

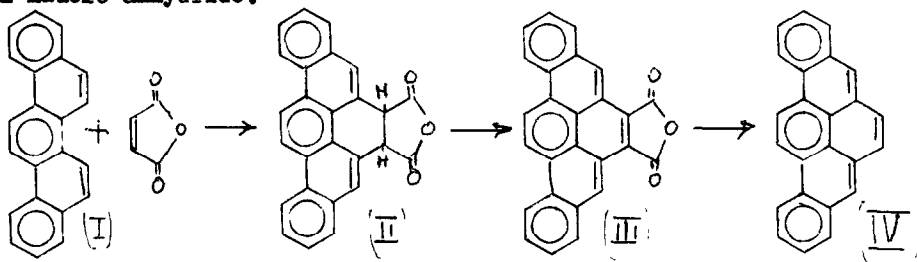
THE REACTION OF PICENE WITH MALEIC ANHYDRIDE

E. Clar \*

Department of Chemistry, The University, Glasgow G12 8QQ

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Maleic anhydride usually does not form stable endocyclic adducts with polycyclic hydrocarbons unless the system contains at least 3 linearly annelated rings<sup>1</sup>. Maleic anhydride also can cause a benzenogenic diene synthesis if the system contains a potential butadiene like the one in perylene<sup>2</sup>. None of these conditions are fulfilled in the case of picene (I). Only the formulation with 3 aromatic sextets<sup>3</sup> indicates the possibility of a reaction with maleic anhydride.



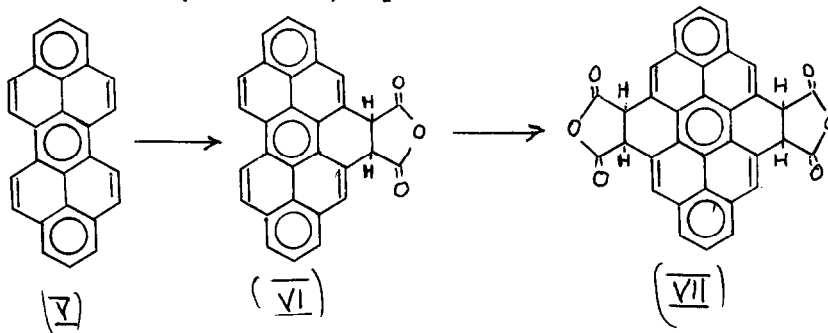
Boiling 10g picene with 230g maleic anhydride and 1g iodine for 3 hr, dissolving a sample in water and extracting the residue with dil NaOH gave an aqueous soln with absorption bands which are typical for a picene derivative  $\nu, 3280; \beta, 2860, 2770 \text{ \AA}$ . It appeared that the primary adduct was partially dehydrogenated to the anhydride (II). This view was confirmed if the reaction was extended over 20 hr. Then the new bands appeared at:  $\alpha, 3980, 3750; \nu, 3330, 3155; \beta, 2955, 2830; \beta', 2430, 2350 \text{ \AA}$ . This spectrum obviously belongs to the anhydride (III). This could be isolated in a pure state if the melt was poured into water, excess maleic anhydride removed and the residue extracted with dil NaOH, filtered and the soln precipitated with HCl. Yield 1g. Sublimation in a vacuum gave red crystals which had M.W., m/e 372 as cal. for  $C_{26}H_{12}O_3$ . The next peak was at

\* Present address: Punta Chullera Km 144, Estepona, Prov. Malaga, Spain.

300 indicating the loss of  $\text{CO}_2$  and  $\text{CO}$ .

Sublimation of the anhydride (III) over molten  $\text{KOH}$  or soda-lime in a vacuum at  $350\text{--}400^\circ$  in a current of  $\text{N}_2$  gave 3,4:9,10-dibenzopyrene (IV) which after recrystallisation from xylene had m.p. and mixed m.p.  $280^\circ$  and gave the same absorption spectrum as an authentic sample of dibenzopyrene (IV)<sup>4</sup>.

If peropyrene (V) is formulated with 3 aromatic sextets an analogous reaction must be expected. In fact peropyrene reacted more readily with maleic anhydride and a small amount of iodine than picene. After a short reaction the alkaline extract showed absorption bands at:  $\text{p}, 4460, 4190, 3980; \beta, 3270, 3140; \beta', 2780, 2660 \text{ \AA}$ . These were replaced by the following bands if the reaction was extended over several hr.:  $\text{p}, 4560, 4300; \beta, 3290, 3160; \beta', 2790, 2670 \text{ \AA}$ . It is obvious that these peropyrene type spectra belong to the partially dehydrogenated mono- and diadduct (VI and VII) resp.



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- 2 E. Clar, *ibid.*, p. 191, Vol. II, p. 28.
- 3 E. Clar, *The Aromatic Sextet*, John Wiley & Sons, 1972, p. 44.
- 4 E. Clar, *Ber. Deut. Chem. Ges.* 72, 1645 (1939); E. Clar, B. A. McAndrew and J. F. Stephen, *Tetrahedron*, 26, 5465 (1970).