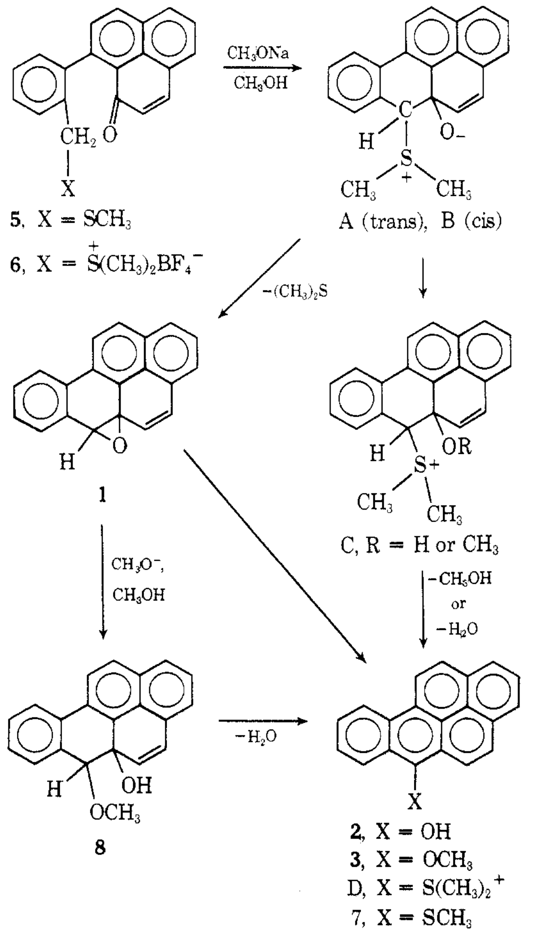
A New Synthesis of 6-Substituted Benzo[*a*]pyrenes Involving 5a,6-Epoxy-5a,6-dihydrobenzo[*a*]pyrene[1]

Summary. A new synthesis of 6-substituted benzo[*a*]pyrene derivatives, which involves as a key step the base-induced cyclization of dimethyl[*o*-(9-phenalenonyl)benzyl]sulfonium tetrafluoroborate, **6**, is described.

Two general methods for the synthesis of arene epoxides have been developed. One stems from chemical reactions[2-4] applied to adjacent dihydrodiols which are obtained by hydroxylation of a phenanthrene-type bond with osmium tetroxide[5,6] or by reduction of a quinone to a mixture of cis and trans diols,[3,7] and the other by the dehydrobromination of polybromoepoxide precursors.[8-10] In this paper we describe efforts to prepare a new type of arene epoxide, 5a,6-epoxy-5a,6-dihydrobenzo[*a*]pyrene, **1**. Although we have not isolated **1**, our method of synthesis of 6-hydroxybenzo[*a*]pyrene, **2**, and 6-methoxybenzo[*a*]pyrene, **3**, described below undoubtedly involves the formation of **1** followed immediately by isomerization to **2** or reaction with methoxide ion to form **3**.

Treatment of phenalenone,[11] **4**, with *o*-(methylthiomethyl)phenyllithium, followed by an oxidative work-up,[12] produced 9-[*o*-(methylthiomethyl)phenyl]phenalenone,[13] **5**. Treatment with methyl iodide followed by silver tetrafluoroborate afforded dimethyl[*o*-(9-phenalenonyl)benzyl]sulfonium tetrafluoroborate,[13] **6**. Reaction of **6** with sodium methoxide in methanol resulted in the formation of **2** (67%) (best isolated as the corresponding acetate[14]), **3**[15] (11%), and 6-methylthiobenzo[*a*]pyrene,[13] **7** (10%).



We interpret these results in the following way. The sulfur ylide formed by treatment of **6** with sodium methoxide attacks the carbonyl group in two ways to yield the trans intermediate, A, and the cis intermediate, B. The predominant isomer, A, rapidly cyclizes to the epoxide, **1**. Most of the epoxide rearranges to **2** but a small amount reacts with sodium methoxide to yield **3**. The cis isomer, **B**, is either protonated or methylated (see below) to form an unstable intermediate C which loses water (or methanol) to yield a dimethyl-6-benzo[*a*]pyrenylsulfonium salt, D. As D is an alkylating agent, it can alkylate B (see above) or methoxide ion and be thereby converted to **7**. An alternate intramolecular alkylation of B to form 5a,6-dihydro-5a-methoxy-6-methylthiobenzo[*a*]pyrene (not shown) is unlikely.[16]

The chemistry involving conversion of **6** to **1** was modeled after the comparable acyclic reaction of Corey and Chaykovsky.[17] In the present case, bases, sodium methoxide (or sodium hydroxide in methanol–acetonitrile), weaker than the bases, butyllithium, and sodium hydride used previously,[17] can be used because the ylide need not be prepared before reaction with the carbonyl component.[18]

References and Notes

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