

starting mixture results in an abrupt increase in the rate of the process, and the nitration products (5-nitro- and 3-nitroacenaphthenes in the ratio 90÷93 : 10÷7) are formed in an almost quantitative yield (> 95 %) in ~40 min. According to the kinetic data, the addition of compound **2** increases the initial nitration rate of acenaphthene by more than three orders of magnitude.

If benzene (without PhNO<sub>2</sub>) is used as the organic phase, the reaction rate decreases, probably due to the lower solubility of **2**. The yield of nitroacenaphthenes under these conditions is ~55 % after 1 h, and 2.5–3 h are required to obtain the nitration products in a quantitative yield. The original compound **2** does not undergo decomposition under the nitration conditions and can be recovered in ~95 % yield after stirring for 1 h at 21 °C with a mixture of benzene and 21.3 % HNO<sub>3</sub> in the presence of NaNO<sub>2</sub> and NaCl. Unlike compound **2**, mercuric chloride shows no catalytic activity.

Sodium chloride plays an important role in the reaction, and compound **2** does not catalyze the nitration of acenaphthene if it is absent. It can be assumed that the chloride anions, by coordinating with the Hg atoms of compound **2**, provide the phase transfer of the cationic electrophilic species responsible for the formation of the nitro-derivatives. Probably, the nitrate anions, unlike Cl<sup>−</sup>, do not form complexes with compound **2** and are

inactive for this reason. It should be noted in this connection that compound **2** can catalyze the transfer of a proton from the hydrochloric aqueous phase to the benzene phase but not from aqueous solutions of nitric or sulfuric acids.

This work has been financially supported by the Russian Foundation for Basic Research, project No. 93-03-18342, and International Scientific Foundation, grant No. MMT 000.

## References

1. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca—London, 1969.
2. O. I. Kachurin, L. I. Velichko, and N. M. Matvienko, *Ukr. Khim. Zh.* [Ukrainian Chemical Journal], 1993, **59**, 642 (in Russian).
3. V. B. Shur, I. A. Tikhonova, P. V. Petrovskii, and M. E. Vol'pin, *Metallorg. Khim.*, 1989, **2**, 1431 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
4. V. B. Shur, I. A. Tikhonova, A. I. Yanovsky, Yu. T. Struchkov, P. V. Petrovskii, S. Yu. Panov, G. G. Furin, and M. E. Vol'pin, *J. Organomet. Chem.*, 1991, **418**, C29.
5. V. B. Shur, I. A. Tikhonova, A. I. Yanovskii, Yu. T. Struchkov, P. V. Petrovskii, S. Yu. Panov, G. G. Furin, and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 1002 [*Dokl. Chem.*, 1991, **321** (Engl. Transl.)].

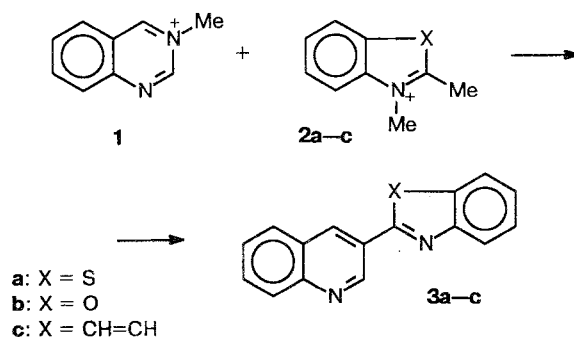
Received December 29, 1993

## Formation of hetarylquinolines from quinazoline derivatives and quaternary salts of heterocyclic bases

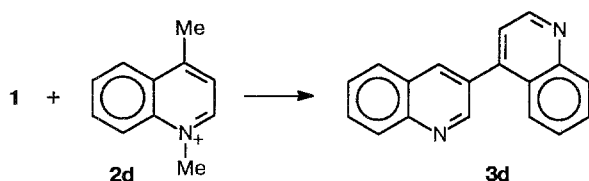
S. P. Gromov\* and M. A. Razinkin

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,  
4 ul. Kosygina, 117977 Moscow, Russian Federation.  
Fax: +7 (095) 936 1255

We have found a new reaction of cyclotransformation of the quinazoline bicycle by the reaction of 2(4)-methylquinazolinium salts with quaternary salts of other heterocyclic bases in pyridine to give 3-hetaryl-substituted quinolines. For example, boiling *N*-methylquinazolinium iodide (**1**) with excess quaternary salt (**2**) gives hetarylquinolines (**3**) in up to 55 % yield.

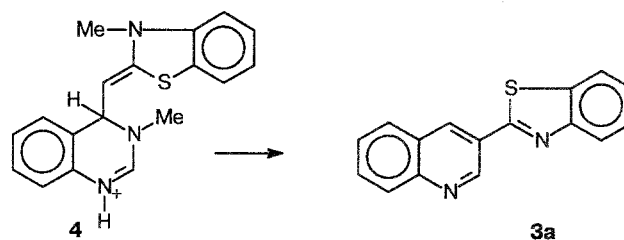


In a similar way, [3,4']biquinolyl (**3d**) was obtained in 19 % yield from 1,4-dimethylquinolinium iodide (**2d**).



Previously,<sup>1</sup> 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 <sup>1</sup>H NMR and confirmed by the agreement of the melting points of compounds **3a,c** with the literature data.<sup>2,3</sup>



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

### References

1. S. P. Gromov and M. A. Razinkin, *Khim. Geterotsikl. Soedin.*, 1992, **5**, 662 [*Chem. Heterocycl. Compd.*, 1992, **5** (Engl. Transl.)].
2. W. Borsche and W. Doeller, *Ann.*, 1938, **537**, 53.
3. E. Carlier and A. Einhorn, *Ber.*, 1890, **23**, 2894.
4. H. C. Van der Plas, *Ring Transformations of Heterocycles*, Academic Press, London, New York, 1973, **1**, 484; **2**, 352.
5. B. M. Krasovitskii and B. M. Bolotin, *Organicheskie lyumino-fory* [*Organic Luminophores*], Khimiya, Moscow, 1984, 334 (in Russian).

Received November 15, 1993;  
in revised form January 25, 1994

## Regio- and stereoselective method for the synthesis of 6 $\alpha$ ,7 $\alpha$ -methylene-6,7-dihydrothebaine

S. Z. Sultanov,<sup>a</sup> V. A. Dokichev,<sup>a</sup> E. E. Shults,<sup>a</sup> U. M. Dzhemilev,<sup>a</sup> G. A. Tolstikov,<sup>a\*</sup> and O. M. Nefedov<sup>b\*</sup>

<sup>a</sup>Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,  
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.  
Fax: +7 (347) 235 6066

<sup>b</sup>N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,  
47 Leninsky prosp., 117913 Moscow, Russian Federation.  
Fax: +7 (095) 135 5328

Thebaine and its derivatives are of substantial interest in practical medicine as analgesics.<sup>1–4</sup>

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

