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Nafion-H Catalyzed Friedel-Crafts Reaction of Methylene Groups: Preparation of [9,9']Spirobixanthene

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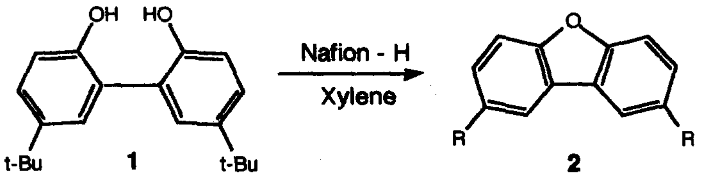
Abstract: Treatment of either p-*tert*-butylcalix[4]arene (**3**), xanthene or 9,10 dihydroanthracene with diphenyl ether in the presence of Nafion-H results in the formation of [9,9]spirobixanthene (**5**).

Nafion-H® is a solid perfluorinated sulfonic acid polymeric resin[1] of superacidic properties.[2] Recently, Yamato *et al.* reported that treatment of substituted dihydroxybiphenyls (**1**) with Nafion-H in boiling xylene resulted in the formation of the corresponding benzofurans (**2**) (eq. 1).[3] For example, reaction of 4,4'-di-*tert*-butyl-2,2'-dihydroxybiphenyl (**1**) with 50 wt % of Nafion-H in boiling xylene resulted in 12% yield of the dibenzofuran **2a** and 75% of the corresponding de-tert-butylated product **2b**. This reaction is notable since it involves the cyclodehydration of two phenolic OH groups under relatively mild conditions.[4]



1

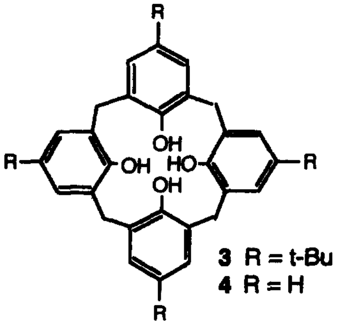
2

a: R = t-Bu
b: R =H

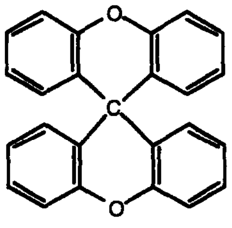
(1)

Calixarenes are macrocyclic compounds formed by a cyclic array of phenolic and methylene groups.[5] We decided to examine the reaction of *p-tert*-butylcalix[4]arene (**3**)[6] with Nafion-H.[7] We reasoned that if the phenolic groups of **3** react similarly to those of **1** this may provide a new synthetic route to macrocyclic systems containing ether groups.

We first reacted **3** (0.25 g) with 40 wt % Nafion-H for 18 hours in boiling xylene. NMR analysis of the residue obtained after filtration of the polymer and evaporation of the solvent indicated the presence of calixarene **4**,[8] i.e., the reaction resulted in de-tert-butylation of the calixarene (82 % yield after recrystallization). This reaction represents an additional method for de-tert-butylation of calixarenes, which is usually accomplished by their treatment with $AlCl_3$ in the presence of phenol or toluene.[8]



3 R = t-Bu
4 R = H



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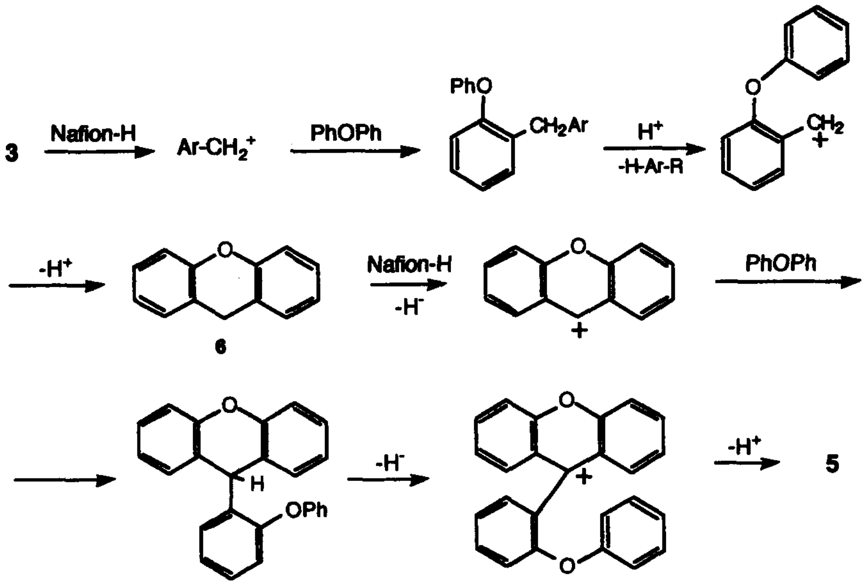
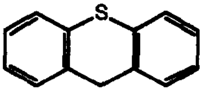
The reaction was then carried out at higher temperatures in order to see whether the calixarene can be forced to undergo dehydration. Reflux of **3** in decalin in the presence of the superacid gave neither de-tert-butylation nor any other apparent reaction. We chose next diphenyl ether as solvent since it has a high boiling point and dissolves **3** at high temperatures. A solution of 1.0 g of **3** in 50 mL diphenyl ether in the presence of 0.5 g Nafion-H was refluxed for 4.5 hours. After filtration of the resin, the reaction mixture was bulb to bulb distilled in vacuo (~ 1 mm Hg). The fraction of the distillate of higher boiling point solidified and was recrystallized from ethanol, yielding 0.2 g of a compound of mp 275-276 °C, which displays in the mass spectrum a molecular peak at m/z 348. The ^{13}C NMR spectra (100 MHz, $CDCl_3$) of the product displayed 6 aromatic signals (δ : 116.12, 123.66, 127.90, 129.46, 131.55, 149.14 ppm) and an aliphatic signal ascribed to the spiro carbon at δ 42.43 ppm. Based on these data we assign the [9,9'] spirobixanthene structure **5** to the compound. When the reaction was repeated in the absence of calixarene, **5** was not obtained. Spirobixanthene has been described once in the literature (mp 282-283 °C)[9] and was prepared by a multistep route, involving in the last step an acid-catalyzed cyclization of 9-(2-phenoxyphenyl)xanthene-9-ol.

Assuming that the reaction mechanism involves electrophilic aromatic substitution on the rings of diphenyl ether,[10] the formation of **5** requires *four* consecutive attacks of a single atom (the nascent spiro carbon) on the ortho positions of two diphenyl ether molecules. If the spiro carbon in **5** is originated from an acid-catalyzed cleavage of a methylene unit of **3**, one must further assume that, under the reaction conditions, two C-H bonds of the CH_2 moiety underwent C-H activation by protolysis.[11] A possible route for the formation of **5** is presented in Scheme 1 in which the calixarene serves as a source of CH_2 units.



Scheme 1

Since according to Scheme 1 under the reaction conditions xanthene (**6**) is an intermediate which undergoes C-H activation, we examined also the Nafion-H catalyzed reaction of diphenyl ether with **6**. Indeed, treatment of 1.5 g **6** with 0.2 g Nafion-H yielded 0.82 g (28 %) of **5**.



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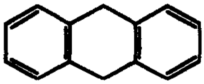

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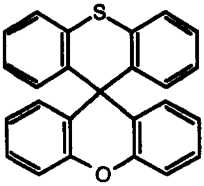

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We examined also whether other systems can undergo an analogous reaction. Treatment of thioxanthene (**7**) under similar conditions did not result in the formation of the corresponding spiro system (**9**) but resulted in the formation of **5** (17 %). Similarly, 9,10-dihydroanthracene (**8**) gave **5** as main product together with small amounts of anthracene. Under the superacidic conditions, these compounds undergo acid-catalyzed Ar-CH_2 cleavage and serve as the source of the spiro carbon. If all Ar-C cleavages are reversible under the superacidic conditions, **5** is likely to be favored over the other possible spiro compounds such as **9** since diphenyl ether it is present in large excess.

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