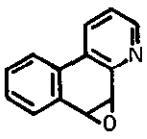
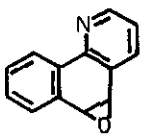
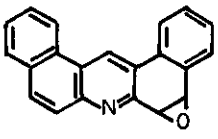
AZA-ARENE OXIDES

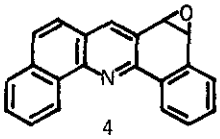
Yoshiyasu Kitahara, Haruhiro Okuda, Naoki Miyata,
Koichi Shudo and Toshihiko Okamoto
Faculty of Pharmaceutical Sciences, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo, Japan

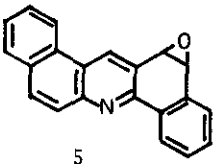
Oxidation of benzo[f]quinoline with ozone gave 2-phenylpyridine-2,2-dicarbaldehyde. The aldehyde was treated with trisdimethylaminophosphine to give benzo[f]quinoline 5,6-oxide(1). Similarly dibenz[a,j]acridine-5,6-oxide(3) was prepared from dibenz[a,j]acridine. Benzo[h]quinoline-5,6-oxide(2) was synthesized by oxidation with sodium hypochlorite in the presence of benzyltriethylammonium chloride. Dibenz[c,h]acridine and dibenz[a,h]acridine were oxidized by m-chloroperbenzoic acid to dibenz[c,h]acridine-5,6-oxide(4) and dibenz[a,h]acridine-12,13-oxide(5), respectively. Oxidation of 10-azabenzo[a]pyrene with osmium tetroxide gave cis-5,6-dihydroxy-5,6-dihydro-10-azabenzo[a]pyrene. The diol was treated with orthoacetic ester-trimethylsilyl chloride to give 10-azabenzo[a]pyrene-4,5-oxide(6).

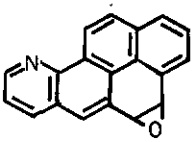

1


2

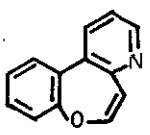

3

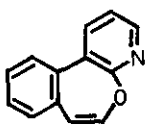

4


5


6

The epoxide(1) was quantitatively and regioselectively isomerized to 5-hydroxybenzo[f]quinoline with the use of trifluoroacetic acid or 24% hydrobromic acid. The reaction of 1 with 36% hydrochloric acid gave 5-hydroxy-6-chloro-5,6-dihydrobenzo[f]quinoline(55%) in addition to 5-hydroxybenzo[f]quinoline(14%). When the epoxide(1) was heated at 75° in 5% sodium hydroxide, trans-5,6-dihydroxy-5,6-dihydrobenzo[f]quinoline. The nucleophilic addition of methoxide in methanol to the epoxide gave trans-5-hydroxy-6-methoxy-5,6-dihydrobenzo[f]quinoline(46%) and trans-5-methoxy-6-hydroxy-5,6-dihydrobenzo[f]quinoline(22%). When 1 was irradiated in dichloromethane by a low pressure mercury lamp, two isomeric oxepins, 7(12%) and 8(6%) were obtained.


7


8