25. *The Photo-oxides of 9 : 10-Dixenylanthracene and 9 : 10-Diphenyl-2-methylanthracene.*

By Denis Duveen and Antoine Willemart.

The preparation of 9 : 10-*dixenylanthracene* and the *photo-oxides* of this hydrocarbon and of 9 : 10-diphenyl-2-methylanthracene are described. The thermal decomposition of these two photo-oxides was effected, and the yields of oxygen liberated determined : these were 95% and 94% respectively of the theoretical amounts.

Previous work (*vide infra*) has shown that the photochemical combination in a *meso*-position of a molecule of oxygen with substituted anthracenes is influenced to no great extent by the number or the nature of *meso*-substituents if these are of a purely alkyl nature. In fact photo-oxides have been obtained in which the substituents were one or two aliphatic, one or two aromatic, or even one aromatic and one aliphatic radical. The single exception is 9 : 9′-dianthranyl (Dufraisse, Velluz, and Velluz, *Bull. Soc. chim.*, 1938, **5**, 600), which can be considered as being a *meso*-anthranylanthracene.

The thermal decomposition of photo-oxides to give oxygen and the original hydrocarbon is, however, largely influenced, as far as the yield of oxygen liberated is concerned, by both the number and the nature of *meso*-substituents, a high yield of oxygen being obtained only in those cases in which the substituents are aromatic in character; *e.g.*, the photo-oxides of 9 : 10-dimethylanthracene and 9 : 10-diphenylanthracene give 0% (Willemart, *Bull. Soc. chim.*, 1938, **5**, 556) and 96% (Dufraisse and Etienne, *Compt. rend.*, 1935, **201**, 280; Dufraisse and Le Bras, *Bull. Soc. chim.*, 1937, **4**, 349) respectively of the theoretical quantity of oxygen.

Striking analogies have frequently been observed between *meso*-diphenylanthracene and hexaphenylethane; *e.g.*, both become coloured on heating and both give addition compounds with sodium and potassium and also with maleic anhydride. This parallel is probably more apparent than real (Dufraisse and Houpillart, *Compt. rend.*, and Dufraisse, *Bull. Soc. chim.*, in course of publication), though it formed an exceedingly useful working tool and was responsible for the original discovery and study of the photo-oxidation of 9 : 10-diphenylanthracene : it was from a consideration thereof that the present work was undertaken.

It is known that the degree of dissociation of a hexa-arylethane into the corresponding free triarylmethyl radical depends, among other factors, on the nature of the substituents. The phenyl group, while necessary to produce dissociation in an appreciable amount, only contributes to this effect to a comparatively small degree, hexaphenylethane in benzene solution being dissociated to the extent of only 5% under the most favourable conditions (Wieland, *Ber.*, 1909, **42**, 3029). On the other hand, the influence of the xenyl radical is much more pronounced, since dixenyltetraphenylethane is dissociated to the extent of 15%, tetraxenyldiphenylethane 80%, and hexaxenylethane 100% (Schlenk, Weickel, and Herzenstein, *Annalen*, 1910, **372**, 1; *Ber.*, 1910, **43**, 1754). In this respect the colours exhibited by solutions of these various hexa-substituted ethanes are instructive colours which are considered to bear a definite relation to the degree of dissociation.

It thus appeared of particular interest to study 9 : 10-*dixenylanthracene* for two main reasons : Firstly, if, as suggested by Ingold and Marshall (J., 1926, 3080), the change in colour on heating which is exhibited by 9 : 10-diphenylanthracene is connected with the formation of a biradical form, this phenomenon should be much accentuated in the case of 9 : 10-dixenylanthracene, which might even be expected to be coloured in the solid state and almost certainly so in solution. We found that the latter hydrocarbon was colourless, became only slightly yellow on heating, and gave colourless solutions in the usual organic solvents. In addition it exhibited absorption bands in agreement with those of the other anthracenic hydrocarbons previously studied, showing only the displacements in the region of the longer wave-lengths predicted from the nature and number of the substituents. This fits in well with the spectroscopic studies of Dufraisse and Houpillart (*loc. cit.*), who failed to find any trace of the existence of a biradical form of 9 : 10-diphenylanthracene.

Secondly, in the thermal decomposition of photo-oxides of *meso*-substituted anthracenes previously studied, whenever the substituents were both aromatic in character a high yield of oxygen was obtained, often approaching but never reaching the theoretical maximum 100%. It seemed likely that the two *meso*-xenyl groups, being powerfully electron-attracting, would have the effect of increasing the yield of oxygen liberated by weakening the fourth bonds of the carbon atoms to which they were attached, the other two bonds being already attached to aromatic electron-attracting groups.

The employment of the usual technique gave the *photo-oxide* of 9 : 10-dixenylanthracene, but only 95% of the theoretical quantity of oxygen could be liberated, a figure which is close to that given by the thermal decomposition of the photo-oxide of 9 : 10-diphenylanthracene. However, we do not regard this as proof that the theoretical maximum cannot be more nearly attained: the preparation of these photo-oxides is always a delicate reaction and their purification is rendered difficult by the sparing solubility of both the original hydrocarbon and the photo-oxides. Although analyses and microscopic homogeneity indicated that the products were chemically pure, it is conceivable that the necessary small amount of impurity was present to lower the yield by a few units %.

We also prepared the photo-oxide of 9 : 10-diphenyl-2-methylanthracene: this decomposed on heating to yield 94% of the theoretical quantity of oxygen. This fact is in harmony with the findings of previous workers regarding both the high yields obtained when the two *meso*-substituents are aromatic in character and the comparative absence of influence of substituents of various natures in the 2-position.

EXPERIMENTAL.

4-Bromodiphenyl was prepared in good yield by Gomberg and Bachman's method (" Organic Syntheses," Collective Vol. I., p. 109).

9 : 10-*Dihydroxy*-9 : 10-*dixenyl*-9 : 10-*dihydroanthracene*.—Dark violet 4-xenyl-lithium was prepared (Gilman, *J. Amer. Chem. Soc.*, 1933, **55**, 1262) by the action of 4-bromodiphenyl (6 g.) on lithium (0·4 g.) in anhydrous ether (30 c.c.) in an atmosphere of pure nitrogen. Anthraquinone (2 g.) was then added in small portions; a vigorous reaction set in and a brown precipitate formed. After 1 hour, the product was poured on ice, the ether allowed to evaporate overnight at room temperature, the solid collected, dried, and extracted with ethyl acetate (150 c.c.), and the extract evaporated to dryness. The residue (6 g.), crystallised twice from boiling toluene (40 c.c.), gave the desired *product* in colourless needles (2·5 g.), m. p. 210—212° (Found: C, 88·15; H, 5·9. $C_{38}H_{28}O_2$ requires C, 88·4; H, 5·4%).

9 : 10-*Dixenylanthracene*.—The above quinol (2·5 g.) was refluxed with acetic acid (40 c.c.) and potassium iodide (2·5 g.). Iodine was immediately liberated and after ½ hour sodium hypophosphite was added to destroy the free iodine and the solution was poured into cold water (500 c.c.). The precipitated *hydrocarbon* was filtered off, dried, and recrystallised (2·4 g.) from boiling xylene (650 c.c.); it (1·8 g.) then had m. p. about 415° (copper block). It gave fluorescent solutions with the usual organic solvents (Found: C, 94·4; H, 6·1. $C_{38}H_{26}$ requires C, 94·6; H, 5·4%).

Photo-oxide of 9 : 10-*Dixenylanthracene*.—A solution of the hydrocarbon (0·5 g.) in carefully purified carbon disulphide (1250 c.c.) was exposed to sunlight until a sample, evaporated to dryness and redissolved in benzene, showed no fluorescence (15—35 minutes according to the actinic activity of the light). The solution was then evaporated to dryness below 30° in a vacuum. Small crystals were left, which could be recrystallised from carbon disulphide, ether, or benzene by concentration of the solutions in a vacuum (Found: C, 88·3; H, 5·55. $C_{38}H_{26}O_2$ requires C, 88·7; H, 5·05%).

The *photo-oxide* (0·1665 g.) liberated oxygen (6 c.c. at N.T.P.) at 190—200° in a vacuum. This represents 95% of the theoretical quantity calculated for $C_{38}H_{26}O_2$. The solid residue had m. p. 414—415°, alone or mixed with the original hydrocarbon.

9 : 10-*Dihydroxy-2-methyl-*9 : 10-*dihydroanthracene*.—This was prepared by the action of phenylmagnesium bromide on 2-methylanthraquinone and purified by crystallisation from toluene; m. p. 246° (copper block). Guyot and Stachling (*Bull. Soc. chim.*, 1905, **33**, 1106) and Schlenk and Bergmann (*Annalen*, 1928, **463**, 185) give m. p. 240° and 238° respectively.

9 : 10-Diphenyl-2-methylanthracene, also previously prepared by the above authors, was obtained by reducing the quinol (4·6 g.) with potassium iodide (4·6 g.) in acetic acid (50 c.c.). It could be satisfactorily recrystallised from alcohol, acetic acid, ethyl acetate or dibutyl ether, and had m. p. 242—243° (copper block).

The Photo-oxide of 9 : 10-*Diphenyl-2-methylanthracene*.—This was prepared by irradiation with sunlight of a solution of the hydrocarbon (1 g.) in pure carbon disulphide (500 c.c.) and purified by recrystallisation from carbon disulphide, ether, or preferably ether–light petroleum. The photo-oxide (0·091 g.), when heated to 170—175° in a vacuum, liberated pure oxygen (5·1 c.c. at N.T.P., representing 94% of the theoretical quantity calculated for $C_{27}H_{20}O_2$). The residue (0·084 g.) melted at 241°, alone or mixed with the original hydrocarbon.

The absorption spectra of the two hydrocarbons were determined with the special apparatus made by Jobin and Yvon and described in detail in *Revue Optique Theorique et Instrumentale*, 1936, **15**, 19 (see also Dufraisse and Houpillart, *ibid.*, 1936, **16**, 321).

We desire to express our appreciation of the kind interest shown by Professor Charles Dufraisse in the present work.

Collège de France, Paris, V°.

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