Synthesis of Unsymmetrical Annulated 2,2’-Bipyridine Analogues with Attached Cycloalkene and Piperidine Rings via Sequential Diels-Alder Reaction of 5,5’-bi-1,2,4-triazines†

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Abstract: Synthesis of bisfunctionalized unsymmetrical 2,2’-bipyridines 8 or their sulfonyl derivatives 12a,b are described. They were prepared via the Diels-Alder reaction of 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydropyridine (6) with 3,3’-bis(methyl-sulfanyl)-5,5’-bi-1,2,4-triazine (1). The reaction leads to the single cycloaddition product 7 which undergoes Diels-Alder reaction with cyclic enamines 2a,b to give unsymmetrical 2,2’-bipyridine derivatives 8, consisting of the two different heterocyclic units: cycloalkeno[c]pyridine and 2,6-naphthyridine.

Keywords: bi-1,2,4-Triazines, Diels-Alder reaction, isocyclic and heterocyclic enamines

Introduction

Functionalized 2,2’-bipyridines have a wide range of applications in many areas of chemistry [2]. Especially interesting and useful are their annulated derivatives with benzo fusion incorporated into larger macropolycyclic structures, since they form stable luminescent complexes with a variety of lanthanide cations [3]. The transition metal complexes of chiral cycloalkenobipyridines have recently been employed as catalysts in a number of asymmetric reactions such as asymmetric cyclopropanation of alkenes [4], asymmetric alkylation of aldehydes [5], asymmetric hydrogenation and hydrosilylation [6] and asymmetric palladium catalysed allylic alkylation [7]. Although, there are several methods to synthesize annulated bipyridines with benzo fusion [8] only a limited number of reports have appeared regarding their analogues with saturated rings attached. The preparation of these ligands often rely on
the transition-metal mediated heteroaryl cross-coupling reactions of specially prepared pyridines [9] or on the Kröhnke-type synthesis starting from $\alpha$, $\beta$-unsaturated ketones [10]. More recent approaches employ cobalt (I) catalysed $[2+2+2]$ cycloadditions between 5-hexenenitrile and 1,3-diynes [11] or the double intramolecular Diels-Alder reactions of $\alpha$, $\beta$-unsaturated hydrazones with 1,3-dialkynes [12]. Alternatively, the construction of the fused pyridine ring can be achieved via intermolecular or intramolecular Diels-Alder (IDA) reactions of 1,2,4-triazines with inverse electron-demand [13]. We have applied this methodology to the direct synthesis of symmetrical and unsymmetrical annulated 2,2'-bipyridines 4 and 5 via the reaction of 5,5'-bi-1,2,4-triazine (1) with cyclic enamines 2a-d [14-16] (Scheme 1). This approach has been based on the regioselective, intermolecular $[4+2]$ cycloaddition of 1 with cyclic enamines 2 to give a common intermediate 3. Subsequent treatment of the latter with the appropriate enamine leads to the annulated 2,2'-bipyridines 4 or 5 respectively.

Scheme 1

![Scheme 1](image.png)

Results and Discussion

This paper describes the extension of the method to the synthesis of annulated 2,2'-bipyridine analogues 8, consisting of the two different heterocyclic units – 2,6-naphthyridine and cycloalkeno[c]pyridine (Scheme 2). The preparation of such compounds could involve the regiospecific conversion of the parent 3,3'-bis(methylsulfanyl)-5,5'-bi-1,2,4-triazine (1) to the single cycloaddition product 7 and the subsequent treatment of the latter with the cyclic enamine 2a,b (route a), or alternatively, the IDA reaction of the easily accessible 3a,b with the appropriate dienophile 6 (route b).

Compound 7 was obtained via the single step $[4+2]$cycloaddition/retro cycloaddition reaction of easily available compound 1 [16] with 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydropyridine (6). The reaction was carried out with 1.5 molar excess of 6 in the boiling dioxane for 1h. The product 7 precipitated from the crude reaction mixture in 92 % yield. In the reaction of 1 with 6 the formation of two isomeric 2,6- or 2,7-tetrahydronaphthyridine derivatives can be anticipated considering it involves the use of an unsymmetric enamine. However, the reaction gives only one reaction product in the excellent yield. Its $^1$H-NMR spectrum exhibited two signals of isolated aromatic protons at $\delta=9.97$ and $\delta=7.94$ ppm respectively. The former signal belongs to 1,2,4-triazine and the latter one is attributed to
the pyridine hydrogen. The separate signal of isolated methylene group appears at δ=3.65, and the multiplet at δ=2.77 can only corresponds to four vicinal hydrogens in saturated pyridine ring. Nuclear Overhauser Enhancement difference spectroscopy provided an unambiguous assignment for this compound. It was found that irradiation of a proton in aromatic pyridine ring (δ=7.94 ppm) led to significant NOE for the signal of the isolated methylene group in the saturated pyridine ring (δ=3.65). These results and the lack of such interactions with the multiplet at δ=2.77 provide evidence for spatial closeness of the pyridine hydrogen and CH₂ and confirm the 2,6-tetrahydronaphthyridine derivative structure of 7.

Scheme 2
Heating 7 with an excess of 1-pyrrolidino-1-cyclopentene (2a, n=1) at 100 °C for 15 hours gives annulated 2,2'-bipyridine dihydroanalogue 8'a as a reaction intermediate. The latter is simply converted into 8a by heating with acetic acid in boiling toluene for 1 hour. Using less reactive 1-pyrrolidino-1-cyclohexene (2b, n=2) [11] and the similar reaction conditions, the annulated 2,2'-bipyridine analogue 8b with a cyclohexene ring attached is prepared in low yield, while the corresponding pyrrolidino derivative 9 is obtained as a main product. This compound is also obtained by treatment of 3,3'-bis(methylsulfanyl)-5,5'-bi-1,2,4-triazine (1) with an excess of 6 without solvent at 100 °C. Compound 9 is obviously formed by conventional nucleophilic replacement of methylsulfanyl group in 1,2,4-triazine part of 7. The single annulation products 3a (n=1) and 3b (n=2) undergo to small extent Diels-Alder reaction with 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydro-pyridine (6) to yield compounds 8a and 8b in low yield. Reaction of such derivatives has been found to result in a rather nucleophilic substitution of methylsulfonyl group in 3a and 3b giving compounds 10a and 10b respectively (Table 1). These results suggest that compound 6 is less reactive and less stable as a dienophile in comparison to cycloalkeno derived enamines 2a and 2b.

### Table 1. Yields of prepared compounds.

| Entry | Reaction | 8a   | 8'a  | 8b  | 9    | 10a | 10b |
|-------|----------|------|------|------|------|-----|-----|
| 1     | 7 + 2a   | <1%  | 60%  | -    | -    | -   | -   |
| 2     | 3a + 6   | 23%  | 8%   | -    | -    | 30% | -   |
| 3     | 7 + 2b   | -    | -    | 10%  | 50%  | -   | -   |
| 4     | 3b + 6   | -    | -    | 5%   | -    | -   | 64% |
| 5     | 1 + 6    | -    | -    | -    | 72%  | -   | -   |
| 6     | 8'a+HOOAc| 98%  | -    | -    | -    | -   | -   |

In order to help us better characterize the cycloaddition reactions of 3a,b with 6 as well as cyclic enamines 2a,b with 7, we calculated the energy differences (ΔE) between the LUMO of diene and HOMO of dienophile, using the AM1 semiempirical method [17]. The results are presented in Table 2. A better orbital overlap should be obtained between the HOMO orbital of cyclic enamines 2a,b and the LUMO orbital of the 7 than in combination of 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydropyridine 6 with 3a,b because the energy gaps are smaller and range from 0.02 to 0.05 eV.

### Table 2. Energy Values of the HOMO of Dienophiles Calculated by the AM1 Semiempirical method, and LUMO<sub>diene</sub> – HOMO<sub>dienophile</sub> Energy Differences (ΔE)

| Dienophile E<sub>HOMO</sub> (eV) | Comp. | ΔE   |
|----------------------------------|-------|------|
| 6: -8.2212                      |       | (E<sub>LUMO diene</sub> 7a - E<sub>HOMO dienophile</sub> 2a,b) |
| 2a: -8.0790                     | 8a    | 7.1193 |
| 2b: -8.0823                     | 8b    | 7.1226 |

- E<sub>LUMO diene</sub> 7a = 2.0871 eV
- E<sub>HOMO dienophile</sub> 2a,b = 4.9680 eV
- E<sub>LUMO diene</sub> 3a,b = 2.0375 eV
- E<sub>HOMO dienophile</sub> 6 = 2.9862 eV
From the above data it is clear that compounds 3a,b are not suitable intermediates for the synthesis of bipyridine derivatives 8a,b. It is well known however that introduction of electron-withdrawing substituents increases deficiency in the 1,2,4-triazine ring and enhances its reactivity in Diels-Alder reaction [12]. We have therefore explored the reaction between 6 and methylsulfonyl derivatives 11a,b, easily available by oxidation of 3a,b with KMnO₄ under phase transfer catalysis conditions [18] (Scheme 3). The reaction of 11a,b with heterocyclic enamine 6 is complete within 1 hour at room temperature leading to unsymmetrical annulated 2,2’-bipyridine analogues 12a and 12b in good yield (Scheme 3).

Scheme 3

Conclusions

In summary, we have developed a new route to unsymmetrical annulated 2,2’-bipyridine analogues with cycloalkene and piperidine rings attached bearing alkylsulfanyl and alkylsulfonyl groups in both pyridine rings. The presence of such leaving groups makes these compounds attractive as building blocks for the synthesis of macrocycles.

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Experimental

General

Melting points are uncorrected. IR spectra were measured with a Magna IR-760 spectrophotometer. The ¹H-NMR spectra were recorded in deuteriochloroform on a Varian-Gemini 200 MHz spectrometer. Mass spectra were measured with an AMD 604 (AMD Intectra GmbH, Germany). Column chromatography was performed on silica gel (230-400 mesh, 60 Merck). All solvents used were dried and distilled according to standard procedures [21]. Merck 60F₂₅₄ plates were used for analytical (TLC) chromatography. 3-Methylsulfanyl-1,2,4-triazine (1)[22], 1-methyl-sulfonyl-3-(3-methylsulfonyl-1,2,4-triazin-5-yl)-6,7-dihydro-5H-cyclopenta[c]pyridine (11a) and 1-methylsulfonyl-3-(3-methyl-sulfonyl-
1,2,4-triazin-5-yl)-5,6,7,8-tetrahydroisioquinoline (11b)[20], 1-methyl-4-pyrrolidin-1-yl-1,2,3,4-tetrahydropropyridine (6) and 1-pyrrolidino-1-cyclopentene (2a) and 1-pyrrolidino-1-cyclohexene (2b) [23] were prepared according to literature methods. Naphthyridine derivatives 8a,b and 12a,b are air sensitive and decompose upon standing.

2-Methyl-5-methylsulfanyl-7-(3-methylsulfanyl-1,2,4-triazin-5-yl)-1,2,3,4-tetrahydro-2,6-naphthyridine (7): A solution of 1 (1.25 g, 4.96 mmol) and 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydropyridine (6, 1.2 g, 7.23 mmol) in dry dioxane (20 mL) was refluxed for 1 h. The solvent was evaporated under reduced pressure and the residue was recrystallized from ethanol-water to give 1.4 g (92 %) of 7 as an orange solid. M. p. 205-206 ºC; IR (KBr) γ cm⁻¹ 1165, 1440, 1540, 2800, 2960; ¹H-NMR δ: 2.42 (s, 3H), 2.60-2.90 (m, 4H), 2.65 (s, 3H), 2.80 (s, 3H), 3.65 (s, 2H), 7.94 (s, 1H), 9.97 (s, 1H); HRMS (EI): m/z calc. for C₁₄H₁₇N₅S₂ (M⁺): 319.09253, found 319.09604.

2-Methyl-5-methylsulfanyl-7-(3-pyrrolidin-1-yl-1,2,4-triazin-5-yl)-1,2,3,4-tetrahydro-2,6-naphthyridine (9): A mixture of 3,3'-bis(methylsulfanyl)-5,5'-bi-1,2,4-triazine (1, 0.50 g, 1.98 mmol) and 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydropyridine (6, 3 mL) was heated at 100 ºC for 16 h. After cooling the mixture was purified by column chromatography using first chloroform and next chloroform-acetone (50:1) to give 0.69 g (72 %) of 9 as a yellow solid. M. p. 205-206 ºC; IR (KBr) γ cm⁻¹ 1251, 1485, 1538, 2873, 2942; ¹H-NMR δ: 2.03-2.07 (m, 4H), 2.47 (s, 3H), 2.66 (s, 3H), 2.76 (s, 4H), 3.60 (s, 2H), 3.74 (broad s, 4H), 7.84 (s, 1H), 9.54 (s, 1H); HRMS (EI): m/z calc for C₁₇H₂₂N₆S (M⁺): 342.16267, found 342.16317.

2-Methyl-5-methylsulfanyl-7-(1-methylsulfanyl-6,7-dihydro-5H-cyclopenta[c]pyridin-3-yl)-1,2,3,4-tetrahydro-2,6-naphthyridine (8a) and 2-methyl-5-methylsulfanyl-7-(1-methylsulfanyl-7a-pyrrolidin-1-yl-5,6,7,7a-tetrahydro-4aH-cyclopenta[c]pyridin-3-yl)-1,2,3,4-tetrahydro-2,6-naphthyridine (8’a): The synthesis of compound 8a was accomplished by two different routes (a and b, respectively):

Route a: A mixture of 7 (0.36 g, 1.18 mmol) and 2a (2.5 mL) was heated at 100 ºC for 16 h. After cooling the mixture was purified by column chromatography using first chloroform and next chloroform-acetone (50:1) to give 8a and 8’a (0.30 g, 60 %). The mixture of the crude dihydro derivative 8’a (0.20g, 0.47 mmol), toluene (10 mL) and HOAc (1mL) was refluxed for 1 h. After cooling the precipitated solid was filtered off and recrystallized from ethanol to give 0.16 g (98 %) of 8a as a yellow solid.

8a: M. p. 209-211 ºC; IR (KBr) γ cm⁻¹ 1200, 1404, 1576, 2766, 2945; ¹H-NMR δ: 2.17 (qui, 2H, J=7.4 Hz), 2.48 (s, 3H), 2.70 (s, 6H), 2.78 (s, 4H), 2.83 (t, 2H, J=7.5 Hz), 3.02 (t, 2H, J=7.5 Hz), 3.62 (s, 2H), 7.84 (s, 1H), 8.06 (s, 1H); HRMS (EI): m/z calc for C₁₉H₂₃N₅S₂ (M⁺): 357.1334, found 357.13433.

8’a: M. p. 170-171 ºC; IR (KBr) γ cm⁻¹ 1240, 1303, 1575, 2803, 2947; ¹H-NMR δ: 1.54-1.60 (m, 2H), 1.66-1.71 (m, 5H), 2.09-2.35 (m, 4H), 2.45 (s, 3H), 2.49 (s, 4H), 2.62 (s, 3H), 2.51-2.75 (m, 4H), 2.72
(m, 3H), 3.55 (s, 2H), 6.91 (d, 1H, \(J=6.1\) Hz), 7.51 (s, 1H); HRMS (EI): \(m/z\) calc for \(\text{C}_{23}\text{H}_{32}\text{N}_{4}\text{S}_{2} (\text{M}^+)\): 428.20684, found 428.20728.

**Route b:** A mixture of 3a (0.26 g, 0.89 mmol) and 6 (2 mL) was heated at 100 °C for 16 h. After cooling the mixture was purified by column chromatography using chloroform and next chloroform: acetone (50:1) to give 8a (0.08 g, 23 %) and 1-methylsulfanyl-3-(3-pyrrolidin-1-yl-1,2,4-triazin-5-yl)-6,7-dihydro-5H-cyclopenta[c]pyridine (10a, 0.085 g, 30 %). M. p. 220-221ºC; IR (KBr) \(\gamma \text{ cm}^{-1} 1289, 1396, 1534, 2870, 2942\); \(^1\text{H-NMR} \delta: 2.0-2.1 (\text{m}, 4\text{H}), 2.09 (\text{qui}, 2\text{H}, \(J=7.4\) Hz), 2.68 (s, 3H), 2.88 (t, 2H, \(J=6.1\) Hz), 2.98 (t, 2H, \(J=6.0\) Hz), 3.74 (broad s, 4H), 8.05 (s, 1H), 9.54 (s, 1H); HRMS (EI): \(m/z\) calc for \(\text{C}_{16}\text{H}_{20}\text{N}_{5}\text{S} (\text{M}+ \text{H})\) calculated 314.1434 found 314.1443.

2-Methyl-5-methylsulfanyl-7-(1-methylsulfanyl-5,6,7,8-tetrahydroisoquinolin-3-yl)-1,2,3,4-tetrahydro-2,6-naphthyridine (8b):

The synthesis of compound 8b has been accomplished by two different routes (a or b).

**Route a:** A mixture of 7 (0.36 g, 1.18 mmol) and 2b (2.5 mL) was heated at 100 ºC for 16 h. After cooling the mixture was purified by column chromatography using first chloroform and next chloroform-acetone (50:1) to give 8b (0.042 g, 10 %) and 9 (0.19 g, 50%).

8b: M. p. 210-212 ºC; IR (KBr) \(\gamma \text{ cm}^{-1} 1292, 1377, 1573, 2766, 2947\); \(^1\text{H-NMR} \delta: 1.78-1.90 (\text{m}, 4\text{H}), 2.48 (s, 3H), 2.59-2.65 (t, 2\text{H}, \(J=6.1\)Hz), 2.67 (s, 3H), 2.69 (s, 3H), 2.77 (s, 4\text{H}), 2.80 (t, 2\text{H}, \(J=6.0\) Hz), 3.62 (s, 2\text{H}), 7.83 (s, 1\text{H}), 7.86 (s, 1\text{H}); HRMS (EI): \(m/z\) calc for \(\text{C}_{20}\text{H}_{25}\text{N}_{3}\text{S}_{2} (\text{M}^+)\): 371.14899, found 371.14830.

**Route b:** A mixture of 3b (0.29 g, 0.95 mmol) and 6 (2 mL) was heated at 100 ºC for 32h. After cooling the mixture was purified by column chromatography using first chloroform and next chloroform-acetone (50:1) to give 8b (0.001 g, 5 %) and 1-methylsulfanyl-3-(3-pyrrolidin-1-yl-1,2,4-triazin-5-yl)-5,6,7,8-tetrahydroisoquinoline (10b, 0.02 g, 64 %). M. p. 131-132 ºC; IR (KBr) \(\gamma \text{ cm}^{-1} 1289, 1396, 1534, 2870, 2942\); \(^1\text{H-NMR} \delta: 1.79-1.92 (\text{m}, 4\text{H}), 2.03-2.17 (\text{m}, 4\text{H}), 2.62 (t, 2\text{H}, \(J=6.1\) Hz), 2.66 (s, 3H), 2.80 (t, 2\text{H}, \(J=6.0\) Hz), 3.75 (broad s, 4\text{H}), 7.86 (s, 1\text{H}), 9.55 (s, 1\text{H}); HRMS (EI): \(m/z\) calc for \(\text{C}_{17}\text{H}_{21}\text{N}_{5}\text{S} (\text{M}^+)\): 327.15177, found 327.15139.

2-Methyl-5-methylsulfonyl-7-(1-methylsulfonyl-6,7-dihydro-5H-cyclopenta[c]pyridine (12a): A mixture of 11a (1.24 g, 3.5 mmol) and 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydro-pyridine (6, 1.16 g, 6.98 mmol) in dioxane (16 mL) was stirred at room temperature for 1 h. The crude product was purified by column chromatography using chloroform-acetone (10:1) as eluent, to give 0.83 g (56 %) of 12a as a yellow solid. M. p. 199-200 ºC; IR (KBr) \(\gamma \text{ cm}^{-1} 1200, 1404, 1576, 2766, 2945\); \(^1\text{H-NMR} \delta: 1.95-2.1 (\text{m}, 2\text{H}), 2.24 (\text{qui}, 2\text{H}, \(J=7.5\) Hz), 2.49 (s, 3H), 2.77 (t, 2\text{H}, \(J=7.5\) Hz), 3.07 (t, 2\text{H}, \(J=7.6\) Hz), 3.37 (s, 3H), 3.39-3.48 (m, 2\text{H}), 3.48 (s, 3H), 3.73 (s, 2\text{H}), 8.20 (s, 1\text{H}), 8.32 (s, 1\text{H}); HRMS (LSIMS): \(m/z\) calc for \(\text{C}_{10}\text{H}_{28}\text{O}_{4}\text{N}_{3}\text{S}_{2} (\text{M}+\text{H})\): 422.12082, found 422.12017.
2-Methyl-5-methylsulfonyl-7-(1-methylsulfonyl-5,6,7,8-tetrahydroisoquinolin-3-yl)-1,2,3,4-tetrahydro-2,6-naphthyridine (12b): A mixture of 11b (0.56 mg, 1.54 mmol) and 1-methyl-4-pyrrolidin-1-yl-1,2,3,6-tetrahydro-pyridine (6, 0.52 g, 3.08 mmol) in dioxane (16 mL) was stirred at room temperature for 0.5 h under nitrogen. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using chloroform-acetone (10:1) as eluent, to give 0.58 g (62 %) of 12b as a yellow solid. M. p. 285-286 ºC; IR (KBr) γ cm⁻¹ 1128, 1302, 1586, 2931, 3011; 1H-NMR δ: 1.78-1.90 (m, 6H), 2.50 (s, 3H), 2.78 (t, 2H, J=5.9 Hz), 2.90-3.00 (m, 2H), 3.25-3.40 (m, 2H), 3.48 (s, 6H), 3.76 (s, 2H), 8.06 (s, 1H), 8.10 (s, 1H); HRMS (LSIMS): m/z calc for C₂₀H₂₆O₄N₃S₂ (M+ H): 436.13647, found 436.13755.

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*Sample Availability:* Available from the author.

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