The Isomerization of 8-Arylbenz[*a*]anthracenes

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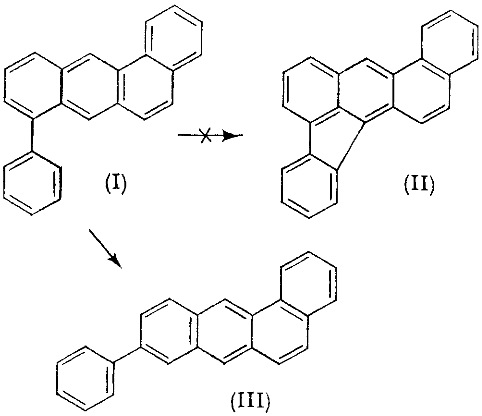
RECENTLY,[1] Buu-Hoï and his co-workers have shown that polycyclic aromatic hydrocarbons are isomerized when treated with $AlCl_3$. While attempting to dehydrogenate 8-phenylbenz[*a*]anthracene[2] (I) to the corresponding naphthafluoranthene[3] (II) using $AlCl_3$, we discovered a new isomerization.

When 1·5 g. of $AlCl_3$ was added to a solution of 300 mg. of (I) in 50 ml. of benzene the solution immediately became pink, but changed to violet as the mixture was shaken and heated at the reflux temperature for 20 min. The mixture was decomposed with dilute HCl to give a pale yellow precipitate. The product was purified by elution chromatography on neutral alumina, Brockman activity I, 80—200 mesh, with benzene as the eluant. The product (III)[4] was finally obtained as light tan leaflets from ethyl acetate, m.p. 244—245°, 240 mg. (80%). Elemental analysis, molecular weight (mass spectrometric), and u.v. and n.m.r. spectra were consistent with the assigned structure of the product (III). A significant bathochromic shift, presumably due to increased conjugation as a result of relief of steric strain, of 10 mμ was observed in the u.v. spectrum of (III) as compared with (I). An identical product is obtained when the reaction is performed using chlorobenzene or carbon disulphide as the solvent.



The three isomeric 8-tolylbenz[*a*]anthracenes when treated as (I) gave in each case a high yield of the corresponding 9-tolylbenz[*a*]anthracene. Thus the shift of aryl group from the 8- to the 9-position appears to occur with maintenance of positional integrity of the substituent on the phenyl ring. This suggests that the isomerization is intramolecular and may proceed through a bridged phenonium ion transition-state.[5]

Since 8-substituted benz[*a*]anthracenes are easier to prepare than the corresponding 9-isomers, this new isomerization appears to provide an attractive method for the preparation of 9-substituted benz[*a*]anthracenes.

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