XCVII.—*Phthalides of the Benzene, Naphthalene, and Carbazole Series. Part I.*

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THE object of this investigation was the synthesis of new phthalides, derived from *o*-xylene, α -ethoxynaphthalene, and 9-ethylcarbazole, by condensing these substances with phthalyl chloride in the presence of aluminium chloride.

It has been found in the cases investigated that, besides the lactone, an acid by-product is formed, the proportion of which to the main product depends on the substances used (being at a minimum in the case of 9-ethylcarbazole) and the temperature of the reaction.

It has been observed in all these cases that the lower the

temperature of the reaction the greater is the amount of acid formed, this being in complete accord with the results obtained by Scheiber (*Annalen*, 1912, **389**, 121) in the case of the condensation of phthalyl chloride with benzene.

The general mechanism of the reaction and its dependence on temperature become clear in the light of the work of Meyer (*Monatsh.*, 1904, **25**, 475, 1177; 1907, **28**, 1211) on the isomeric chlorides and esters of *o*-benzoylbenzoic acid; of Goldschmidt and Lipschitz (*Monatsh.*, 1904, **25**, 1174) on those of fluorenyl- and naphthoyl-benzoic acids, and of Scheiber (*loc. cit.*) and Ott (*Annalen*, 1912, **392**, 275), who isolated asymmetric phthalyl chloride, and thus brought into accord the evidence, obtained by chemical and physical methods, as to the structure of phthalyl chloride.

The phthalyl chloride, prepared in the ordinary way, is the symmetric isomeride, and reacts at a low temperature according to the equation

The decomposition by water of the product of the reaction at this stage is represented by the equation

If the reaction is continued at a higher temperature, two intramolecular changes take place in the presence of aluminium chloride:

and

the reaction then proceeding according to the equations

and

This conception of the reaction explains, not only the formation of the acid, but also the fact that the lactone is obtained whether the reacting mixture is heated immediately the substances are brought together or after they have been kept in the cold for some time.

The condensation of *o*-xylene with phthalyl chloride leads to the formation of *o*-xylylphthaloylic acid and di-*o*-xylylphthalide.

The acid has already been described by Meyer (*Ber.*, 1882, **15**, 637) and Limpricht (*Annalen*, 1900, **312**, 100), and shown to have the constitution represented by formula I, from which the di-*o*-xylylphthalide may be considered to have the structure II, since phthalides may be regarded as the condensation products of the ketonic acids, accompanying them, with another molecule of the hydrocarbon (Pechmann, *Ber.*, 1881, **14**, 1865):

In a similar way, the action of phthalyl chloride on α -ethoxynaphthalene produces *o*-1-ethoxynaphthoylbenzoic acid, the corresponding hydroxy-acid of which has been investigated by Deichler and Weizmann (*Ber.*, 1903, **36**, 556), and proved to have the structure III; the di-1-ethoxynaphthylphthalide, which is also formed, has the constitution denoted by IV, on grounds similar to those advanced in the case of di-*o*-xylylphthalide.

On treatment with aluminium chloride, the ethoxy-groups of the di-1-ethoxynaphthylphthalide are replaced by hydroxy-groups, and the α -naphthaphthalein (V) thus obtained is identical with that prepared by Grabowski (*Ber.*, 1871, **4**, 725).

On heating the α -naphthaphthalein at 290°, it is changed into α -naphthafuran (VI), identical with that obtained by Grabowski (*Ber.*, 1871, **4**, 661) and Meyer (*Ber.*, 1893, **26**, 207).

This method of formation of α -naphthaphthalein and α -naphthafuran from di-1-ethoxynaphthylphthalide establishes their respective structures:

The products of the reaction of phthalyl chloride with 9-ethylcarbazole are more numerous than those obtained in the previous cases, and lead to the formation of 9-ethylcarbazole-3-phthaloylic acid (VII) and 9-ethylcarbazole-3:6-diphthaloylic acid (VIII), which may be formulated similarly to the 9-methyl homologues prepared by Ehrenreich (*Monatsh.*, 1911, **32**, 1103) and the carbazolephthaloylic acids obtained by Stümmer (*Monatsh.*, 1907, **28**, 411) and Scholl and Neovius (*Ber.*, 1911, **44**, 1249):

The two phthalides, di-9-ethylcarbazyolphthalide (IX) and tri-9-ethylcarbazyldiphthalide (X), which were also isolated, may be regarded as derived from their corresponding acids, VII and VIII; therefore their structures will be similar to those advanced in the previous cases:

From 9-ethylcarbazole-3:6-diphthaloylic acid (VIII) the corresponding quinone, 2:3:6:7-diphthaloyl-9-ethylcarbazole (XI), has been prepared:

The linear configuration is assigned to this quinone on grounds identical with those put forward by Ehrenreich (*loc. cit.*) in the case of diphthaloyl-9-methylcarbazole, and by Scholl and Neovius (*loc. cit.*) in that of diphthaloylcarbazole.

Substances VII and VIII have also been prepared by condensing 9-ethylcarbazole with phthalic anhydride in the presence of aluminium chloride.

9-Ethylcarbazole-3:6-diphthaloylic acid and its corresponding quinone (XI) are the subjects of Cassella & Co.'s patent (D.R.-P. 261737), but no details are given in the patent specifications.

EXPERIMENTAL.

The phthalyl chloride used in these condensations was prepared by Graebe's method (*Annalen*, 1887, **238**, 329), special care being taken to remove as much as possible of the phthalic anhydride dissolved in the chloride.

Di-o-xylylphthalide (II).—Thirty grams of phthalyl chloride and 40 grams of *o*-xylene were dissolved in 250 c.c. of carbon disulphide, and 25 grams of finely powdered aluminium chloride were gradually added. The reaction was allowed to proceed at the ordinary temperature, and was completed in five to six hours.

The reaction mixture was decomposed with ice and hydrochloric acid, and a current of steam passed through to remove the excess of *o*-xylene and solvent.

The residue was collected, dried, powdered, and extracted with dilute ammonia. On acidifying the alkaline solution, after filtering, a white powder was precipitated, which crystallised from hot water in small, white prisms, melting at 161–162°, identical with *o*-xylylphthaloylic acid prepared by Meyer (*loc. cit.*) and Limpricht (*loc. cit.*).

The residue, insoluble in ammonia, was crystallised from ethyl alcohol, from which it separated as a gelatinous mass, which crystallised on rubbing with a glass rod. After two recrystallisations, *di-o-xylylphthalide* was obtained as a white, crystalline powder, melting at 107–108°. It is soluble in alcoholic potassium hydroxide and all ordinary organic solvents, and gives with cold concentrated sulphuric acid an orange coloration, which turns brown on heating:

0.1310 gave 0.4011 CO_2 and 0.0756 H_2O . $\text{C}=83.54$; $\text{H}=6.40$.

$\text{C}_{24}\text{H}_{22}\text{O}_2$ requires $\text{C}=84.10$; $\text{H}=6.48$ per cent.

o-1-Ethoxynaphthoylbenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OEt}$.—The condensation of α -ethoxynaphthalene (2 mols.) with phthalyl chloride (1 mol.) was carried out in a similar way as in the previous experiment, with the difference that the reaction was completed by heating the mixture on the water-bath for two hours. After the decomposition of the reaction mixture, and distillation with steam in the usual way, the residue was extracted several times with dilute ammonia, and the solution was filtered and then acidified with dilute hydrochloric acid. The reddish powder which was precipitated was dissolved in dilute sodium hydroxide, forming a dark green solution. The sodium salt of *o*-1-ethoxynaphthoylbenzoic acid isolated from the solution was obtained in white crystals after one recrystallisation from water. The pure sodium salt of the acid forms a colourless solution in water.

In a similar manner the ammonium salt is obtained in large, white, glistening plates.

The free acid crystallises from ethyl alcohol in large, white plates. From toluene the acid is obtained as small, white crystals, melting at 155 – 156° , and giving with concentrated sulphuric acid in the cold an orange-red coloration, which deepens on heating:

0.1867 gave 0.5108 CO_2 and 0.0839 H_2O . $\text{C}=74.61$; $\text{H}=4.99$.

$\text{C}_{20}\text{H}_{16}\text{O}_4$ requires $\text{C}=74.97$; $\text{H}=5.03$ per cent.

On heating *o*-1-ethoxynaphthoylbenzoic acid with aluminium chloride suspended in carbon disulphide (Hartmann and Gattermann, *Ber.*, 1892, **25**, 3531), the ethoxy-group was replaced by a hydroxyl group, and *o*-1-hydroxynaphthoylbenzoic acid, yellowish crystals melting at 185 – 186° , was obtained identical with the acid prepared by Deichler and Weizmann (*loc. cit.*).

On acidifying the dark green mother liquor, after the removal of the sodium salt, a brownish-red substance was precipitated, which, on digesting with animal charcoal in benzene and crystallising from the latter (brownish-yellow crystals melting at 209 – 210°), was found to be α -naphthaphthalein.

Di-1-ethoxynaphthylphthalide (IV).—The residue, insoluble in ammonia, was recrystallised several times from glacial acetic acid, from which it was finally obtained as a white, coarse, crystalline substance, melting at 159° :

0.1781 gave 0.5268 CO_2 and 0.0883 H_2O . $\text{C}=80.32$; $\text{H}=5.51$.

$\text{C}_{32}\text{H}_{26}\text{O}_4$ requires $\text{C}=80.97$; $\text{H}=5.53$ per cent.

The phthalide is soluble in all ordinary organic solvents. Although it is insoluble in aqueous alkaline solutions, it dissolves

when heated with alcoholic potassium hydroxide. With concentrated sulphuric acid, the phthalide gives a green coloration in the cold and a brownish-red on heating.

α -Naphthaphthalein (V).—The displacement of the ethoxy-groups by hydroxyl groups in di-1-ethoxynaphthylphthalide was effected by treating it with aluminium chloride suspended in carbon disulphide.

The dihydroxy-compound was obtained from benzene in small, brownish-yellow crystals, melting at 209—210°. It is soluble in alkalis with a deep green colour, and gives a brownish-red coloration, identical with that obtained on heating the ethoxyphtalide, with cold concentrated sulphuric acid:

0.1215 gave 0.3542 CO₂ and 0.0460 H₂O. C=79.5; H=4.21.

C₂₈H₁₈O₄ requires C=80.36; H=4.32 per cent.

This phthalein is identical with *α -naphthaphthalein* obtained by Grabowski (*loc. cit.*) by fusing *α -naphthol* with phthalic anhydride. Grabowski gives C₂₈H₁₈O₄· $\frac{1}{2}$ H₂O as its composition. *α -Naphthaphthalein* is also obtained by the careful fusion of di-1-ethoxynaphthylphthalide with potassium hydroxide.

α -Naphthfluoran (VI).—On heating *α -naphthaphthalein* for half an hour at 290°, it ceases to be soluble in alkalis. On digesting the fused dark mass with animal charcoal in benzene, and crystallising from the latter, a substance, white crystals, melting at 300°, was obtained, which was identical with *α -naphthfluoran*, prepared by Grabowski (*loc. cit.*) and Meyer (*loc. cit.*) by fusing *α -naphthol* with phthalyl chloride.

9-Ethylcarbazole-3-phthaloylic acid (VII) and *9-ethylcarbazole-3·6-diphthaloylic acid* (VIII).—*9-Ethylcarbazole* was prepared by Graebe and Behägel's method (*Annalen*, 1880, **202**, 24), with the introduction of the modifications applied by Ehrenreich (*loc. cit.*) in the case of *9-methylcarbazole*.

The acids were obtained by condensing phthalyl chloride (1 mol.) with *9-ethylcarbazole* (2 mols.) in the presence of aluminium chloride suspended in carbon disulphide, and in larger quantities by using phthalic anhydride instead of phthalyl chloride, the chief products in the former case being the phthalides IX and X.

The reaction mixture from the first condensation was decomposed and distilled with steam (care has to be taken to add an excess of acid and pass steam for about two hours, as the aluminium complex is very stable), and the residue was extracted with ether to remove unchanged ethylcarbazole, and washed several times with hot water to remove any phthalic acid. The residue, a greyish-yellow powder, was digested with warm dilute ammonia, and the solution filtered. On acidifying the alkaline solution, a

white powder was precipitated, which was found to consist of two acids, one soluble and the other practically insoluble in benzene.

The latter crystallised from ethyl alcohol in rhombic crystals, melting at 266—268°. The acid soluble in benzene was obtained from this solvent in white needles, which, on being recrystallised from ethyl alcohol, melted at 188—189°. Both acids were obtained as the main product on using phthalic anhydride. The acid of lower melting point was found to be 9-ethylcarbazole-3-phthaloylic acid, whilst the other acid was 9-ethylcarbazole-3: 6-diphthaloylic acid.

In agreement with Ehrenreich's experience (*loc. cit.*) in the case of 9-methylcarbazole-3-mono- and -3: 6-diphthaloylic acids, the authors find that, in the condensation of ethylcarbazole with phthalic anhydride, the use of benzene instead of carbon disulphide as a solvent, and of equimolecular quantities instead of 1 mol. of ethylcarbazole to 2 mols. of phthalic anhydride, considerably increases the proportion of the monophthaloylic acid.

The acid, m. p. 266—268°:

0.1306 gave 0.3489 CO₂ and 0.0501 H₂O. C=72.86; H=4.27.

0.5104 „ 13.7 c.c. N₂ at 17° and 752 mm. N=3.07.

C₃₀H₂₁O₆N requires C=73.30; H=4.29; N=2.85 per cent.

The *silver* salt, which is amorphous, white, and stable to light, was prepared by treating a boiled ammoniacal solution of the acid with dilute silver nitrate:

0.4128 gave 0.1230 Ag. Ag=29.80.

C₃₀H₁₉O₆NAg₂ requires Ag=30.61 per cent.

The acid, m. p. 188—189°:

0.1517 gave 0.4267 CO₂ and 0.0668 H₂O. C=76.72; H=4.89.

0.4860 „ 16.5 c.c. N₂ at 18° and 758 mm. N=3.91.

C₂₂H₁₇O₈N requires C=76.94; H=4.98; N=4.08 per cent.

The *silver* salt of the ethylcarbazolephthaloylic acid resembles closely the silver salt of the diphthaloylic acid in appearance and properties:

0.3801 gave 0.0883 Ag. Ag=23.24.

C₂₂H₁₆O₃NAg requires Ag=23.97 per cent.

2: 3: 6: 7-Diphthaloyl-9-ethylcarbazole (XI).—One part of 9-ethylcarbazole-3: 6-diphthaloylic acid and 25 parts of concentrated sulphuric acid were heated at 99° for five hours. The product was poured on ice, filtered, and extracted with warm dilute sodium hydroxide. The residue, a dark powder, was found to be insoluble in alcohol and benzene, sparingly soluble in glacial acetic acid, and soluble in pyridine and nitrobenzene; from the latter it separated in monoclinic crystals, which, on being washed

with light petroleum, were found to be of a yellowish-grey colour. The substance did not melt at 300° , and with concentrated sulphuric acid it gave a bluish-violet colour, which changed to violet on adding concentrated hydrochloric acid:

0.1213 gave 0.3501 CO_2 and 0.0373 H_2O . $\text{C}=78.72$; $\text{H}=3.61$.

$\text{C}_{30}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{C}=79.10$; $\text{H}=3.73$ per cent.

Di-9-ethylcarbazylphthalide (IX).—The main product of the reaction of phthalyl chloride and 9-ethylcarbazole, insoluble in ammonia, was extracted with ethyl alcohol, and a canary-yellow, crystalline compound was obtained from the alcoholic solution. After several recrystallisations from alcohol, the substance decomposed, on heating, above 155° . With concentrated sulphuric acid it gave a mauve colour in the cold, and a bluish-green on heating.

The substance is soluble in alcoholic potassium hydroxide, benzene, and acetic acid:

0.1844 gave 0.5581 CO_2 and 0.0876 H_2O . $\text{C}=82.52$; $\text{H}=5.28$.

0.4742 „ 21.6 c.c. N_2 at 17° and 755 mm. $\text{N}=5.25$.

$\text{C}_{36}\text{H}_{28}\text{O}_2\text{N}_2$ requires $\text{C}=83.04$; $\text{H}=5.42$; $\text{N}=5.38$ per cent.

On fusion with potassium hydroxide, benzoic acid and some tarry matter were formed.

Tri-9-ethylcarbazylidiphthalide (X).—In the preceding preparation, the portion which was insoluble in alcohol was extracted with benzene and crystallised from benzene and light petroleum. On recrystallising twice from this solvent, a light yellow, crystalline substance was obtained, which decomposed at above 235° . It is sparingly soluble in alcohol or alcoholic potassium hydroxide, and moderately so in acetic acid. With concentrated sulphuric acid it gives a dark violet colour in the cold and a green on heating. After fusing with potassium hydroxide, benzoic acid and tarry matter are obtained:

0.1711 gave 0.5088 CO_2 and 0.0765 H_2O . $\text{C}=81.10$; $\text{H}=4.98$.

0.3612 „ 14.8 c.c. N_2 at 17° and 756 mm. $\text{N}=4.72$.

$\text{C}_{58}\text{H}_{43}\text{O}_4\text{N}_3$ requires $\text{C}=82.33$; $\text{H}=5.12$; $\text{N}=4.96$ per cent.

The residue, which was insoluble in benzene, was found to be soluble in chloroform, pyridine, and nitrobenzene. On digesting with alcohol, a brownish powder was obtained. It does not melt at 300° , and gives a dark green coloration with concentrated sulphuric acid, the solution becoming yellow when diluted with water. The substance has not yet been identified.