Dihydro-intermediates in the Preparation of Dibenzo[*a*,*e*]fluoranthenes from 7-Arylbenz[*a*]anthracenes

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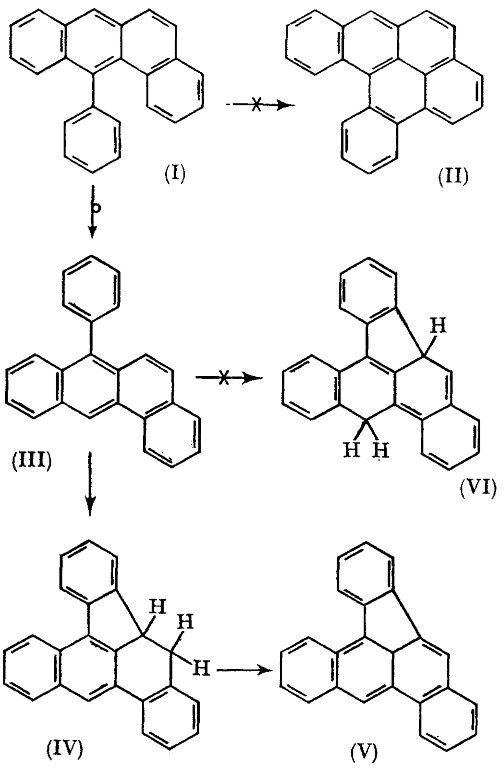
BUU-HÖI and his co-workers[1] recently reported that the product obtained when 12-phenylbenz[*a*]anthracene (I) is dehydrogenated with $AlCl_3$ is dibenzo[*a*,*e*]fluoranthene (V) and not dibenzo[*a*,*l*]pyrene (II) as has been reported previously.[2] They reasoned that (I) rearranged to 7-phenylbenz[*a*]anthracene (III) which then led to (V). Experimental data has since been presented to verify this suggestion.[3]



We have now been able to isolate dihydro-intermediates in high yields from the reactions of 7-arylbenz[*a*]anthracenes into dibenzo[*a*,*e*]fluoranthenes.

A mixture of (III) (500 mg.), $AlCl_3$ (1·5 g.), and benzene (50 ml.), was heated at the reflux temperature for 25 min. and decomposed with dilute HCl. The product was purified by elution chromatography on neutral alumina, Brockman activity I, 80—200 mesh, using light petroleum (30—60°)–benzene (1 : 1) as the eluant. The product, identified as (IV) by means of elemental analysis, u.v., i.r., n.m.r. spectroscopy, and molecular weight determination (mass spectrometric), weighed 370 mg. (75%), m.p. 190—191°. The precise molecular weight determination establishes that (IV) is indeed a dihydro-compound. The u.v. spectrum shows a 1,3-diarylnaphthalene structure while the i.r. spectrum shows the methynyl hydrogen and methylene hydrogen atoms. The choice of structure (IV) over other possible structures can be made on the basis of the n.m.r. spectrum, which shows clearly that the methylene hydrogen atoms are split. This is consistent with structure (IV) where an aliphatic hydrogen atom is adjacent to the methylene hydrogen atoms. Other plausible structures, such as (VI), have an isolated methylene group which would appear as a singlet and are therefore rejected. Structure (IV) clearly represents a rearrangement of hydrogen atoms from structure (III). If one attempts to draw an alternate structure for the dihydro-compound (IV) without rearrangement of hydrogen atoms, an amusing fact is revealed; namely, one simply cannot do it.

When (IV) was dehydrogenated with 2,3-dichloro-5,6-dicyanobenzoquinone, compound (V) was obtained essentially quantitatively.

The isolation of dihydro-intermediates from the reactions of 7-arylbenz[*a*]anthracenes with $AlCl_3$ appears to be general. In each case we were able to isolate the corresponding dihydro-compound when the three isomeric monomethylphenylbenz[*a*]anthracenes were treated with $AlCl_3$ and each could be dehydrogenated to the corresponding monomethyldibenzo[*a,e*]fluoranthene using 2,3-dichloro-5,6-dicyanobenzoquinone. Acceptable elemental analyses were obtained for all new hydrocarbons and the ultraviolet spectra confirmed the assigned structures.

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[3] F. A. Vingiello and A. K. Youssef, *Chem. Comm.*, **1967**, 863.