

## Two Relatively Stable *p*-Quinodimethanes

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*Summary* Thermally stable *p*-quinodimethanes (**1b**) and (**2b**) have been prepared which owe their relative stability to the presence of the methyl groups in the 5,8- [for (**1b**)] and 1,4-positions [for (**2b**)].

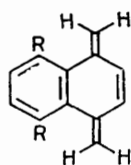
THE existence of 1,4-naphthoquinodimethane (**1a**) and 9,10-anthraquinodimethane (**2a**) as reactive intermediates in some reactions is well established.<sup>1</sup> The high reactivity of these molecules and their tendency to polymerise at ambient temperatures has made attempts to isolate and

characterise them difficult. However, Pearson and his co-workers<sup>2</sup> have succeeded in measuring their spectroscopic properties at low temperatures.

We have now prepared two related compounds which are relatively stable thermally. Treatment of the anthraquinone (**3**)<sup>3</sup> with an excess of methylmagnesium iodide followed by zinc(II) acetate and chloroacetic acid gave (**2b**) (43%) and not the reported product.<sup>4</sup>

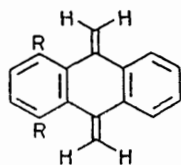
Compound (**2b**), † m.p. 100–101 °C, is thermally stable up to its melting point and its <sup>1</sup>H n.m.r. spectrum [ $\tau$ (CDCl<sub>3</sub>) 2.40–2.57 (2H, m), 2.67–2.83 (2H, m), 2.93 (2H, s),

† All new compounds gave the expected mass spectra and elemental analyses.



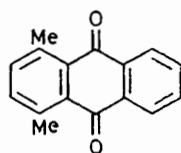
(1)

a; R = H  
b; R = Me

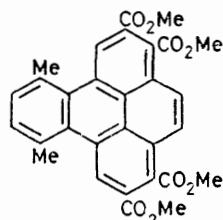


(2)

a; R = H  
b; R = Me



(3)



(4)

4.24 (2H, s), 4.52 (2H, s), and 7.49 (6H, s)] exhibits signals characteristic of the quinodimethane structure. The u.v. and i.r. spectra are similar to those described for (2a).<sup>2</sup> Ozonolysis of (2b) gave (3) and treatment with dimethyl acetylenedicarboxylate in refluxing nitrobenzene gave the expected adduct (4),<sup>5</sup>† m.p. 211–213 °C. However, (2b) is remarkably resistant to reduction and can be recovered unchanged after treatment with H<sub>2</sub>-Pd at 50 °C and 3 atm.

The corresponding naphthoquinodimethane compound (1b) was prepared (11%) from 5,8-dimethylnaphthoquinone<sup>6</sup> using an excess of methylmagnesium iodide or methyl-lithium, followed by HCl-dioxan, as a pale yellow, crystalline solid, m.p. 86–88 °C (EtOH);  $\tau$ (CDCl<sub>3</sub>) 2.47 (2H, s), 3.43 (2H, s), 4.18 (2H, s), 4.63 (2H, s), and 7.40 (6H, s);  $\nu_{\text{max}}$  (KBr) 1615, 907, 892, 795, and 755 cm<sup>-1</sup>;  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 2.4 (7.076), 237 (4.105), and 275 (3.90) nm. It slowly decomposes at room temperature but is stable indefinitely at 0 °C.

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<sup>1</sup> H. U. Wagner and R. Gompper, in 'The Chemistry of Quinone Compounds,' pt. 2, ed. S. Patai, Wiley, New York, 1974.

<sup>2</sup> J. M. Pearson, H. A. Six, D. J. Williams, and M. Levy, *J. Amer. Chem. Soc.*, 1971, **93**, 5034.

<sup>3</sup> A. W. H. Wardop, G. L. Sainsbury, J. M. Harrison, and T. D. Inch, *J.C.S. Perkin I*, 1976, 1279.

<sup>4</sup> P. de Bruyn, *Compt. rend.*, 1950, **231**, 295.

<sup>5</sup> For similar reactions, see: I. T. Millar and K. E. Richards, *J. Chem. Soc.*, 1967, 855.

<sup>6</sup> O. C. Musgrave and C. J. Webster, *J. Chem. Soc. (C)*, 1971, 855.