

A SIMPLE SYNTHESIS OF 9-METHYLPHENANTHRENES

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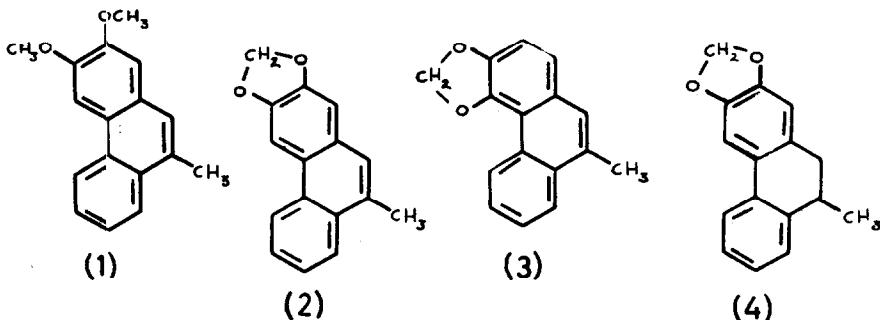
(Received 7 October 1964)

Among the various reactions postulated to proceed via a benzyne-type intermediate¹, the Diels-Alder addition to dienes such as butadiene and furan has attracted considerable attention as a potentially useful synthetic procedure. Stiles and his co-workers² have shown that when benzene diazonium-2-carboxylate³ is decomposed thermally in the presence of phenylacetylene, phenanthrene can be isolated in 8% yield, and when 1-phenylpropyne is used in place of phenylacetylene, a 3.6% yield of 9-methylphenanthrene can be realised.

We have studied the addition of benzyne, generated by the diazotisation of anthranilic acid in aprotic solvents⁴, to isoeugenol-methyl ether, and to isosafrole. Both of these styrenes are known⁵ to add to maleic anhydride.

The most satisfactory conditions were realised by adding concurrently solutions of anthranilic acid and isoamyl nitrite in acetonitrile to a refluxing solution of the styrene, in the same solvent. With isoeugenol methyl ether we were able easily to isolate 2,3-dimethoxy-9-methylphenanthrene (1) in 5% yield⁶ m.p. 141-143° (lit⁷ m.p. 131°). The ultraviolet and infrared spectra, and in particular the N.M.R. spectrum were all compatible with this structure.

In the case of isosafrole, the corresponding phenanthrene (2), m.p. 140-141°, was obtained in 6% yield. Unreacted isosafrole (49%) was recovered. The ultraviolet, infrared and N.M.R. spectra were all very similar in relevant detail to the corresponding spectra of (1). A second crystalline compound, m.p. 108-109° was isolated (1.3% yield) from the mother liquors of (2). The ultraviolet spectrum was only slightly



different from that of (2), and the N.M.R. spectrum suggested that this material is 3,4-methylenedioxy-9-methylphenanthrene (3), the product expected from the alternative mode of addition of the dienophile, benzyne to the diene, isosafrole.

Examination of the residues from the reaction of isoeugenol methyl ether with benzyne by chromatography eventually yielded a small amount of a low melting point solid whose spectral properties suggest that it is 3,4-dimethoxy-9-methylphenanthrene, which is reported⁸ to melt at 59°. We have not yet been able to fully characterize this material.

When the reaction with isosafrole was repeated in a mixture of toluene and methyl ethyl ketone as solvent, the phenanthrene (2) was accompanied by the 9,10-dihydrophenanthrene (4). The latter was converted into (2) either by heating alone or with palladium-black in an inert solvent, or by heating it under reflux with either nitrobenzene or acetonitrile.

With both isoeugenol methyl ether and isosafrole in acetonitrile, a nitrogen-containing byproduct (m.p. > 360°) is formed in about 10% yield (based upon the anthranilic acid). Nothing is yet known about this substance except that it exhibits a very strong blue fluorescence.

Not many 9-methylphenanthrenes have been reported in the literature; those that have been described have usually been prepared by rather laborious procedures. The synthetic work described in this communication offers a convenient route to this interesting type of phenanthrene, and it is being investigated further.

References

1. Brief summaries and useful references are given for example, by M. E. Kuehne and T. Kitagawa, J. Org. Chem., 29, 1270 (1964) and Stiles et. al - see reference 2.
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