-methyldiphenylacetylene (6b)

Oil. ^{1}H-NMR: δ= 1.31 (t, *J*= 7.2, 3H); 3.23 (br. q, *J*= 7.2, 2H); 4.56 (br. s, 1H); 6.50-6.68 (m, 2H); 7.11-7.45 (m, 6H). MS *m/z* (%): 235 (M$^+$, 91), 220 (100), 205 (28), 204 (25), 178 (9), 128 (5), 109 (9), 102 (7). HRMS for $C_{17}H_{17}N$ calcd. 235.1361, found 235.1362.

4-Chloro-2’-ethylaminodiphenylacetylene (6c)

Oil. ^{1}H-NMR: δ= 1.32 (t, *J*= 7.1, 3H); 3.25 (br. q, *J*= 7.1, 2H); 4.51 (br. s, 1H); 6.58-6.71 (m, 2H); 7.17-7.49 (m, 6H). MS *m/z* (%): 255 (M$^+$, 43), 240 (100), 205 (29), 204 (32), 190 (3), 178 (8), 163 (3), 144 (6), 128 (7), 102 (9). HRMS for $C_{16}H_{14}ClN$ calcd. 255.0815, found 255.0813.

2-Ethylamino-4’-nitrodiphenylacetylene (6e)

Mp: 63-64°C. ^{1}H-NMR: δ= 1.34 (t, *J*= 7.3, 3H); 3.27 (br. q, *J*= 7.3, 2H); 4.52 (br. s, 1H); 6.64 (d, *J*= 7.7, 1H); 7.20-7.42 (m, 3H); 7.60-7.68 (m, 2H); 8.19-8.25 (m, 2H). MS *m/z* (%): 266 (M$^+$, 77), 251 (73), 236 (3), 219 (9), 205 (100), 204 (73), 191 (7), 176 (9), 163 (5), 144 (7). HRMS for $C_{16}H_{14}N_2O_2$ calcd.266.1055, found 266.1053.

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