Stable Hydrocarbon Analogues of 9-Anthrone: Methyl Substituted 9-Alkylidene-9,10-dihydroanthracenes

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Summary Simple hydrocarbon analogues of 9-anthrone have been isolated, stabilisation being afforded through *peri* interactions involving methyl groups.

9-Alkylidene-9,10-dihydroanthracene derivatives are generally unstable relative to 9-alkylanthracenes. They have been isolated only in crowded systems[1,2] where the geometry and rigidity of the latter forms are disadvantageous. The two forms afford interesting structural analogy with 9-anthrones and 9-anthranols where the opposite order of stability generally applies, favouring the anthrone.

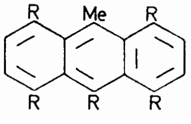
This Communication reports the simplest stable alkylidene dihydroanthracenes so far obtained. All are hydrocarbons incorporating *peri* interactions of groups no larger than methyl. All have at least one hydrogen at position-10.

A series of methylanthracenes of type (**1**) was investigated. This involved several structural possibilities in which from 2 to 4 of the groups R were methyl and the rest hydrogen. Those systems not already known were synthesised from appropriately substituted 9-anthrones. This entailed either 1,2-addition of methylmagnesium iodide or reduction of the anthrone with lithium aluminium hydride; this was followed in each case by dehydration with toluene-*p*-sulphonic acid[3] or with phosphoryl chloride in pyridine.

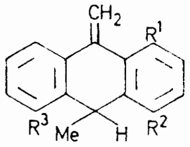
The nature of the products differed with the degree of crowding. Those systems which incorporated no more than one *peri* methyl–methyl interaction, *e.g.* the 1,4,9- and 1,9,10-trimethyl and the 1,4,5,9-tetramethyl series, were obtained exclusively as anthracene tautomers. These were identified by their characteristic electronic absorption and by low field aromatic or methyl proton resonances [δ 8·3 (10-H) and 3·0 (10-Me)].

Those products which incorporated at least two *peri* interactions and in which crowding could be relieved by a methyl-substituted carbon -9 or -10 becoming tetrahedral behaved differently. They were obtained as methylene-dihydroanthracene tautomers (**2**), (**3**), (**4**), and (**5**). These were identified by the methylene, methine, and methyl proton resonances associated with the central ring (δ 5·41—5·81, 3·95—4·44, and 1·25—1·45 respectively, the chemical shifts varying with the number of *peri* methyl substituents). Compounds (**2**)—(**5**) exhibited benzenoid absorption in their u.v. spectra (λ_{max} 255 nm) and they were remarkably stable. On treatment with toluene-*p*-sulphonic acid in boiling toluene[2] they remained substantially unchanged. Equilibrium with their respective anthracene tautomers was established only slowly under these conditions and the proportion of the latter at equilibrium was $<2\%$ (by electronic absorption).

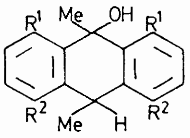
Treatment of the alcohol (**6**) with phosphoryl chloride in pyridine gave (**7**), a further stable tautomer of (**4**); the latter was obtained from the isomeric alcohol (**8**). The ^{1}H n.m.r. spectra of the two hydrocarbons were readily differentiable. After acid-catalysed equilibration of the compounds, the spectrum of (**7**) was smoothly converted into that of (**4**). The equilibrium proportion of the former was too small to be detected by n.m.r. spectrometry as was that of its anthracene tautomer (previous paragraph).



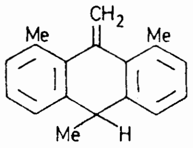
(1)



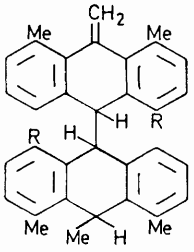
	R¹	R²	R³
(2);	Me	H	Me
(3);	Me	Me	H
(4);	H	Me	Me
(5);	Me	Me	Me



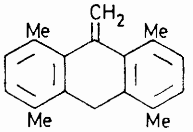
	R¹	R²
(6);	Me	H
(8);	H	Me



(7)



(9); R = H
(10); R = Me



(11)

1,8,9-Trimethyl- and 1,4,8,9-tetramethyl-anthracenes belong to a third category. They were isolated in the anthracene form but after treatment with toluene-*p*-sulphonic acid they were efficiently converted into the dimers (**9**) and (**10**). These were identified by ^{1}H n.m.r. spectroscopy and mass spectrometry. The ease of dimerization presumably reflects the fact that in the monomers there is no stable tautomeric possibility in which the crowded carbon-9 can become tetrahedral, whereas this possibility is manifested in one-half of each dimer. The analogous 1,4,5,8,9-pentamethylanthracene[3,4] did not undergo dimerization evidently because of hindrance by the methyl groups at positions-4 and -5. On treatment with acid it formed a tautomeric mixture (*ca.* 1 : 1) with (**11**). Both tautomers were characterised as were the other new compounds reported in this work.

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