NOTES.

*Octadeuteronaphthalene.* By G. R. CLEMO and A. McQUILLEN.

IN the preparation of hexadeuterobenzene from dideuteroacetylene and its purification by means of picric acid (this vol., p. 851) about 3 g. of crude picrate mixture were obtained from 22·5 g. of heavy water. This has now been investigated and, although more material will be necessary for a full examination, pure octadeuteronaphthalene and a more complex hydrocarbon have been isolated. The picrate mixture was separated by fractional crystallisation from alcohol into (a) a pure *picrate*, forming dark red needles, m. p. 205° [Found : C, 64·1; water (heavy and ordinary), 33·25; N, 9·05. $C_{24}H_3D_{12}O_6N_3$ requires C, 63·6; water, 32·4; N, 9·27%], and (b) an orange mixture of picrates. The free hydrocarbon of (a) was regenerated by shaking the ethereal solution of the picrate with very dilute aqueous ammonia, and was purified by sublimation in a vacuum at 100°, forming yellow plates, m. p. 135°, giving a green fluorescence in the solid state and a blue one in ethereal solution. Lack of material has so far prevented full analysis, but $C_{18}D_{12}$ is indicated for the hydrocarbon, and it is significant that in crystalline form and fluorescent properties it corresponds closely to 1 : 2-benzanthracene, m. p. 141°.

The mixture (b) also was converted into the hydrocarbons as above and these were taken up in ether, some tellurium derived from the catalyst thus being removed. The ethereal extract was converted into picrate, which after repeated crystallisation gave two yellow fractions, (c) of moderate solubility in alcohol and (d) of high solubility. The free hydrocarbon from (c) was purified by sublimation for 5 days at 100° and ordinary pressure, yielding colourless plates, m. p. 77·5°. Recrystallisation from 75% methyl alcohol, followed by sublimation at 50° in a vacuum, gave pure *octadeuteronaphthalene*, m. p. 77·5° (Found : C, 87·3, 88·8; D, 12·3, 12·4. $C_{10}D_8$ requires C, 88·2; D, 11·8%. $C_{10}H_8$ requires C, 93·8; H, 6·2%). The microanalysis was as difficult as that of benzene and it was necessary to use a considerable length of platinum catalyst to ensure efficient combustion.

The fraction (d) gave liquid hydrocarbons, from which no sublimate was obtained after heating for 48 hours at 100° in a vacuum.—ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM, NEWCASTLE-UPON-TYNE. [*Received, July 29th,* 1935.]

Action of Maleic Anhydride on Diphenylisobenzfuran. By EDWARD DE BARRY BARNETT.

WHEN 4 g. of maleic anhydride in 25 c.c. of dichloroethylene were added slowly at the ordinary temperature to 9 g. of 1 : 2-diphenyl*iso*benzfuran in 75 c.c. of dichloroethylene, reaction took place almost instantly with the production of a transitory red colour and the separation of almost colourless crystals, m. p. 279° (decomp.) after recrystallisation from ethyl acetate (Found : C, 78·0; H, 4·7. $C_{24}H_{16}O_4$ requires C, 78·2; H, 4·4%).
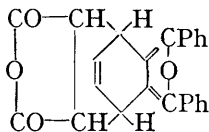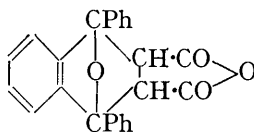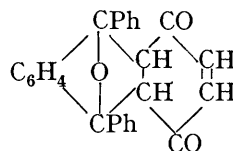
(I.)   (II.)   (III.)

This *adject* might be represented by formula (I) or (II), but its stability towards bromine is much more in harmony with the latter, as also is its method of preparation, since Guyot and Catel (*Bull. Soc. chim.*, 1906, **35**, 1125) and Guyot and Valette (*Ann. Chim.*, 1911, **23**, 363) have shown that the lateral carbon atoms are the centres of reactivity of the *iso*benzfuran ring system. Although the adject is stable in the solid state, it dissociates into its components extremely easily even in inert solvents such as ethyl acetate, and in this way resembles the adjects of maleic anhydride and the fulvenes (Kohler and Kalbe, *J. Amer. Chem. Soc.*, 1935, **57**, 917). This ease of dissociation is remarkable, since it must involve the disturbance of the aromatic structure.

Diphenyl*iso*benzfuran also reacted with benzoquinone extremely easily, *e.g.*, in ethereal solution at − 10°. The *product* (presumably III) dissociated in solution so easily that purification was difficult, but a sample recrystallised from chloroform and dried at 105° melted at 203° (decomp.) (Found : C, 82·1; H, 5·1. $C_{26}H_{18}O_3$ requires C, 82·5; H, 4·8%).—SIR JOHN CASS TECHNICAL INSTITUTE, LONDON, E.C. 3. [*Received, July 3rd,* 1935.]

The Influence of Substituents on the Energy of Activation. By D. H. PEACOCK.

HERTEL and DRESSEL (*Z. physikal. Chem.*, 1933, **23**, B, 281) examined the rates of addition of trinitroanisole and methyl trinitroanisole to dimethylaniline and some of its para-substituted derivatives. They found that the ratios of the velocities of reaction of the bases used with the two nitro-compounds were constant, and concluded that the difference between the energies of activation for a given pair of bases with trinitroanisole was equal to the difference for the same pair of reactants with methyl trinitroanisole, and further that the energy of activation was additive in character. They used the equation $\log k = - A/T + B$ and found that for all their reactions the values of B lay between 10·9 and 11·5. They therefore assumed that B was constant for all the reactions studied and used the value 11·2. For this assumption there does not seem to be any sufficient theoretical or experimental justification. Although the differences in the experimental values of B are small, they are sufficient to produce large variations in the differences in A upon which the authors base their conclusions. This is especially noticeable when the values of the energy of activation of a particular base with methyl trinitroanisole are compared with those for the same base and trinitroanisole. Using Hertel and Dressel's method of calculation, it appears that the introduction of the methyl group into trinitroanisole raises the energy of activation by a constant amount. If, however, the energies of activation are calculated in the usual way from the temperature coefficients of the reactions concerned, the introduction of the methyl group raises the energy of activation in two cases and lowers it in two others. Similar variations in the effect of introduction of a methyl group have been observed before (Peacock, *J.*, 1924, **125**, 1976).

It must, however, be emphasised that the assumption of constancy in B is not in itself sufficient to lead to constant differences in A. This result requires also constancy in the ratios of the velocities of reaction of the bases used with the two nitro-compounds. Constant ratios for reaction velocities have been observed in other cases and the observation certainly requires explanation. The simplification introduced by Hertel and Dressel seems, however, to require more justification than they have given.—UNIVERSITY COLLEGE, RANGOON, and UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, May 28th,* 1935.]