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STABLE ANTHRAQUINODIMETHANES

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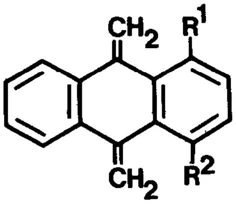
Quinodimethanes *e.g.* (1) are generally unstable compounds which polymerize readily. They have been isolated in pure form only in conjunction with highly crowded or polar substituents[1,2]. This communication reports the simplest stable anthraquinodimethanes so far obtained. All are hydrocarbons having no other substituents than methyl groups *peri* to the potentially reactive methylene centres at positions-9,10.

Reaction of 1,4-dimethylanthraquinone with methylmagnesium iodide gave the diol (2). On treatment with phosphoryl chloride in pyridine or with hydrogen chloride in tetrahydrofuran it was converted into the crystalline quinodimethane (3) (52, 79% respectively). The product (λ_{max} 235, 276nm; M^+ 232) was identified by p.m.r. resonances of appropriate intensities, the methylene groups appearing as an AB system (δ5.71, 5.43, J 2 Hz) and the methyl groups as a singlet (δ2.50).

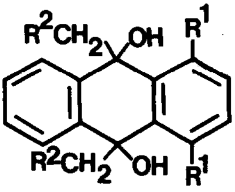
Unlike (1) which can be handled only at low temperatures and in high dilution,[3,4] (3) was stable above its melting point (105°). It could be sublimed without decomposition at atmospheric pressure and was unaffected by indefinite storage in the solid phase.

Analogous quinodimethanes having methyl substituents in the 1,5-, 1,8-, 1,4,8- and 1,4,5,8-positions were prepared similarly, dehydration being effected by phosphoryl chloride in pyridine, and all were stable. Even the monomethyl derivative (4) could be isolated, albeit in lower yield (14%) than the more highly substituted examples. Freshly prepared samples were stable at temperatures up to the melting point (90°) but decomposed after several weeks' standing at room temperature. Decomposition led to intractable, presumably polymeric materials.

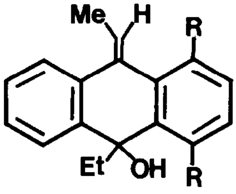
Not surprisingly the 9,10-diethylidene compound (5) was also stable (m.p. 156-158°). It was obtained by treatment of the appropriate diol (6) with acidified methanol. Milder treatment (hydrochloric acid in tetrahydrofuran) afforded the intermediate (7) which, under the former conditions gave (5) as the only product (78%).



	R^1	R^2
1	H	H
3	Me	Me
4	Me	H

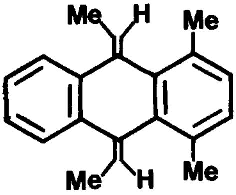


	R^1	R^2
2	Me	H
6	Me	Me
8	H	Me



7 R=Me

9 R=H



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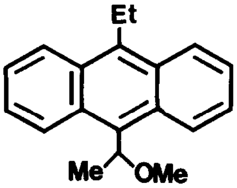

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Comparison of this behaviour with that of the analogous compounds (8), (9) provides a further example of the stabilising influence of the *peri* methyl groups. Treatment of (8)[5] or (9) with acidified methanol gave no quinodimethane, only the product (10) hypothetically derivable from it by addition of methanol.

Satisfactory elemental analyses and spectra have been obtained for all new compounds reported in this work.

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