Letters to the Editor

Cyclic trimeric perfluoro-*o*-phenylenemercury as the phase transfer catalyst for nitration with dilute nitric acid

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Nitration with dilute nitric acid in the presence of nitrites as initiating additives is a widely used method for obtaining nitro-derivatives of phenols, amines, and other highly reactive aromatic compounds.[1] In the case of solid compounds poorly soluble in water, one has to use organic solvents and perform the process in two-phase systems. Under these conditions, phase transfer catalysts are useful (*e.g.*, *cf.* Ref. 2).

It was recently found that cyclic trimeric *o*-phenylenemercury $(o\text{-}C_6H_4Hg)_3$ (**1**) and perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**2**), containing three Hg atoms in a planar nine-membered cycle, readily coordinate halide anions.[3–5] It turned out also[3] that compound **1** can catalyze the azo-coupling of $PhN_2^+X^-$ (X = Cl, Br) with β-naphthol in the CH_2Br_2—H_2O two-phase system, which indicates that polymetallamacrocycles of this type show promise as phase transfer catalysts for electrophilic reactions.

It was found in the present work that compound **2** has high catalytic activity in the phase transfer nitration of acenaphthene with dilute nitric acid in the presence of sodium nitrite and NaCl.

The experiments were performed with vigorous stirring at 21±1 °C. A 0.5 *M* solution of acenaphthene in a benzene—nitrobenzene mixture (100 : 15, v/v; 5 mL) was used as the organic phase. Nitric acid (21.3 %, 2.5 mL) containing NaCl (0.13 mol per one mol of HNO_3) was used as the acidic aqueous phase. Catalyst **2** (0.01 mol per one mol of acenaphthene) was added. This amount of **2** did not dissolve completely in the organic phase. Just before the experiment, $NaNO_2$ (0.04 mol per one mol of HNO_3) was added to the acidic aqueous phase.

The nitration in the absence of compound **2** proceeds very slowly: the yield of nitro derivatives does not exceed 1 % after 3 h. The addition of a catalyst to the

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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 $90 \div 93 : 10 \div 7$) 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 $PhNO_2$) 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_3 in the presence of $NaNO_2$ 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^-, 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.

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

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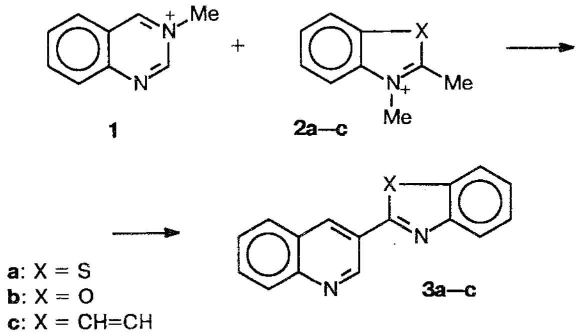
We have found a new reaction of cyclotransformation of the quinazoline bicycle by the reaction of 2(4)-methylquinazolinium salts with quaternary salts of other heterocyclic bases in pyridine to give 3-hetaryl-substituted quinolines. For example, boiling *N*-methylquinazolinium iodide (**1**) with excess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



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