

By application of the related procedure, we have also obtained bromobenchrotrene from benchrotrene and compound **3** in a 57% yield. The product was identified by mass and ^1H NMR spectra.

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New highly efficient phase transfer catalyst for nitration with dilute nitric acid

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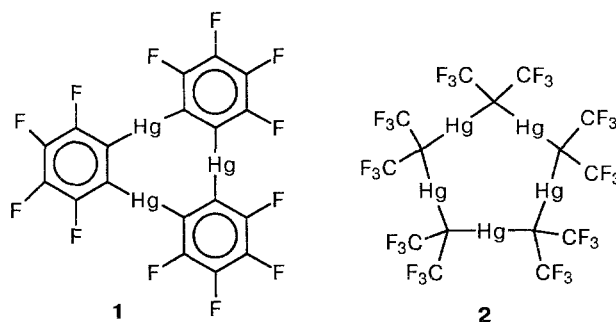
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One of the methods of preparation of nitroderivatives of phenols, arylamines and other highly active aromatic substrates is nitration with dilute nitric acid in the presence of initiating additives of nitrous acid¹.

Recently we reported that it is possible to increase the rate of the process^{2,3} carrying out this reaction under phase transfer catalysis conditions. We found that³ the cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃ (**1**), which is able to form complexes with halide anions⁴, is an efficient phase transfer catalyst for nitration of acenaphthene with 21.3 % HNO₃ in the presence of sodium nitrate and NaCl (organic phase: a mixture of benzene and nitrobenzene). The reaction proceeds at room temperature and after ~40 min leads to almost quantitative formation of nitroacenaphthenes. The role of the chloride anions in this reaction is

essential. It consists in coordination with mercury atoms of the catalyst to form lipophilic complex anion, which is the phase transfer carrier of cationic electrophilic species responsible for the formation of nitroproducts.



In the present work we report a new highly effective phase transfer nitration catalyst, mercury-containing macrocycle **2**, which is able also to bind the halide anions with formation of complexes.

In the typical experiment, to 5.8 mL of 0.23 M solution of acenaphthene in a benzene–nitrobenzene mixture (100 : 8.4 v/v) 0.008 g of **2** and 2.5 mL of 21.3 % HNO₃, containing NaCl (0.75 mol per mol of HNO₃) were added. Then to the reaction mixture, NaNO₃ (0.034 mol per mol of HNO₃) was introduced and vigorous stirring at 21±1°C was started.

In the course of the reaction, rapid nitration of acenaphthene was observed, leading to the formation of 5-nitro- and 3-nitro-derivatives (in the ratio of (90–93) : (10–7)), the yield of which after ~10 min was almost quantitative (98%). Under similar conditions, but in the absence of **2**, the conversion of acenaphthene to nitroproducts did not exceed 1 % even after 2 h. According to the kinetic data, compound **2** increases the initial rate of acenaphthene nitration (determined by the slope of the tangent to the initial area of the kinetic curve) by 3300 times.

An important feature of **2**, distinguishing it from **1**, is that in this case acenaphthene nitration also proceeds without NaCl, although at a lower rate. The yield of nitroproducts under such conditions reaches ~100 % only after 2 h. However, if 31.2 % HNO₃ is used instead of 21.3 % HNO₃, the process of nitration is finished quantitatively after 3 min. Thus, one can suppose, that **2**, in contrast to **1**, coordinates efficiently enough not only chloride, but also nitrate anions. This assumption conforms with the fact that macrocycle **2**, in contrast to **1**,³ is able to transfer protons into the ben-

zene phase both from the aqueous solutions of hydrochloric acid and from the aqueous solutions of nitric acid. This transfer of proton into the organic phase can be monitored by the change in the color of the benzene layer, which contains dissolved triphenylcarbinol, from colorless to yellow due to formation of triphenylmethyl cation.

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Reaction of 1,4-diphenylbut-1-en-3-yne with Ru₃(CO)₁₂. Crystal structure of Ru₃(CO)₈{μ₃-2η¹-η⁴-PhCH=CHC=C(Ph)C(Ph)=CCH=CHPh}

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In continuation of systematic investigations of reactions of heteroatom-substituted and functionalized alkynes with metal carbonyl clusters, we initiated a study of the behavior of enynes in these reactions. Our interest

in enynes is due to the fact of their participation as intermediates in the oligomerization/cyclization reactions of alkynes promoted by metal complexes; moreover, the presence of an olefinic bond in enynes offers