211. *Synthetic Experiments in the Rubrene Series.*

By Ernst Bergmann.

On interaction with phenylmagnesium bromide, 1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* is converted into a keto-acid, which can be cyclised to give 9 : 10-*diphenylnaphthacene*-11 : 12-*quinone*. This quinone, which is the fundamental substance for the synthesis of rubrene and similar compounds, is more readily obtained by dehydration of the *addition product* of 1 : 2-diphenyl*iso*benzfuran and α-naphthaquinone.

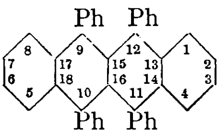
1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride is converted by the former method into 9-*phenylnaphthacene*-11 : 12-*quinone*, which, on reaction with phenyllithium, takes up only one phenyl group.

Several side reactions occurring in the above syntheses are discussed.

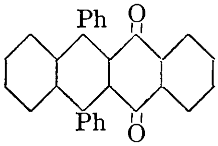
Recently rubrene has been proved to be 9 : 10 : 11 : 12-tetraphenylnaphthacene (I) by two independent syntheses (Dufraisse and Velluz, *Compt. rend.*, 1935, **201**, 1394; *Bull. Soc. chim.*, 1936, **3**, 1905; Allen and Gilman, *J. Amer. Chem. Soc.*, 1936, **58**, 937) in both of which the decisive step is the preparation of 9 : 10-diphenylnaphthacene-11 : 12-quinone (II). As has already been pointed out by the American authors, neither method can be extended to give tetra-arylnaphthacenes containing different substituents at the top and at the bottom of the formula. We tried, therefore, to develop new synthetic methods, and report the results so far obtained.

1 : 2-Diphenyl*iso*benzfuran (III) reacts with maleic anhydride (Weiss and Abeles, *Monatsh.*, 1932, **61**, 162; Barnett, J., 1935, 1326 ; Dufraisse and Prion, *Bull. Soc. chim.*,

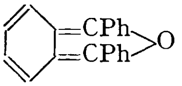
1938, **5**, 611) to give the addition product (IV), and this on dehydration yields 1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylic anhydride*. The reaction of this anhydride with phenylmagnesium bromide according to the method of Weizmann and co-workers (J., 1935, 1367; 1936, 567) gives a keto-acid (V), which can be cyclised by means of benzoyl chloride in α-chloronaphthalene solution (I. G. Farbenindustrie A.G., German Pat. 590,579; *Chem. Zentr.*, 1934, II, 3846; compare Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531**, 48, 127) to give 9 : 10-*diphenylnaphthacene*-11 : 12-*quinone* (II). When concentrated sulphuric acid is used as the dehydrating agent, oxidation takes place and instead of (II), a *dihydroxydiphenyldihydronaphthacenequinone* is obtained, whose bright red colour, recalling that of dihydroxynaphthacenequinone, may be evidence in favour of formula (VI). The hydroxylating action of concentrated sulphuric acid has been observed in similar cases; it is responsible for the formation of halochromic solutions from 9 : 10-diphenylanthracene and hot sulphuric acid (Schlenk and Bergmann, *Annalen*, 1928, **463**, 174; compare Ingold and Marshall, J., 1926, 3084).



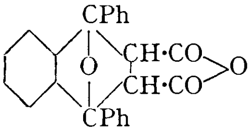
(I.)



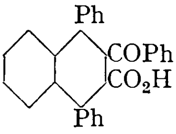
(II.)



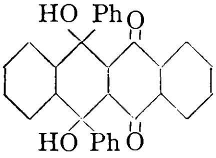
(III.)



(IV.)

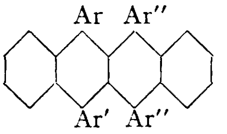


(V.)



(VI.)

The *iso*benzfuran (III) is prepared from phenylphthalide and phenylmagnesium bromide. Evidently a substituent other than phenyl may be present in either reagent, and therefore the preceding method of synthesis is capable of producing tetra-arylnaphthacenes of the types



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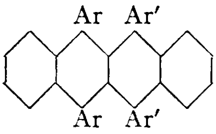
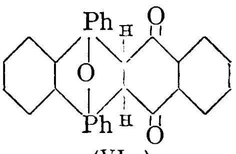
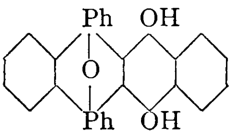


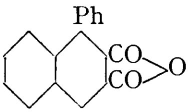
The synthesis described above can be considerably shortened by the direct addition of (III) to α-naphthaquinone; the analogous addition to benzoquinone has been studied by Barnett (*loc. cit.*). When the resulting *compound* (VI*a*) is treated with hydrobromic acid in glacial acetic acid solution, two reactions occur, namely, removal of 1 mol. of



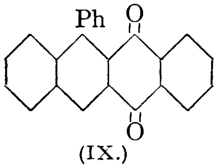
(VI*a*.)



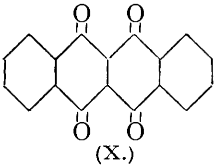
(VII.)



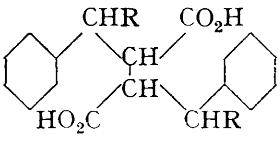
(VIII.)



(IX.)



(X.)



(XI.)

water, yielding the desired quinone (II), and isomerisation to (VII). The migration of hydrogen atoms in products of type (VI*a*) has been studied in detail, *e.g.*, by Diels, Alder, and Stein (*Ber.*, 1929, **62**, 2337).

Similarly, 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (VIII), which is prepared by the interaction of phenylpropiolic acid and acetic anhydride (Michael and Bucher, *Amer. Chem. J.*, 1898, **20**, 93; Schaarschmidt, *Ber.*, 1915, **48**, 1826), when treated successively with phenylmagnesium bromide and concentrated sulphuric acid, is easily converted into 9-*phenylnaphthacene*-11 : 12-*quinone* (IX). Phenyl-lithium introduces only one phenyl group into (IX): we hope to convert the quinone into triarylnaphthacenes under more drastic conditions.

Naphthacenediquinone (X) gives no phenylated products on interaction with phenyl-lithium; only dihydroxynaphthacenequinone has been isolated, formed by partial reduction (compare Gabriel and Leupold, *Ber.*, 1898, **31**, 1283).

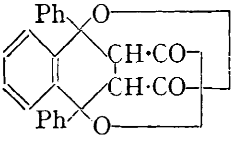
An even more prolific synthesis is being explored, namely, the interaction between Grignard compounds and the diketones which should be accessible by double cyclisation of αβ-dibenzylsuccinic acid or its symmetrically diarylated derivatives (XI, R = H or Ar). The tetra-arylnaphthacenes so formed should be identical with the substances obtained by the " rubrene reaction " from $CPh_2Cl\cdot C⁝CAr$.

EXPERIMENTAL.

1 : 2-Diphenyl*iso*benzfuran (III) was prepared by Guyot and Catel's method (*Bull. Soc. chim.*, 1906, **35**, 1125) from phenylphthalide and phenylmagnesium bromide, but the results were not always satisfactory. Sometimes, instead of (III), its oxidation product, *o*-dibenzoylbenzene, was obtained.

The addition of (III) to maleic anhydride took place smoothly, but dehydration of the product proved troublesome. (*a*) The addition product (IV) (12 g.) was suspended in methanol (120 c.c.), saturated with hydrogen chloride at 0°, and boiled for 3 hours in a current of the gas. The precipitate was filtered off, washed with sodium carbonate solution, and boiled with methanol (30 c.c.) and 15% methyl-alcoholic potassium hydroxide (16·5 c.c.) for 4 hours. The solvent was distilled off, and the residue dissolved in water and precipitated with acid. The oily acid solidified and was purified by means of glacial acetic acid. The first crop only consisted of the desired 1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylic anhydride*, prismatic plates (1·6 g.), m. p. 273—275° (Found: C, 82·2; H, 4·1. $C_{24}H_{14}O_3$ requires C, 82·3; H, 4·0%).

(*b*) In a second experiment, the product (11·2 g.) obtained after the treatment with methyl-alcoholic potassium hydroxide was boiled with thionyl chloride (50 c.c.) for 3 hours. Part of the product (3·2 g.) crystallised on cooling; recrystallised from glacial acetic acid containing some acetic anhydride, it formed quartz-like crystals, m. p. 250—252°. The *substance* was not acidic and was probably a dilactone (annexed formula) (Found: C, 77·9; H, 4·5. $C_{24}H_{16}O_4$ requires C, 78·2; H, 4·3%). The orange-red residue obtained on evaporation of the excess of thionyl chloride was recrystallised from glacial acetic acid. Two substances were obtained and were separated mechanically: the colourless portion had m. p. 250—252° and was identical with the above dilactone(?); the reddish crystals had m. p. 273—275° and did not depress the m. p. of the above anhydride.



(*c*) The most satisfactory result was obtained as follows: The addition product (IV) (2·2 g.) was kept for 2 days at 37° in glacial acetic acid (30 c.c.) saturated with hydrogen bromide. The precipitate was filtered off (*A*), and the filtrate diluted with water, giving a precipitate of 1 : 4-diphenylnaphthalene-2 : 3-dicarboxylic anhydride, which crystallised from ligroin in clusters of needles, m. p. 275°.

Precipitate (*A*) was recrystallised from butyl alcohol and then from nitrobenzene, giving the acid, m. p. 295° (decomp.), corresponding to the above anhydride. On prolonged heating with butyl alcohol, (*A*) was converted into *butyl hydrogen* 1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylate*, leaflets, m. p. 238° (Found: C, 79·8; H, 5·8. $C_{28}H_{24}O_4$ requires C, 79·3; H, 5·7%).

9 : 10-*Dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydronaphthacene*-11 : 12-*quinone* (VI).—A Grignard solution prepared from bromobenzene (0·4 c.c.) and magnesium (0·1 g.) was added to a hot benzene solution of the above anhydride (1·3 g.), and the mixture heated for 1 hour. After

decomposition with ice and sulphuric acid, the keto-acid was isolated in the usual way. It was not obtained crystalline. This crude product was treated with concentrated sulphuric acid (10 c.c.) (it exhibited a red-green dichroic colour reaction) at room temperature for 3 hours and then poured on ice. The red powder obtained, m. p. above 360°, was dried and crystallised from ethyl benzoate; yield, 0·77 g. (Found : C, 82·3, 82·1; H, 4·4, 4·1. $C_{30}H_{18}O_4$ requires C, 81·5; H, 4·1%). When the crude keto-acid was treated with benzoyl chloride in α-chloronaphthalene solution (Vollmann and co-workers, *loc. cit.*), 9 : 10-diphenylnaphthacene-11 : 12-quinone (II) was obtained in moderate yield.

Addition of 1 : 2-*Diphenyl*iso*benzfuran to* α-*Naphthaquinone*.—The *iso*benzfuran (5·4 g.) and the quinone (3·2 g.) were heated in boiling xylene (20 c.c.) for 2 hours. The *addition product* (VI*a*) (6·8 g.) separated, on cooling, in well-shaped rhombic crystals, which were conveniently recrystallised from butyl acetate. The intensely fluorescent solution was dark red at the b. p., lemon-yellow at room temperature. The crystals were yellow, but gave at 150° a red, nearly black, liquid (Found : C, 83·5; H, 4·8. $C_{30}H_{20}O_3$ requires C, 84·1; H, 4·7%). In accordance with similar observations of Barnett (*loc. cit.*), the substance showed a tendency to dissociate into its constituents; *e.g.*, on treatment with phenylmagnesium bromide, diphenyl*iso*benzfuran (III) was regenerated, some unchanged material recovered, and a brown-red substance of unknown nature obtained, which crystallised from benzyl alcohol in needles, m. p. above 360°.

9 : 10-*Diphenylnaphthacene*-11 : 12-*quinone* (II) *and* 11 : 12-*Dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydronaphthacene Oxide* (VII).—The addition product (VI*a*) (2 g.) was kept at 37° for 2 days with a mixture of glacial acetic acid (20 c.c.) and 40% hydrobromic acid (5 c.c.). The crystalline part of the product (1·2 g.) was collected and recrystallised from butyl acetate. The first crop consisted of stout yellow prisms (0·5 g.), m. p. 282°; according to their m. p. and analysis they were *diphenylnaphthacenequinone* (II) (Found : C, 87·8, 88·0; H, 4·6, 4·9. $C_{30}H_{18}O_2$ requires C, 87·8; H, 4·4%). On being cooled to — 10°, the butyl acetate mother-liquor deposited a second *substance* (0·4 g.) in colourless needles, m. p. 150°, which according to the analysis had formula (VII) (Found : C, 83·9; H, 4·9. $C_{30}H_{20}O_3$ requires C, 84·1; H, 4·7%). A second crop of this substance was obtained when water was added to the original glacial acetic acid mother-liquor and the precipitate was recrystallised from propyl alcohol; m. p. 150°.

9-*Phenylnaphthacene*-11 : 12-*quinone* (IX).—1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride (VIII) (7·5 g.) was dissolved in the necessary quantity of boiling toluene, and a solution of phenylmagnesium bromide (from 0·7 g. of magnesium and 3 c.c. of bromobenzene) added. After 2 hours' boiling, the product was decomposed and worked up in the usual way. The keto-acid formed was a resin, giving a dark red-violet colour reaction with concentrated sulphuric acid. It (3·8 g.) was kept at the ordinary temperature for 20 hours with this acid (38 c.c.) and then poured into ice-water. The brown precipitate was collected, washed with sodium carbonate solution and water, dried, and recrystallised first from butyl alcohol and then from glacial acetic acid; m. p. 215°. Thin individual crystals were yellow, thicker ones brown; they consisted of octahedra with rounded corners (Found : C, 86·1; H, 4·5. $C_{24}H_{14}O_2$ requires C, 86·2; H, 4·2%).

Interaction with phenyl-lithium. The quinone (IX) (1 g.) was introduced into a phenyl-lithium solution prepared from lithium (0·23 g.) and bromobenzene (3·1 c.c.; 10 mols.). It dissolved slowly; after 6 days, the mass was poured into ice-cold dilute sulphuric acid. The product was an oil, which crystallised on trituration with methyl alcohol; it was purified by means of toluene, forming prisms, m. p. 248° (decomp.), which dissolved in concentrated sulphuric acid with an intense brown colour. The *substance* is probably 11-hydroxy-12-keto-9 : 11-diphenyl-11 : 12-dihydronaphthacene, the carbonyl group at C_{11} in (IX) being less sterically hindered than that at C_{12} (Found : C, 86·9; H, 5·2. $C_{30}H_{20}O_2$ requires C, 87·4; H, 4·9%).

Naphthacenediquinone (X), prepared by Deichler and Weizmann's method (*Ber.*, 1903, **36**, 719) (1·2 g.), was added to phenyl-lithium [from 0·72 g. of lithium and 9·5 c.c. (20 mols.) of bromobenzene]. A vigorous reaction took place. After 6 days the product was worked up as described above. It separated from ethyl malonate in bright red needles, which were identified by m. p. and mixed m. p. (357°) as dihydroxynaphthacenequinone. From the residue obtained from the ethereal layer, no definite substance could be isolated.

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