CII.—*Contributions to the Study of Acenaphthylene and its Derivatives.*

By BERTRAM CAMPBELL.

THE yellow hydrocarbon, acenaphthylene, $C_{12}H_8$, was first obtained by von Behr and van Dorp (*Ber.*, 1873, **6**, 753) by passing acenaphthene vapour over red-hot lead monoxide,

In 1912, Dziewoński and Rapalski (*Ber.*, 1912, **45**, 2491) succeeded in obtaining it in larger yield by passing the vapour of acenaphthene through a silica tube heated to redness.

Several wet methods have been tried in the course of the present investigation, but none of these has given satisfactory results. When a current of oxygen was passed through a boiling solution of acenaphthene in xylene in the presence of a catalyst (cobalt oxide or platinum-black) for periods of from two to fourteen hours, some oxidation took place, but, so far as the yield of acenaphthylene was concerned, the method was unsatisfactory.

The acenaphthylene used in this investigation was prepared by Dziewoński and Rapalski's method, and was freed from the saturated hydrocarbon by the fractional crystallisation of the picrates. The picrate of acenaphthylene was decomposed by

ammonia, and the hydrocarbon purified by crystallisation from alcohol. In this way, it was obtained in square yellow plates, melting at 93°.

In outlining the investigation of the derivatives of acenaphthylene, the dihalogen additive products were considered suitable substances for starting materials. Of these, only the dibromide, $C_{12}H_8Br_2$, has been prepared (Blumenthal, *Ber.*, 1874, **7**, 1092), and it was soon found that, in attempting to obtain other derivatives from it (for example, the dicyanide), no reaction ensued other than the partial decomposition of the dibromide (almost white) into monobromide (yellow):

Indeed, by boiling a solution of the dibromide in light petroleum (b. p. 65—70°) for seven hours, some decomposition resulted. Attention was therefore directed to other 1:2-dihalogen compounds of acenaphthene.

The 1:2-dichloride, $C_{12}H_8Cl_2$ (m. p. 115°), was prepared by the addition of chlorine to acenaphthylene. The position of the halogen atoms in the molecule was established by the oxidation of the substance to naphthalic acid:

By the action of alcoholic potassium hydroxide on 1:2-dichloroacenaphthene, monochloroacenaphthylene was obtained as a yellow oil resembling the corresponding monobromo-derivative.

When iodine was added to acenaphthylene in ethereal solution, an unexpected change took place, for, instead of obtaining the di-iodide, a pale yellow, amorphous substance was obtained, which contained no iodine. Subsequent work pointed to the fact that polymerisation of the acenaphthylene had occurred, giving rise to a hydrocarbon, which agreed in general properties with the poly-acenaphthylene ($C_{12}H_8$)₂₂, described by Dziewoński and Leyko (*Ber.*, 1914, **47**, 1679).

EXPERIMENTAL.

Acenaphthylene (1 mol.) was dissolved in carbon tetrachloride, and chlorine (1 mol.), which had been saturated with the solvent vapour, was added. The solvent was allowed to evaporate, and the product, after refining with animal charcoal, was crystallised from light petroleum, when it was obtained in white, glistening plates,

920 CONTRIBUTIONS TO THE STUDY OF ACENAPHTHYLENE, ETC.

which melted sharply at 115° . It crystallised from alcohol in white needles:

0.1435 gave 0.1841 AgCl. Cl = 31.74.

$C_{12}H_8Cl_2$ requires Cl = 31.8 per cent.

Oxidation of 1:2-Dichloroacenaphthene.

The above substance (1 mol.) was boiled under a reflux condenser for two hours with the calculated quantity of potassium permanganate (1 mol. $K_2Mn_2O_8$) in aqueous solution. The colourless solution, after filtration, was acidified with hydrochloric acid, and the white, crystalline precipitate was collected and washed. It was dissolved in aqueous sodium carbonate, reprecipitated with hydrochloric acid, collected, washed, and dried at 110° . It melted at 266° . On heating in a dry tube, it sublimed, and it dissolved in cold concentrated sulphuric acid, giving a yellow solution with a blue fluorescence. These properties agree with those of naphthalic anhydride.

1:2-Dichloroacenaphthene (1 mol.) was boiled with a slight excess of alcoholic sodium ethoxide for one hour. The yellow solution, after cooling, was poured into iced water, and the yellow, oily drops which separated were extracted with ether. After being washed with water, the ethereal solution was boiled with animal charcoal, dried, and evaporated, when a yellow oil remained:

0.1034 gave 0.0793 AgCl. Cl = 18.99.

$C_{12}H_7Cl$ requires Cl = 19.05 per cent.

Action of Iodine on Acenaphthylene.

Ethereal solutions of molecular proportions of iodine and acenaphthylene were mixed, and the solvent was allowed to evaporate spontaneously. The greyish-black residue was washed several times with alcohol to remove free iodine. There remained a yellowish, insoluble residue, which readily dissolved in cold benzene, giving a reddish-brown solution. On pouring into alcohol, a lemon-yellow precipitate was obtained, which was collected, washed, and dried. On examination, it was found to contain no iodine. After several precipitations from benzene solution by means of alcohol, it was obtained as a pale yellow powder, which was found to be very readily soluble in chloroform, carbon

tetrachloride, xylene, aniline, or *o*-nitrotoluene, but insoluble in alcohol, ether, or glacial acetic acid. It showed no signs of melting at 260°. Although an analysis was not made, its properties agree in detail with those of polyacenaphthylene described by Dziewoński and Leyko (*loc. cit.*).

In conclusion, the author desires to take advantage of this opportunity to express his best thanks to Professor H. B. Baker for the facilities afforded for the carrying out of the above work, which, although temporarily interrupted, it is hoped to continue later.

ROYAL COLLEGE OF SCIENCE,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. [Received, May 10th, 1915.]