

Synthesis of anthracene ethers from anthracene methyl ethers *via* an acid-catalyzed exchange reaction†

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Selective synthesis of anthracene ethers was achieved under mild conditions *via* an acid-catalyzed ether–ether exchange reaction and its scope and limitations, as well as its potential in synthesizing anthracene-based crown ethers, tested.

Linearly fused aromatic hydrocarbons, commonly known as acenes, have very prominent positions in both computational chemistry¹ and organic material chemistry.² Theoretical studies have come to the consensus that the HOMO and LUMO of higher oligoacenes are nearly degenerate although the actual size of the band gap is still an ongoing controversy. Even as the simplest member of this distinguished family, anthracene and its derivatives have proved extremely versatile in material science. They have been used as the key component in light emitting diodes,³ field-effect transistors,⁴ sensors,⁵ and organic gellators.⁶

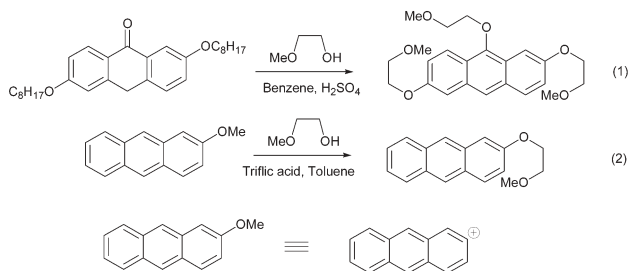
Despite all the incentives provided by both theory and application, the synthesis of acenes remains a difficult problem.⁷ We recently launched a project directed towards the synthesis, physical studies and potential application of acenes. In this Communication, we wish to report a new ether–ether exchange reaction on the anthracene core. We believe this reaction is a valuable addition to the hitherto-limited arsenal at synthetic chemists' disposal to tackle acene synthesis and derivatization.

The discovery of the exchange reaction is serendipitous. Our original goal was to aromatize 2,6-dialkoxy anthrone following a known procedure (eqn. (1) in Scheme 1).⁸ However, after the reaction, we realized that not only the aromatization has taken place, but both octyloxy groups on the starting anthrone were also replaced by 2-methoxyethoxy groups, evidently from excess 2-methoxyethanol employed in the reaction. The progress of the

reaction was monitored by TLC and no intermediate products can be detected. Further inquiry revealed that this reaction is not particular to 9-alkoxyanthracene; 2-methoxyanthracene also undergoes such a transformation to give 2-(2-methoxyethoxy)-anthracene under the same conditions. The net reaction conveys 2-methoxyanthracene as an anthryl cation synthon. In contrast, 2-methoxynaphthalene remains unchanged under the same conditions.

We then set out to optimize the reaction conditions. It soon became clear that using a non-oxidative strong organic acid is crucial since the alkoxy-substituted anthracene products are prone to oxidative degradation. A high boiling aprotic solvent can facilitate the removal of methanol to make the exchange irreversible. The optimal combination for exchange reaction is one equivalent of trifluoromethanesulfonic acid (with respect to anthracene) and two equivalents of alcohol (relative to the number of –OMe to be replaced) in boiling toluene. The procedure was thus applied to all the reactions in the following studies unless otherwise mentioned.

Table 1 shows our results from reactions conducted with 2-methoxyanthracene. Oligoether, halogen, and polyfluorinated alkyl groups are all compatible with the reaction conditions. Compounds **1e** and **1f** are synthesized without employing protecting groups for the free hydroxy group. An alkylation pathway would require the use of less accessible ω -halogenated alcohols as the alkylating agent. The efficient incorporation of polyfluorinated chain (entry 7) is especially noteworthy.



Scheme 1 Discovery and optimization of the exchange reaction.

† Electronic supplementary information (ESI) available: Detailed synthetic procedure and characterization for all new compounds. See <http://www.rsc.org/suppdata/cc/b412090f/>

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Table 1 Simple ether–ether exchange reaction on 2-methoxyanthracene

Entry	Substrate	Alcohol	Product yield (%)
1		HO(CH ₂) ₂ OCH ₃	1a (80%)
2		HO(CH ₂) ₃ OCH ₃	1b (79%)
3		HO(CH ₂) ₂ Br	1c (67%)
4		HO(CH ₂) ₄ CH(CH ₃) ₂	1d (62%)
5		HO(CH ₂) ₂ O(CH ₂) ₂ OH	1e (52%)
6		HO(CH ₂) ₆ OH	1f (45%)
7		HO(CH ₂) ₂ C(F)(CF ₃) ₂	1g (86%)

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