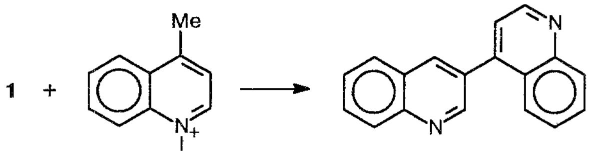
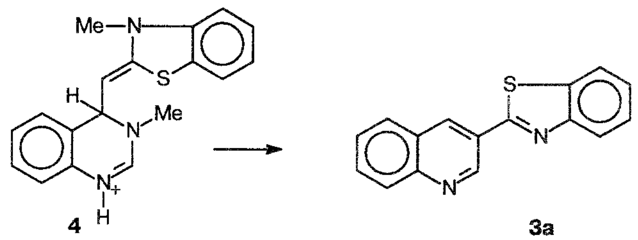
In a similar way, [3,4′]biquinolyl (**3d**) was obtained in 19 % yield from 1,4-dimethylquinolinium iodide (**2d**).



2d **3d**

Previously,[1] we have observed the formation of compounds analogous to adduct **4** in the reaction of a quaternary salt of a heterocyclic base with *N*-methylquinazolinium iodide **1** by the action of triethylamine in MeCN. These products then underwent opening of the pyrimidine ring of the quinazoline bicycle. It could be assumed that compound **4**, formed by the nucleophilic attack of position 4 of the quinazoline bicycle of quaternary salt **2a** by the enamine carbon atom of the anhydro base, is one of the possible intermediates in the synthesis of arylquinolines **3**. In fact, boiling adduct **4** in pyridine also gives compound **3a**, although in a low yield (5 %).

The structure of the hetarylquinolines **3** obtained was established by ^{1}H NMR and confirmed by the agreement of the melting points of compounds **3a,c** with the literature data.[2,3]



4 **3a**

The reaction studied is a previously unknown type of transformation of the pyrimidine ring by *C*-nucleophiles,[4] which opens up a new way to synthesize luminophores based on di- and polyhetaryls.[5]

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Regio- and stereoselective method for the synthesis of 6α,7α-methylene-6,7-dihydrothebaine

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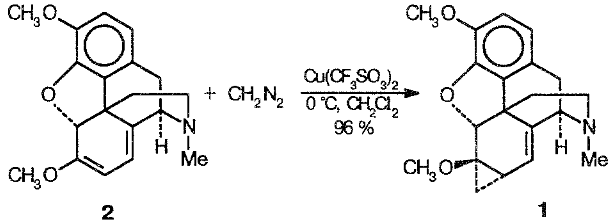
Thebaine and its derivatives are of substantial interest in practical medicine as analgesics.[1–4]

We have elaborated a regio- and stereoselective method for synthesizing a hitherto unknown member of the series of hydrophenanthrene alkaloids, *viz.*, 6α,7α-methylene-6,7-dihydrothebaine (**1**), in 96 % yield from thebaine (**2**) and diazomethane by the action of



2 **1**

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copper triflate. The $Cu(CF_3SO_3)_2$-catalyzed [1+2]-cycloaddition of the carbene generated from CH_2N_2 occurs strictly selectively (with ~100 % selectivity) to the trisubstituted C(6)=C(7) double bond in the *cis*-position relative to the benzodihydrofuran fragment of the original thebaine molecule.

The catalysts $Pd(OAc)_2$, $Pd(acac)_2$, and $Rh_2(CF_3CO_2)_4$ turned out to be inefficient in this reaction.

A solution of CH_2N_2 (obtained from 2.2 g of *N*-nitroso-*N*-methylurea) in CH_2Cl_2 (22 mL) was added dropwise at 0 °C over 10 min to a stirred solution of thebaine **2** (0.5 g, 1.6 mmol) and $Cu(CF_3SO_3)_2$ (0.012 g, 0.033 mmol) in CH_2Cl_2 (10 mL). The solvent was evaporated, and the product was chromatographically purified on a column with SiO_2 ($CHCl_3$ as the eluent) to give 0.5 g (96 %) of compound **1**, m.p. 156.5—157.5 °C. ^{13}C NMR ($CDCl_3$), δ: 15.86 d; 22.59 t; 24.61 t; 25.91 s; 34.27 t; 42.04 s; 43.28 q; 47.52 t; 54.64 q; 56.60 q; 64.23 d; 85.12 d; 101.70 d; 113.91 d; 118.94 d; 127.55 s; 132.26 s; 142.83 s; 143.74 s; 148.63 s. ^1H NMR ($CDCl_3$), δ: 0.23—0.40 (m, 1 H); 0.98—1.30 (m, 2 H); 1.66—2.70 (m, 6 H); 2.31 (s, 3 H, NCH_3); 3.32—3.58 (m, 1 H, NCH); 3.35 (s, 3 H, OCH_3); 3.75 (s, 3 H, OCH_3); 4.48 (s, 1 H, OCH); 4.98 (d, 1 H, =CH); 6.58 (s, 2 H, Ph). IR, ν/cm^{-1}: 910, 1020, 1055, 1230, 1280, 1375, 1455, 1610, 1640, 1645, 2850—2965. MS, *m/z*: 325.

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