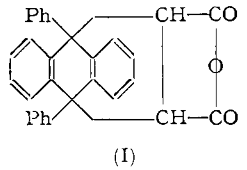
835. *The Addition of Maleic Anhydride to 9 : 10-Diphenylanthracene.*

By J. W. COOK and LEON HUNTER.

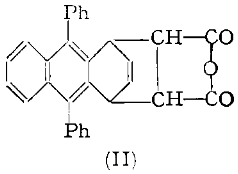
Maleic anhydride adds at the 1 : 4-positions of 9 : 10-diphenylanthracene, both in xylene solution and also when the reactants are fused together. Spectroscopic evidence of the structure (II) of the adduct is supported by the preparation of epoxides from two of its esters.

ANTHRACENE and many of its simple derivatives react with maleic anhydride and other dienophiles by addition at the 9 and 10 positions. Bachmann and Kloetzel (*J. Amer. Chem. Soc.*, 1938, **60**, 481) found that 9 : 10-diphenylanthracene reacted slowly and incompletely with maleic anhydride, but by using 30 mol. of maleic anhydride in boiling xylene they obtained an adduct, m. p. 249—250°, in 78% yield, and assumed for this the structure (I). Dufraisse, Velluz, and Velluz (*Bull. Soc. chim.*, 1938, **5**, 1073) were unable to isolate a product by the " usual technique," but when equal weights of 9 : 10-diphenylanthracene and maleic anhydride were fused together they obtained an adduct, m. p. 315—317°. They attributed the difference in m. p. to the fact that they had used a block for their m. p. determination whereas the American workers had used a capillary tube. Dufraisse suggested that in the latter case complete dissociation had taken place during heating and pointed out that the m. p. recorded by Bachmann and Kloetzel is very close to that of diphenylanthracene (m. p. 250—251°).

Gillet (*ibid.*, 1950, **17**, 1141) examined the ultra-violet absorption spectrum of a sample of adduct prepared by Dufraisse's method, and found that it was not benzenoid in character, like the spectra of the adducts of anthracene and 9-phenylanthracene, but closely resembled that of 1 : 4-diphenylnaphthalene. Gillet therefore proposed the structure (II), which is that of a derivative of 1 : 4-diphenylnaphthalene.



(I)



(II)

More recently, the reaction has been discussed from a theoretical standpoint by Brown (*J.*, 1952, 2229), who concluded that under the conditions used by Bachmann and Kloetzel addition of maleic anhydride should take place almost exclusively at the 9 and 10 positions. Brown accepted the structure (I) for their product and advanced an explanation for the formation of (II) at the higher temperature used by the French workers.

It was clearly of interest, therefore, to re-examine the reaction under both sets of conditions, to determine whether or not the products are identical, and to establish their structures. We have found that the same product was formed under both sets of conditions; this was shown by comparison not only of the adducts, but of three derivatives. Moreover, in each case the adduct had an absorption spectrum corresponding closely with that of 1 : 4-diphenylnaphthalene and is therefore represented by formula (II). This structure [but not (I)] contains an isolated ethylenic bond which should be susceptible to oxidative attack. We were unable to isolate pure products of permanganate oxidation or of ozonisation, but the presence of the double bond was shown by titration with perphthalic acid and also by characterisation of the epoxides obtained by monoperphthalic acid oxidation of the dimethyl and diethyl esters.

Evidently the two *meso* phenyl groups (which are not coplanar with the anthracene rings) completely suppress the addition of maleic anhydride which normally takes place at the 9 and 10 positions. Addition at the less reactive (but by no means inert) 1 and 4 positions is paralleled by the 1 : 4-addition of maleic anhydride to naphthalene derivatives (Kloetzel *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 273, 1991; Abadir, Cook, and Gibson, *J.*, 1953, 8). The theoretical aspects of the reaction (Brown, *loc. cit.*) need reconsideration in the light of these findings.

EXPERIMENTAL

1 : 4-*Dihydro*-9 : 10-*diphenylanthracene*-1 : 4-endo-αβ-*succinic Anhydride* (II).—(a) *Preparation in boiling xylene* (cf. Bachmann and Kloetzel, *loc. cit.*). A solution of 9 : 10-diphenylanthracene (10 g.) and maleic anhydride (80 g.) in xylene (250 c.c.) was boiled under reflux for 3 hr. and then poured into 40% potassium hydroxide solution. The solvent was removed in steam and the suspended potassium *endo*succinate, together with unchanged diphenylanthracene, was collected and dried in a vacuum desiccator. The hydrocarbon was extracted with benzene and the residual potassium salt (11·4 g.) was converted into the acid by refluxing it with dilute mineral acid. Crystallisation from moist ethyl acetate gave 1 : 4-*dihydro*-9 : 10-*diphenylanthracene*-1 : 4-endo-αβ-*succinic acid* as crystals, m. p. 260° (Maquesne block) or 241—242° (capillary tube) (Found : C, 77·5; H, 4·75. $C_{30}H_{20}O_4,H_2O$ requires C, 77·9; H, 4·8%). Recrystallisation from acetic anhydride gave the anhydride (II), m. p. 310—315° (Maquesne block) or 244—245° (capillary tube). Light absorption in ethanol : $\lambda_{max.}$ 288, 291, 293 mμ : log ε = 4·1, 4·08, 4·07.

(b) *Preparation without a solvent* (Dufraisse, Velluz, and Velluz, *loc. cit.*). Powdered 9 : 10-diphenylanthracene (0·5 g.) and maleic anhydride (0·5 g.) were intimately mixed and heated to fusion. After a few seconds the product was cooled, powdered, and extracted with ether and benzene to remove unchanged reactants. The *endo*succinic anhydride (II) formed crystals (from benzene), m. p. 309—315° (Maquesne block) or 245—247° (capillary tube). Light absorption in ethanol : $\lambda_{max.}$ 242 *, 288, 291, (294) mμ : log ε = 4·74, 4·07, 4·06, (4·04).

The *dimethyl ester* was prepared by boiling this anhydride (0·7 g.) with 2% methanolic sulphuric acid (60 c.c.) for 6 hr. It crystallised from methanol in flat rectangular prisms with a double m. p. (187° and then 215—216°) (Found : C, 81·1; H, 5·4. $C_{32}H_{26}O_4$ requires C, 81·0; H, 5·5%). The *diethyl ester*, similarly prepared, formed crystals, m. p. 222—224° (Found : C, 81·45; H, 6·05. $C_{34}H_{30}O_4$ requires C, 81·25; H, 6·0%).

The *cis*-dimethyl ester (0·1 g.) was isomerised by boiling its solution in sodium methoxide (2 g. of sodium in 50 c.c. of methanol) for 15 hr. (cf. Diels and Alder, *Annalen*, 1931, **486**, 191; Hückel and Goth, *Ber.*, 1925, **58**, 447). The solution was concentrated, poured into water, and acidified. The precipitated acid was re-esterified with methanol–sulphuric acid and gave the trans-*dimethyl* ester as clusters (from methanol), m. p. 186—187° depressed by mixing with the *cis*-ester (Found : C, 80·75; H, 5·55%).

The anhydride prepared in xylene solution was similarly converted into the *cis*-dimethyl ester, double m. p. 189° and 215°, the *trans*-dimethyl ester, m. p. 186°, and the *cis*-diethyl ester, m. p. 221—224°, and the m. p.s showed no depression when mixed with corresponding derivatives of the anhydride prepared without a solvent.

Degree of Unsaturation of Adduct (II).—A weighed amount of the diethyl ester (*ca.* 0·4 g.) was added to 50 c.c. of a 0·5% solution of monoperphthalic acid in chloroform. Oxidation was complete only after 95 hr. at room temperature. Excess of perphthalic acid was estimated by adding potassium iodide and titrating the liberated iodine. The number of double bonds given by two determinations was 1·048 and 1·025.

The epoxide was not isolated in a satisfactorily pure condition from the titrated solution. For preparative purposes, the diethyl ester (150 mg.) was added to 0·5% monoperphthalic acid in

---

* Because of a defect in the spectrophotometer absorption in this region was not measured with the sample prepared in xylene solution.

chloroform (50 c.c.) and kept at room temperature for 4 days. Acids were removed by extraction with sodium carbonate solution, and the washed chloroform solution was dried (Na_2SO_4) and evaporated. The residual gum crystallised from light petroleum (b. p. 60—80°) in crystals, m. p. 237—238°, of *diethyl* 3 : 4-*epoxy*-1 : 2 : 3 : 4-*tetrahydro*-9 : 10-*diphenylanthracene*-1 : 4-endo-αβ-*succinate* (Found : C, 78·5; H, 5·75. $C_{34}H_{30}O_5$ requires C, 78·7; .H, 5·8%).

The *epoxide* similarly prepared from the *cis*-dimethyl ester had m. p. 218—219° (from hexane) (Found : C, 78·45; H, 5·5. $C_{32}H_{26}O_5$ requires C, 78·35; H, 5·3%).

Microanalyses were by Mr. J. M. L. Cameron and Miss M. W. Christie.

UNIVERSITY OF GLASGOW.

[*Received, August* 18*th*, 1953.]