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INTRAMOLECULAR INVERSE ELECTRON DEMAND DIELS-ALDER REACTIONS OF PYRAZINES

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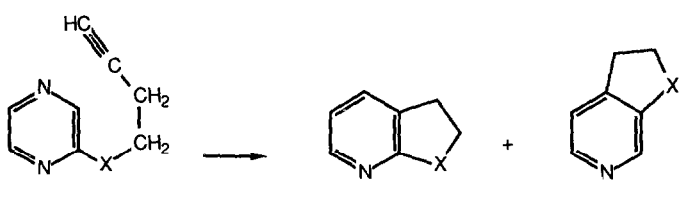
Abstract: Thermally induced intramolecular Diels-Alder cyclisations of (alkynyloxyalkyl)pyrazines to dihydropyranopyridines have been studied in the solvent undecane. The introduction of a phenyl group in the α-position of the 3-butynyloxymethyl side chain leads to a 3-4 fold increase of the reaction rate, while the influence of a γ-phenyl group on the rate is negligible. The (3-butynyloxymethyl)pyrazine reacts about 7 times slower than the (3-propynyloxyethyl)pyrazine; the presence of a trimethylsilyl group at the terminus of the alkyne decreases in general the rate of the intramolecular cyclisations. The mechanisms are discussed.

There are several reports in the literature which described Diels-Alder reactions of substituted electron-rich and electron-poor pyrazines with triple bond dienophiles[1,2]. Substituted pyridines are obtained, probably via the intermediacy of a cycloadduct, being formed by addition of the triple bond across the C_2-C_5-positions. The intramolecular version of cycloaddition reactions has also been investigated. Pyrazines, containing as substituent a five membered side-chain with a dienophilic terminal alkyne group have been found to react on heating in nitrobenzene to form a mixture of the *b* and *c* annelated bicyclic pyridines **1** and **2**[3]. Similar reactions have also been reported with appropriately substituted pyrimidines and pyridines[4].



X = O, S, SO_2, N, C,

1,2,4-Triazines containing a six membered ω-dienophilic side-chain are reported to give in an intramolecular Diels-Alder reaction bicyclic systems with two six-membered rings: 2,3-

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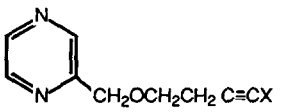
dihydropyrano[2,3-*b*]pyridines[5], 3,4-dihydro-2*H*-thiopyrano[2,3-*b*]pyridines[6] and 5,6,7,8-tetrahydroquinolines[7]. However, for these cyclisations higher reaction temperatures are required than for the formation of the bicyclic compounds **1** and **2**. This is due to the significant loss of entropic assistance, associated with intramolecular reactions, as a result of lengthening of the side-chain[5,8].

Intramolecular Diels-Alder cyclisations in pyrazines containing a six-membered alkynyloxyalkyl side-chain have never been studied. In this paper we report on studies with the aim of seeing whether enhancement of the nucleophilic properties of the triple bond in the side-chain by introducing a trimethylsilyl group at the terminal carbon atom or a bulky phenyl group in the α, β or γ–position of the side-chain would change the course and rate of the cycloaddition. For that purpose we prepared the pyrazines (**3a,b-7a,b**) and studied the thermolytic behaviour of these compounds.



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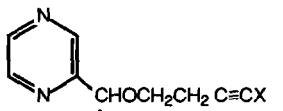

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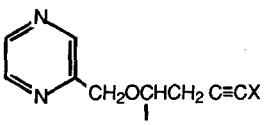
a X = H
b X = $SiMe_3$



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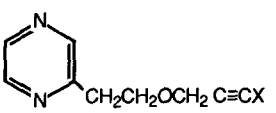

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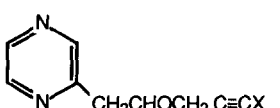

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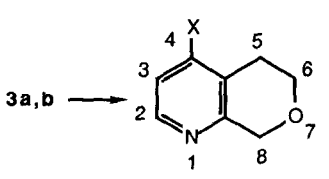
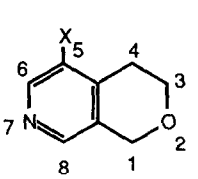
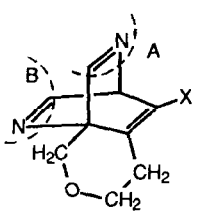
Heating of (3-butynyloxymethyl) pyrazine **3a** (prepared from chloromethylpyrazine[9, 10] and the sodium salt of 3-butyn-1-ol) in undecane at 195°C for 135 hrs gave in good yield a mixture of the 8*H*-5,6-dihydropyrano[3,4-*b*]pyridine (**8a**, 40%) and 1*H*-3,4-dihydropyrano[3,4-*c*]pyridine (**9a**, 22%). Attempts to perform this thermal rearrangement in nitrobenzene were found to be less successful; much decomposition took place and only in very low yields **8a** (3%) and **9a** (3%) were obtained.



8a,b



9a,b



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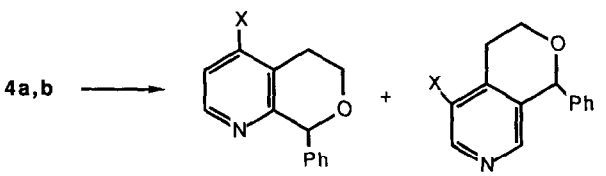
When heating the trimethylsilyl derivative **3b** (obtained by reacting the lithium salt of **3a** with trimethylsilyl chloride) in undecane a mixture of the 4-trimethylsilyl derivative **8b** (28%) and the 5-trimethylsilyl derivative **9b** (23%) is formed. The required reaction time for complete conversion of **8b** is very long (280 hrs!) (See table 1).

Comparing the reaction conditions for the intramolecular cycloaddition in **3a** and **3b** it is evident that in the intramolecular cyclisation of **3b** a considerable steric effect must be operative. Despite the activating influence of the trimethylsilyl group on the nucleophilic reactivity of the alkyne bond[11, 12] the required reaction time for conversion of **3b** is about twice as long as that for **3a**. In the formation of the intermediate cycloadduct **10** considerable steric hindrance develops between the trimethylsilyl group and the C=N bridge. Studies with Dreiding models confirm this steric effect. From **3a** as well as **3b** product **8a**, **8b** is always favoured over **9a**, **9b**, implying that loss of hydrogen cyanide from cycloadduct **10** indicated by "A" is faster than of that indicated by "B". This result is in agreement with previous observations[3]. It is known that trimethylsilyl derivatives of pyridine are useful synthetic intermediates[13,14]. The methodology to obtain trimethylsilyl derivatives of fused pyridines by intramolecular Diels-Alder reactions with appropriately substituted pyrazines is a new entry to this type of compound.

In the literature it has been observed that the presence of two methyl groups on the α- or β-position in an ω-alkyne side-chain attached to a furan ring leads to a rate enhancement in intramolecular Diels-Alder reactions[15,16]. This *gem* dimethyl effect was also found with *gem* dicyano groups present in the α-position of an ω-alkyne side chain attached to a 1,2,4-triazine[6,7] or pyrimidine ring[4] and was ascribed to the so-called Thorpe-Ingold effect.

In order to evaluate the effect of a phenyl group present on the α- and γ-position of the 3-butynyloxymethyl side chain we prepared the compounds **4** and **5**; for comparison also the propynyloxyethylpyrazines **6** and **7** were synthesized. Compound **4a** was prepared by reacting α-bromo-α-phenylmethylpyrazine **11** (obtained from benzylpyrazine[17] and N-bromo-succinimide) with sodium propargyloxide. Heating **4a** in undecane at 195° it was found that a shorter reaction time is required than for **3a** (see table 1) and that a reaction mixture is obtained containing the *b*-fused product **12a** (38%) as well as the *c*-fused product **13a** (13%).

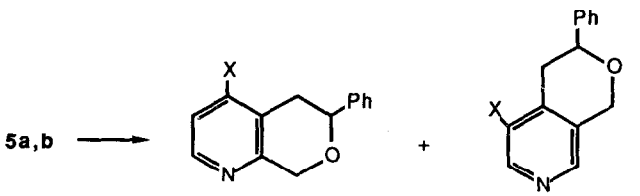


12a,b **13a,b**

From these results it is evident that the α-phenyl group has a rate-enhancing effect on the intramolecular Diels-Alder reaction. The Thorpe-Ingold effect, as well as the circumstance that, from all possible orientations of the side-chain, the one in which there is minimisation of the steric interaction between the phenyl and pyrazinyl group is the most favourable for the

cyclisation explain this rate enhancement.

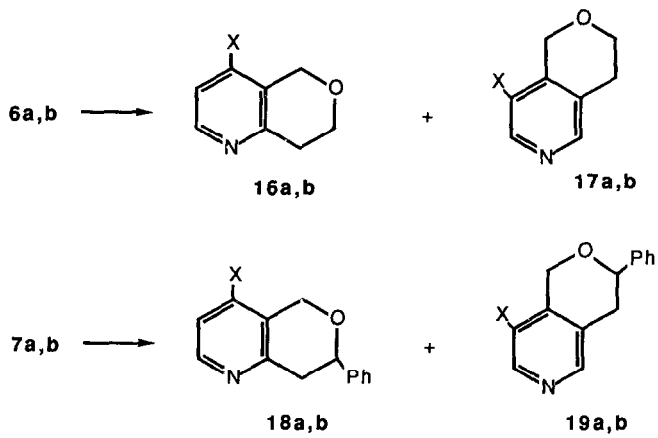
Similar results were obtained with the trimethylsilyl derivative **4b**. Also in the formation of **12b** and **13b** from **4b** a rate enhancement, when compared to **3b**, was observed although steric interference of the trimethylsilyl group plays a more significant role than in the formation of compounds **8b** and **9b**. Thermolysis of (1-phenyl-3-butynyloxy)methylpyrazine **5a** (prepared from chloromethylpyrazine and the sodium salt of 1-phenyl-3-butyn-1-ol[18]) and its trimethylsilyl derivative **5b**, when heated at 195° in undecane, required the same reaction time for complete conversion as found for **3a** and **3b**. Mixtures of the phenyl-[3,4-*b*] and [3,4-*c*] pyridines **14a, b** and **15a,b** were found, the *b*-fused systems being the major products (see table 1). This result shows that in the thermolytic reaction the influence of the γ–phenyl group on the rate of the reaction is negligible.



14a,b **15a,b**

Since the α–phenyl group increases the rate of reaction (**4a/3a** = 4) and the influence of the γ–phenyl group on the rate of cycloaddition is negligible (**3a/5a**=1) we became interested in the effect of a phenyl group present on the β–position of an alkynyloxyalkyl side chain.

For that purpose we synthesized the parent compound β-(2-propynyloxy)ethylpyrazine **6a** by reaction of the sodium salt of β-pyrazinylethanol[12,13] with 3-bromopropyne, and β-(2-propynyloxy)-β-phenylethylpyrazine **7a** by reacting the sodium salt of α-phenyl-β-pyrazinylethanol[20] with 3-bromopropyne.



16a,b **17a,b**

18a,b **19a,b**

We compared the rate of cycloaddition of **6a** and **7a** and their trimethylsilyl derivatives **6b** and **7b**. From the results of Table 1 it can be seen that the rate of **6a/7a** is about 1 indicating that the β–phenyl group has little influence on the rate of the intramolecular cycloaddition. It is interesting that compounds **6a,b** in which oxygen is present in the γ–position of the unsubstituted side chain are more reactive than compounds **3a,b**.

Table 1 Reaction conditions and yields of products in the Diels-Alder cyclisations with (alkynyloxyalkyl)pyrazines (**3-7**) in the solvent undecane.

Starting material	Reaction time(hrs)* at 195°C	Yield of product
3a	135	**8a** (40%); **9a** (22%)
3b	280	**8b** (28%); **9b** (23%)
4a	36	**12a** (38%); **13a** (13%)
4b	160	**12b** (34%); **13b** (14%)
5a	135	**14a** (31%); **15a** (20%)
5b	280	**14b** (33%); **15b** (31%)
6a	19	**16a**(21%); **17a**(31%)
6b	65	**16b**(16%); **17b**(61%)
7a	15	**18a** (30%); **19a** (53%)
7b	32	**18b** (20%); **19b** (50%)

* for complete conversion of starting material

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM 390 spectrometer. Me_4Si was used as internal standard (δ=0 ppm). Mass spectral data were obtained on a AEI MS 902 spectrometer equipped with VG ZAB console. Column chromatography was carried out over Merck silica gel 60 (230-400 mesh ASTM). Undecane was purchased from Aldrich Chemie (Brussels, Belgium).

(3-Butynyloxymethyl)pyrazine **3a**

To a solution of 4.92 g (0.07 mol) of 3-butyn-1-ol in 40 ml of dry tetrahydrofuran were added 1.27 g (0.055 mol) of sodium. The mixture was stirred for 2 h at room temperature under nitrogen. To the resulting suspension a solution of 6 g (0.047 mol) of 2-chloromethylpyrazine[9,10] in 10 ml of dry tetrahydrofuran was added. The mixture was stirred at 40°C for 2 h. After cooling 50 ml of ether and 10 ml of water were added. The pH of the water layer was diminished to 8 with a few drops of dilute hydrochloric acid. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. After column chromatography of the residue (solvent system ether/petroleum ether 40-60°, 1:10) 4.0 g (53%) of **3a** was obtained.
Ms Calcd. for $C_9H_{10}N_2O$ (M^+): m/e 162.0793. Found: m/e 162.0784. Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.64; H, 6.21; N, 17.27. Found: C, 66.35; H, 6.50; N, 17.54.
^{1}H NMR ($CDCl_3$) δ 8.84 (s, 1H), 8.57 (s, 2H), 4.8 (s, 2H), 3.80 (t, J=7.5 Hz, 2H), 2.58 (dt, J_1=7.5 Hz, J_2=2.5 Hz, 2H), 2.12 (t, J=2.5 Hz, 1H).

α–Phenyl-α–(3-butynyloxy)methylpyrazine **4a**

To a solution of 0.72 g (0.01 mol) of 3-butyn-1-ol in 20 ml of dry tetrahydrofuran were added 0.26 g (0.011 mol) of sodium. The mixture was stirred for 2 h at room temperature under

nitrogen. To the resulting suspension was added, in five portions, a solution of 1.5 g (0.006 mol) of α-bromo-α-phenylmethylpyrazine at 50°C during a period of 3.5 h. The mixture was stirred at 50°C for additional 0.5 h. After cooling 50 ml of ether and 10 ml of water were added. The pH of the water layer was reduced to 8 with a few drops of dilute hydrochloric acid. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. After column chromotography (solvent system, ether/petroleum ether 40-60°, 2:3) 0.24 g (17%) of **4a** was obtained.
Ms Calcd. for $C_{15}H_{14}N_2O$(M^+): m/e 238.1106. Found: m/e 238.1099. Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.82; N, 11.75. Found: C, 75.69; H, 6.10; N, 12.03. ^1H NMR ($CDCl_3$) δ 8.85 (s, 1H), 8.42 (s, 2H), 7.57 - 7.18 (m, 5H), 5.52 (s, 1H), 3.62 (t, J=6.6 Hz, 2H), 2.52 (dt, J_1=6.6 Hz, J_2=2.1 Hz, 2H), 1.91 (t, J=2.1 Hz, 1H).

(1-Phenyl-3-butynyloxy)methylpyrazine **5a**
To a solution of 6.0 g (0.041 mol) of 1-phenyl-3-butyn-1-ol[18] in 80 ml of dry tetrahydrofuran was added 1.0 g (0.043 mol) of sodium. The mixture was stirred at 45°C for 1 h and refluxed for an additional 1 h under nitrogen. To the resulting suspension was added a solution of 4.5 g (0.035 mol) of chloromethylpyrazine in 10 ml of dry tetrahydrofuran. The mixture was stirred at 70°C for 2 h. After cooling 50 ml of ether and 10 ml of water were added. The pH of the water layer was reduced to 8 with a few drops of hydrochloric acid. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. Column chromatography (solvent system ether/petroleum ether 40-60°, 1:2) of the residue gave 5.0 g (60%) of **5a** (mp 61-62°C, after recrystallization from petroleum ether 40-60°).
Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.75. Found: C, 75.70; H, 5.86; N, 11.87. ^1H NMR ($CDCl_3$) δ 8.90 (s, 1H), 8.50 (s, 2H), 7.38 (br s, 5H), 4.60 (m, 3H), 2.72 (m, 2H), 2.0 (t, J=2.5 Hz, 1H).

β-(2-Propynyloxy)ethylpyrazine **6a**
To a solution of 4.0 g (0.032 mol) of β-pyrazinylethanol[19] in 20 ml of dry tetrahydrofuran were added 0.82 g (0.036 mol) of sodium. The mixture was stirred at room temperature for 3 h. To the resulting suspension a solution of 4.22 g (0.036 mol) of 3-bromopropyne in 10 ml of dry tetrahydrofuran was added and the resulting mixture was stirred at 50°C for 1 h. After cooling, 50 ml of ether and 10 ml of water were added. The pH of the water layer was reduced to 8 with a few drops of dilute hydrochloric acid. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. After column chromatography of the residue (ether as eluent) 1.09 g (21%) of **6a** was obtained.
Ms Calcd. for $C_9H_{10}N_2O$ (M^+): m/e 162.0793. Found: m/e 162.0791. Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.64; H, 6.21; N, 17.27. Found: C, 6.39; H, 6.30; N, 16.98. ^1H NMR ($CDCl_3$) δ 8.67-8.40 (m, 3H), 4.18 (d, J=2.5 Hz, 2H), 3.97 (t, J=6Hz, 2H), 3.11(t, J=6 Hz, 2H), 2.5 (t, J=2.5 Hz, 1H).

β-(2-Propynyloxy)-β-phenylethylpyrazine **7a**
To a solution of 2.0 g (0.01 mol) of α-phenyl-β-pyrazinylethanol[20] in 10 ml of dry tetrahydrofuran were added 0.28 g (0.012 mol) of sodium. The mixture was stirred at room temperature for 3 h. To the resulting suspension was added a solution of 1.3 g (0.011 mol) 3-bromopropyne in 10 ml of dry tetrahydrofuran. The resulting mixture was stirred at 60°C for 3 h. After cooling 50 ml of ether and 10 ml of water were added. The pH of the water layer was reduced to 8 with few drops of hydrochloric acid. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. After column chromatography of the residue (solvent system ether/petroleum ether 40-60°, 1:1) 0.69 g (25%) of **7a** (mp. 33-35°C) was obtained.
Ms Calcd. for $C_{15}H_{14}N_2O$ (M^+): m/e 238.1106. Found: m/e 238.1109. Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.75. Found: C, 75.72; H, 5.96; N, 11.76. ^1H NMR ($CDCl_3$) δ 8.62-8.42 (m, 3H), 7.35 (br s, 5H), 5.02 (dd, J_1=9Hz, J_2=6Hz, 1H); 4.15 and 3.85 (two dd, J_1=15.3Hz, J_2= 2.5 Hz, 2H), 3.22 (m, J_1= 15 Hz, J_2=9Hz, J_3=6Hz, 2H), 2.30 (t,J=2.5Hz, 1H).

α-Bromo-α-phenylmethylpyrazine **11**
To a solution of 4.2 g (0.025 mol) of benzylpyrazine[17] in 50 ml of dry carbon tetrachloride were added 4.8 g (0.028 mol) of N-bromosuccinimide and 0.05 g of dibenzoyl peroxide. After cooling to 0°C the suspension in carbon tetrachloride was filtered and the filtrate evaporated under reduced pressure. After column chromatography (solvent system ether/petroleum ether 40-60°, 1:4) 2.0 g (32%) of **11** (mp 69-70°C, after recrystallization from petroleum ether 40-60°) was obtained. Anal. Calcd. for $C_{11}H_9BrN_2$: C, 53.03; H, 3.64; N, 11.32. Found: C, 53.13; H, 3.67; N,

11.32. ^{1}H NMR ($CDCl_3$) δ 8.80 (d, J=1.2Hz, 1H), 8.55 (m, 2H), 7.62-7.24 (m, 5H), 6.22 (s, 1H).

Table 2 Yield, mass spectral and ^{1}H NMR data of the silylated compounds **3b**, **4b**, **5b**, **6b** and **7b**.

Compound	Yield %	Ms (M^+) Calcd. Found	^{1}H NMR ($CDCl_3$)
3b	74	234.1188 234.1186	8.82 (s, 1H), 8.53 (s, 2H), 4.73 (s, 2H), 3.73 (t, J=7.0 Hz, 2H), 2.59 (t, J=7.0 Hz, 2H), 0.14 (s, 9H)
4b*	67	310.1501 310.1493	8.90 (s, 1H), 8.45 (s, 2H), 7.55-7.24 (m, 5H), 5.57 (s, 1H), 3.65 (t, J=6.9Hz, 2H), 2.62 (t, J=6.9 Hz, 2H), 0.14 (s, 9H)
5b	81	295.1266** 295.1267**	8.94 (s, 1H), 8.50 (s, 2H), 7.38 (br s, 5H), 4.64 (m, 3H), 2.73 (m, 2H), 0.13 (s, 9H).
6b	72	234.1188 234.1190	8.68-8.40 (m, 3H), 4.15 (s, 2H), 3.94 (t, J=6Hz, 2H), 3.08(t, J=6Hz, 2H), 0.13 (s,9H).
7b	73	310.1501 310.1513	8.58-8.38 (m, 3H), 7.30 (br s, 5H), 5.00 (dd, J_1=9Hz, J_2=6Hz, 1H), 4.09 and 3.90 (two dd, J=15.3 Hz, 2H), 3.20 (m, J_1=15Hz, J_2=9Hz, J_3=6Hz, 2H), 0.13 (s, 9H)

* Mp 41-42°C, Anal. Calcd. for $C_{18}H_{22}N_2OSi$: C, 75.60; H, 5.92; N, 11.75 Found: C, 75.69; H, 6.10; N, 12.03

** No molec. peak M^+ was found. Only the fragmentation peak M^+-15 was observed.

General procedure for preparation of the trimethylsilyl derivatives **3b**, **4b**, **5b**, **6b** and **7b**

To 0.002 mol of compounds (**3a** - **7a**) dissolved in 10 ml of dry tetrahydrofuran and cooled below -70°C, under nitrogen, a commercial ether-cyclohexane solution of phenyl lithium (0.003 mol) was added dropwise while keeping temperature below -65°C. After 5 min 0.003 mol of trimethylsilyl chloride dissolved in 5 ml of dry tetrahydrofuran was added dropwise, keeping temperature below -65°C. After the addition the temperature of the mixture was allowed to rise to -40°C. The mixture was stirred at this temperature for 0.5 h and the temperature was allowed to rise gradually to 0°C during the next hour. Then 50 ml of ether and 2 ml of 10% aqueous hydrochloric acid were added. The pH of the water layer was adjusted between 8 to 9 with solid sodium bicarbonate. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The liquid residue was purified by column chromatography using as solvent system ether/petroleum ether 40-60°, 1:1 to give **3b**, **5b-7b** as an oil and **4b** as a solid. Yields, mass spectral and ^{1}H NMR data are given in Table 2.

General procedure for the intramolecular Diels-Alder reaction of pyrazines (**3-7**)

A solution of 0.3 g of pyrazines (**3-7**) in 1 ml of undecane (compounds **3a-7a** dissolved in undecane only at 195°C, the silylated compounds **3b-7b** dissolved at room temperature) was heated under nitrogen under conditions depending on the substrate (see Table 1). The resulting solution was chromatographed [solvent system ether/petroleumether 40-60°; ratio 1:1 (for **8a**, **9a**, **12a**, **13a**, **14a**, **15a**, **16b**, **17b**, **18a** and **19a**); ratio 1:2 (for **8b**, **9b**, **12b** and **13b**); ratio 1:10 (for **14b** and **15b**) and ratio 1:3 (for **18b** and **19b**); only ether for **16a** and **17a**. Mass spectral, ^{1}H NMR and elemental analyses data of the obtained compounds are summarized in Table 3.

Table 3 Mass spectral, ^1H NMR and elemental analyses data of Diels-Alder products

Products	Mp °C	Ms (M^+) Calcd. Found	Anal. Calcd./ Found	^1H NMR ($CDCl_3$) δ
8a	oil	135.0684 135.0686		8.49 (d, J=5.4 Hz, 1H), 7.49 (d, J=7.2 Hz, 1H), 7.16 (dd, J_1 = 7.5 Hz, J_2=4.8 Hz, 1H), 4.83 (s, 2H), 4.00 (t, J=6.0Hz, 2H), 3.85 (t, J = 6.0Hz, 2H)
9a	oil	135.0684 135.0678		8.41 (d, J=5.6Hz, 1H), 8.33 (s, 1H), 7.08 (d, J=5.6Hz, 1H), 4.78 (s, 2H), 3.98 (t, J=6.0Hz, 2H), 2.85 (t, J=6.0Hz, 2H)
8b	oil	207.1080 207.1082		8.38 (d, J=4.8 Hz, 1H), 7.23 (d, J=4.8 Hz, 1H), 4.80 (s, 2H), 3.98 (t, J=5.7 Hz, 2H), 2.92 (t, J=5.7 Hz, 2H), 0.33 (s, 9H)
9b	oil	207.1080 207.1089		8.51 (s, 1H), 8.28 (s, 1H), 4.85 (s, 2H), 4.04 (t, J=6.0Hz, 2H), 2.94 (t, J=6.0Hz, 2H), 0.34 (s, 9H)
12a	35-38	211.0997 211.0996	C, 79.59/79.86 H, 6.20/6.46 N, 6.63/6.74	8.42 (d, J= 4.8 Hz, 1H), 7.50 (d, J=7.5 Hz, 1H), 7.34 (br s, 5H), 7.10 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 1H), 5,81 (s, 1H), 4.30-3.73 (m, 2H), 3.28-2.68 (m, 2H)
13a	45-48	211.0997 211.0988	C, 79.59/79.87 H, 6.20/6.38 N, 6.63/6.57	8.42 (d, J=4.8 Hz, 1H), 8.08 (s, 1H), 7.38 (br s, 5H), 7.12 (d, J=4.8, 1H), 5.75 (s, 1H), 4.35-3.75 (m, 2H), 3.32-2.63 (m, 2H)
12b	oil	283.1392 283.1392		8.40 (d, J=4.8 Hz, 1H), 7.34 (br s, 5H), 7.22 (d, J=4.8 Hz, 1H), 5.86 (s, 1H), 4.30-3.78 (m, 2H), 3.32-2.75 (m, 2H), 0.34 (s, 9H)
13b	53-55	283.1392 283.1393	C, 72.03/72.33 H, 7.46/7.66 N, 4.94/4.98	8.50 (s, 1H), 8.02 (s,1H), 7.34 (br s, 5H), 5.76 (s, 1H), 4.27-3.67 (m. 2H), 3.36-2.68 (m, 2H), 0.35 (s, 9H)
14a	51-53	211.0997 211.1001	C, 79.59/79.49 H, 6.20/6.03 N, 6.63/6.46	8.46 (d, J=4.8 Hz, 1H), 7.54-7.25 (m, 6H), 7.15 (dd, J_1=7.5 Hz, J_2=4.8Hz, 1H), 5.02 (s, 2H), 4.78 (dd, J_1=9Hz, J_2=5.4 Hz, 1H), 3.30-2.80 (m, 2H)
15a	93-96	211.0997 211.0998	C, 79.59/79.60 H, 6.20/6.23 N, 6.63/6.84	8.44 (d, J=5.4 Hz, 1H), 8.37 (s, 1H), 7.38 (br s, 5H), 7.08 (d, J=5.4 Hz, 1H), 4.94 (s, 2H), 4.71 (dd, J_1=7.5 Hz, J_2=6.6 Hz, 1H), 3.08 (d, J= 6.6 Hz, 2H)
14b	oil	283.1392 283.1397		8.44 (d, J=4.5 Hz, 1H), 7.42 (br s, 5H), 7.26 (d, J=4.5, 1H), 5.08 (s, 2H), 4.78 (t, J=6.6 Hz, 1H), 3.09 (d, J=6.6 Hz, 2H), 0.34 (s, 9H)
15b	oil	283.1392 283.1396		8.55 (s, 1H), 8.35 (s, 1H), 7.47 (br s, 5H), 5.02 (s, 2H), 4.75 (t, J=6.6 Hz, 1H), 3.08 (d, J=6.6 Hz, 2H), 0.33 (s, 9H)

16a	oil	135.0684 135.0690		8.41 (d, J=4.8 Hz, 1H), 7.28 (d, J=4.8 Hz, 1H) 7.07 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 1H), 4.85 (s, 2H), 4.07 (t, J=6 Hz, 2H), 3.0 (t, J=6 Hz, 2H).
17a	oil	135.0684 135.0691		8.36 (m, 2H), 6.88 (d, J=5.4 Hz, 1H), 4.7 (s, 2H), 3.97 (t, J=6 Hz, 2H), 2.8 (t, J=6 Hz, 2H)
16b	oil	207.1080 207.1072		8.41 (d, J=4.8 Hz, 1H), 7.22 (d, J=4.8 Hz, 1H), 4.88 (s, 2H), 4.08 (t, J=6 Hz, 2H), 3.07 (t, J=6 Hz, 2H), 0.34 (s, 9H)
17b	oil	207.1080 207.1072		8.45 (s, 1H), 8.36 (s, 1H), 4.85 (s, 2H), 4.04 (t, J=6 Hz, 2H), 2.88 (t, J=6 Hz, 2H), 0.36 (s, 9H)
18a	47-49	211.0997 211.0995	C, 79.59/79.45 H, 6.20/6.30 N, 6.63/6.60	8.46 (d, J=4.8 Hz, 1H), 7.40 (br s, 5H), 7.30 (d, J=7.5 Hz, 1H), 7.12 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 1H), 4.96 (s, 2H), 4.83 (t, J=7.0 Hz, 1H), 3.20 (d, J=7.0 Hz, 2H)
19a	31-32	211.0997 211.0994	C, 79.59/79.73 H, 6.20/6.36 N, 6.63/6.56	8.48 (m, 2H), 7.44 (br s, 5H), 7.04 (d, J=5.4 Hz, 1H), 4.98 (s, 2H), 4.75 (t, J=6.9 Hz, 1H), 3.02 (d, J=6.9 Hz, 2H)
18b	oil	283.1392 283.1398		8.53 (d, J=4.8 Hz, 1H), 7.48 (br s, 5H), 7.30 (d, J=4.8 Hz, 1H), 5.18 and 4.96 (two d, J=18.5 Hz, 2H), 4.92 (t, J=7.2 Hz, 1H), 3.32 (d, J=7.2 Hz, 2H), 0.34 (s, 9H)
19b	118- 120	283.1392 283.1392	C, 72.03/71.89 H, 7.46/7.47 N, 4.94/4.78	8.50 (s, 1H), 8.38 (s, 1H), 7.38 (br s, 5H), 5.12 and 4.90 (two d, J=18.5 Hz, 2H), 4.71 (t, J=7.2 Hz, 1H), 3.02 (d, J=7.2 Hz, 2H), 0.33 (s, 9H)

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