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Triflic acid promoted synthesis of polycyclic aromatic compounds

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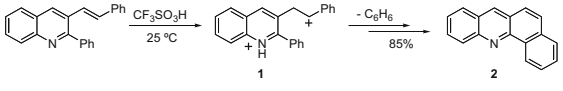
ABSTRACT

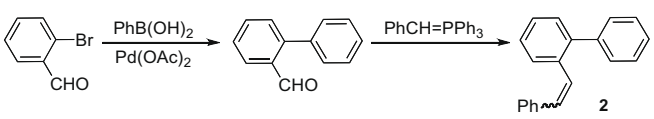
The triflic acid (CF_3SO_3H) promoted cyclizations of 2-styrylbiaryls are found to be useful for the synthesis of polycyclic aromatic compounds, including functionalized derivatives of polycyclic aromatic compounds and heterocyclic systems. The reaction involves cationic cyclization followed by an elimination of benzene from the intermediate product.

Polycyclic aromatic hydrocarbons and related compounds have been of great interest due to their relationships to chemical carcinogenesis.[1] Besides their biological activities, these substances have likewise been considered important components in material science applications. Due to their extended π-systems, they can exhibit novel optical properties.[2] Consequently, there is the continued need for new synthetic routes leading to these types of compounds and their functionalized derivatives.[3] We recently described a new superacid-promoted route to aza-polycyclic aromatic compounds (Eq. 1).[4,5] This chemistry involves the formation of superelectrophilic intermediates (i.e., **1**), followed by cyclization and elimination of benzene to give the condensed aromatic compounds (i.e., **2**). Because the precursor substrate possesses an N-heterocyclic ring that is fully protonated in acid, the cyclizations occur via the dicationic, superelectrophilic intermediates such as **1**. These results raised an interesting question: is it possible to achieve similar condensation reactions through monocationic reactions (without N-heterocyclic rings) to prepare polycyclic aromatic hydrocarbons? In the following Letter, we address this question and describe a new superacid-promoted synthetic route to polycyclic aromatic hydrocarbons, substituted derivatives, and heterocyclic systems.



(1)

In our initial investigation of this reaction, 2-styrylbiphenyl (**2**) was prepared and reacted with superacidic CF_3SO_3H.[6] This substrate (along with other olefins used in this study) was synthesized using Suzuki and Wittig coupling reactions (Eq. 2).[4] When compound **2** is reacted in superacid, the product mixture is complex, but some phenanthrene (**3**, ca. 5–10% yield) is detected by GCMS (Eq. 3). Other major products from the reaction include 9,10-dihydro-9-phenylphenanthrene (**4**) and 9-benzyl-9*H*-fluorene (**5**). With the formation of product **5**, it is clear that both possible carbocationic intermediates (**7a**,**b**) are generated in the acid. The phenanthrene (**3**) is formed by *ipso*-protonation of the phenyl group of compound **4** and elimination of benzene. Other minor products (ca. 5% yield) include biphenyl and dibenz[*a*,*c*]anthracene (**6**). Although it is not exactly clear how these products are formed, the presence of compound **6** suggests some type of dimerization and cleavage reaction steps. Compound **2** was also reacted in the gas-phase by flash vacuum pyrolysis (200 °C, 10^{-2} Torr) over the solid acid Nafion-H. Overall a similar product mixture was observed; however, the dibenz[*a*,*c*]anthracene (**6**) was not formed. Since intermolecular reactions are less likely in the gas-phase, this supports the idea that an intermolecular reaction gives compound **6** in the condensed phase.



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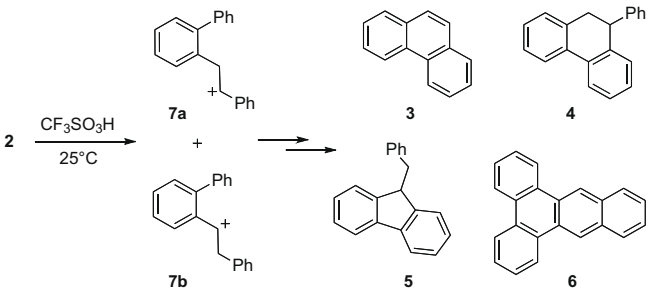
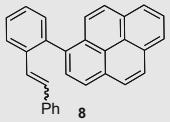
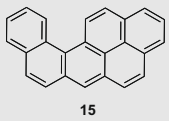
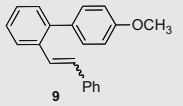
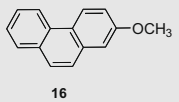
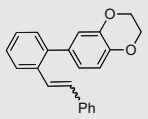
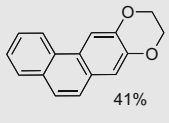
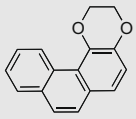
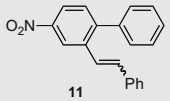
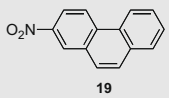
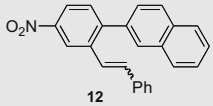
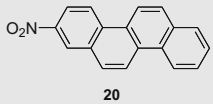
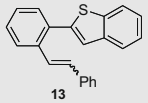
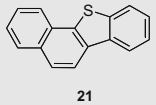
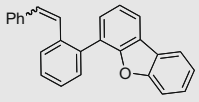
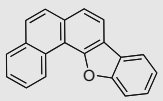


(3)

The formation of some phenanthrene (**3**) from 2-styrylbiphenyl (**2**) was a promising initial result, so a number of styryl-substituted arenes were prepared and reacted with CF_3SO_3H (Table 1). Substrate **8** gives naphtho[1,2-*a*]pyrene (**15**) as the major product in fair yield. This system (**8**) differs from 2-styrylbiphenyl (**2**) most notably by the increased nucleophilic character of the pyrenyl group versus the phenyl group (in **2**). Similarly, reactions of the aryl ether derivatives **9** and **10** provide good yields of the condensation products (entries 2 and 3). In the case of substrate **9**, the reaction with CF_3SO_3H gives 2-methoxyphenanthrene (**16**), while compound **10** produces two regioisomers (**17** and **18**) from reaction at the 5- and 8-positions of the benzodioxane ring. Nitro-functionalized substrates give the polycyclic aromatic compounds in good yields, with the preparation of 2-nitrophenanthrene (**19**) and 2-nitrochrysene (**20**). Cyclization of **12** occurs regioselectively at the 1-position of the naphthyl ring. Although the yields were low, heterocyclic systems (**21** and **22**) were prepared from cyclization of a benzothiophene derivative (**13**) and the dibenzofuran derivative (**14**). Most of the condensation reactions were done by reacting a $CHCl_3$ solution the substrate with CF_3SO_3H at 25 °C. However, in some cases, the reaction conditions needed to be tailored for particular substrates. For example, compound **12** gave complex product mixtures when the reaction was done at temperatures warmer than 0 °C.

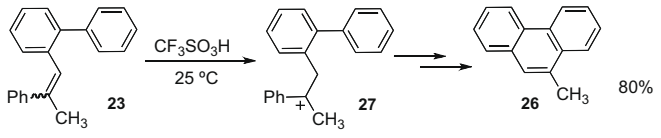
In order to obtain better yields for the conversions, we reasoned that the 2-phenyl-1-propenyl system should lead to regioselective protonation and more efficient cyclizations. Several 2-phenyl-1-propenyl derivatives were prepared and reacted with superacid (Eqs. 4,5,6). When compounds **23** and **24** were reacted with CF_3SO_3H, the polycyclic aromatic hydrocarbons (**26** and **28**) are formed in reasonably good yields. The conversion of compound **23** to 9-methylphenanthrene (**26**) is a marked improvement over the analogous reaction of 2-styrylbiphenyl (**2**) to give phenanthrene (**3**, Eq. 2). This improvement may be understood by considering the regioselectivity of protonation. Compounds **23** and **24** are

Table 1
Cyclizations of styryl-substituted precursors **8**–**14** to the condensed products **15**–**22** in CF_3SO_3H

Entry	Starting material	Product(s)	Yield[d] (%)
1	 **8**	 **15**	52[a]
2	 **9**	 **16**	71[a]
3	 **10**	 41% **17**  **18**	34[a]
4	 **11**	 **19**	81[a]
5	 **12**	 **20**	78[b]
6	 **13**	 **21**	42[c]
7	 **14**	 **22**	12[a]

[a] Reaction done at 25 °C.
[b] Reaction done at 0 °C.
[c] Reaction done at 65 °C.
[d] Isolated yields of pure products. Products were characterized by ^1H and ^{13}C NMR and by high resolution and low resolution mass spectra.

protonated exclusively at the 1-carbon position of the olefinic groups, leading to the stable 3° carbocations (i.e., **27**). This leads to efficient conversions to the phenanthrenes. In the case of compound **24,** however, the product mixture also contains a small amount of 9-methyl-2-phenylphenanthrene (**29**; visible by NMR),



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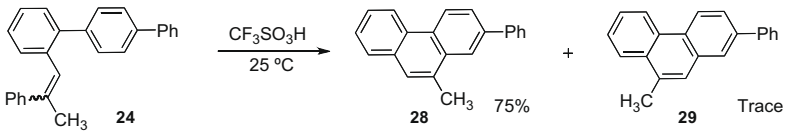
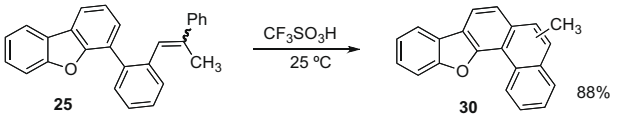


(5)



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