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EXPERIMENTS IN THE ARYL NAPHTHACENE SERIES. PART III

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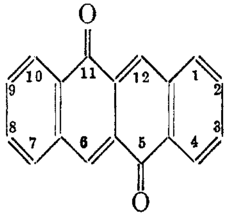
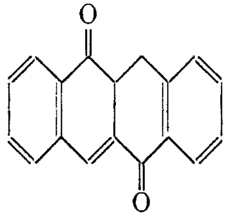
In Part I (1) experiments with 6,11-diphenylnaphthacene-5,12-quinone have been described which contribute to our knowledge of the rubrenes proper, the 5,6,11,12-tetraaryl naphthacenes (4). In order to make the 5,11-diaryl naphthacenes equally available by synthesis, it was necessary to find a suitable 5,11-dicarbonyl derivative of naphthacene, which was to be treated with organometallic compounds. In view of the observation that the ana-quinone (I) of naphthacene (naphthacene-5,11-quinone) does not react "normally" with organometallic compounds, its hydrogenation products have been investigated. A preliminary report has been given in Part II (2) on the experiments with the dihydro derivative (II) of (I), the 5,11-diketo-5,11,11a,12-tetrahydronaphthacene. These experiments have been continued, but neither phenyl- nor *p*-tolyllithium have given with (II) the expected reaction: in neither case, could more than one aryl group be introduced into the naphthacene system by means of the aryl lithium compounds.

On interaction with phenyllithium, (II) gave a compound $C_{24}H_{16}O$ (m.p. 255°), which could be transformed with acetyl chloride into a yellow substance of the formula $C_{26}H_{18}O_2$ and of m.p. 268°. This composition and the color support the previously suggested formula of 11-phenyl-5-acetoxynaphthacene (IV); the substance $C_{24}H_{16}O$, therefore, is 11-phenyl-5-hydroxynaphthacene (III a) or its ketonic form, 11-phenyl-5-keto-5,12-dihydronaphthacene (III b). The mechanism of the reaction appears to be the following: The saturated carbonyl group at C_{11} reacts normally, and subsequently splits off water between C_{11} and C_{11a}. The resulting dihydronaphthacene derivative (III b) may stabilize itself by enolization.



I



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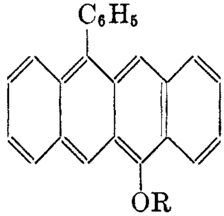
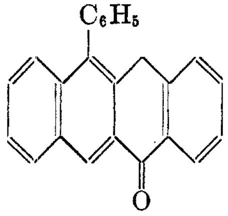
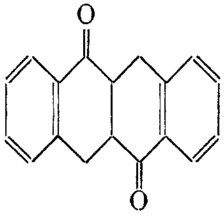


IIIa: R=H IV: R=CH_3CO



IIIb



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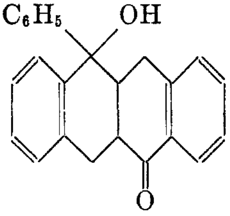

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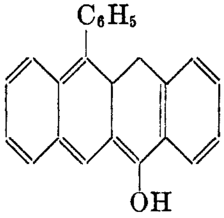

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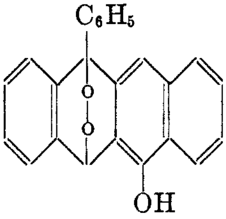
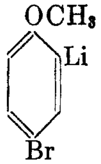


VIII



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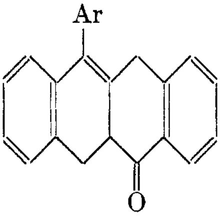

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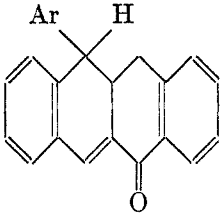

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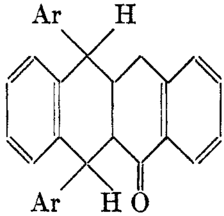
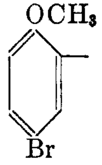
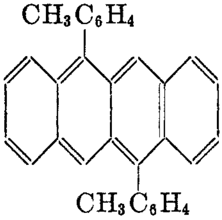


XII

Ar =





XIII

With *p*-tolyllithium, the reaction of (II) proceeded analogously. A substance $C_{25}H_{18}O$, m.p. 248°, was formed, which could be acetylated to give a compound $C_{27}H_{20}O_2$; evidently, these are the analogs of (III) and (IV), respectively.

In view of the possible desmotropy between (III a) and (III b), the observation should be recorded that in one of the reactions of (II) with phenyllithium, instead of the substance of m.p. 255°, a brown isomer, m.p. 230°, has been obtained in small quantities, which may be the desmotropic form.

All these experiments tend to show that carbonyl derivatives of the naphthacene series which contain a double bond in α,β-position to the carbonyl group, do not react "normally" with organometallic reagents. Recourse was therefore taken to the tetrahydro derivative (V) of (I), the 5,5a,6,11,11a,12-hexahydro-5,11-diketonaphthacene. This substance, m.p. 220–222°, was made available from *sym.* dibenzylsuccinic acid; its interaction with a number of aryl lithium compounds proved rather complex.

With phenyllithium, again only one phenyl group could be introduced into the molecule. The well-crystallized product of m.p. 295–298° had the curious formula $C_{24}H_{16}O_3$. Two of the three oxygen atoms are of peroxydic nature, as the liberation of iodine from potassium iodide solution shows. As a possible formula (VIII) is suggested, which would be understandable if the following mechanism of reaction is assumed: one carbonyl group in (V) reacts with phenyllithium in the expected manner; the product (VI) loses one molecule of water and is subsequently enolized to (VII), which in contact with air is dehydrogenated and converted into the peroxide (VIII) in the same way as most naphthacenes are.

Still more complicated was the reaction with the organometallic compound derived from *p*-bromoanisole and lithium. This compound was the 2-lithio-4-bromoanisole (IX), in analogy with the recent observations of Wittig and his co-workers (7). Its crystalline reaction product with (V) had the formula $C_{32}H_{26}Br_2O_3$, showing that two aromatic nuclei had entered the molecule; two of the oxygen atoms are accounted for by the two methoxyl groups, the third is not hydroxylic in nature, as the substance is resistant to boiling acetyl chloride. Its formula is assumed to be (XII), 6,11-di-(2′-methoxy-5′-bromophenyl)-5-keto-5,5a,6,11,11a,12-hexahydronaphthacene; such a substance would be formed by the following successive steps: normal reaction at C_{11} and dehydration to (X), which, however, rearranges to (XI), possessing an α,β-unsaturated carbonyl system. This reacts by the usual 1,4-addition process with a second molecule of the lithium compound (IX) and gives, by hydrolysis and simultaneous ketonization, (XII).

Only with *p*-tolyllithium, could the desired reaction be achieved. From (V) a deep yellow hydrocarbon $C_{32}H_{24}$ was obtained, which according to its formula, its color, and the high melting point (335–336°) is regarded as the desired 5,11-di-*p*-tolylnaphthacene (XIII).

EXPERIMENTAL

Benzylsuccinic acid was prepared according to Cordier (3). An alcoholic solution of sodium ethoxide (from 7.5 g. of sodium and 100 cc. of anhydrous alcohol) was treated in quick succession with ethyl benzylmalonate (75 g.) (5) and ethyl bromoacetate (51 g.). After 6–8 hours on the water-bath, the reaction was complete. The alcohol was evaporated, the residue treated with a little dilute sulfuric acid and extracted with ether. The crude triethyl 1-phenylpropane-2,2,3-tricarboxylate (96 g.) was hydrolyzed by heating for 4 hours with alcoholic potash (75 g. of KOH in 300 cc. of alcohol). The product was diluted with water (200 cc.), acidified, and extracted with boiling ether. The tricarboxylic acid was thus obtained as an oil (89 g.), which crystallized partly on standing. Decarboxylation was effected by heating at 165–170° for 1 hour. Twenty grams of the tricarboxylic acid gave 15 g. of benzylsuccinic acid, m.p. 160–161°, after recrystallization from benzene.

Dimethyl benzylsuccinate was obtained in good yield from the acid (53 g.) and methanol (90 cc.), saturated with gaseous hydrochloric acid, on the water-bath for one hour; boiling point 128–135°/1.5 mm.

Anal. Calc'd for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8.
Found: C, 65.8; H, 7.0.

Benzylidenebenzylsuccinic acid. To a mixture of dimethyl benzylsuccinate (28 g.), benzaldehyde (13.4 g.) and ether (60 cc.), 2.8 g. of sodium powder was added. The initial reaction was violent; it was completed by heating on the water-bath for 3 hours. Water (100 cc.), and after 1 hour 33% sodium hydroxide solution (20 cc.), were added, and the hydrolysis was completed on the water-bath, for 1.5 hours. After cooling, hydrochloric acid (75 cc. of concentrated acid and 75 cc. of water) was added, and the oily product isolated after 12 hours standing at 0°, and triturated with isopropyl ether. The crystals had, after recrystallization from 50% acetic acid, the expected m.p. 160–162°; yield 10 g.

sym. *Dibenzylsuccinic acid.* The two diastereomerides of this acid have already been observed by Stobbe and von Vigier (6); our experience is that catalytic hydrogenation of benzylidenebenzylsuccinic acid gives sometimes the high-melting isomer (m.p. 210°; Stobbe 204°), sometimes a low-melting product (m.p. 170°), which, however does not depress markedly the melting point of the 210° substance. No attempt has been made to find whether these two products represent two distinct and pure isomers (Stobbe's second isomer had the m.p. 203°), and whether and how their formation depends on the conditions of hydrogenation (speed of hydrogen absorption, etc.), as it was observed that both cyclize to the same diketone (V). The hydrogenations were carried out in propyl or isopropyl alcohol as solvent, with palladium on barium sulfate as catalyst, at the boiling point of the solvent. The 210° product is best recrystallized from benzene, the 170° product from isopropyl alcohol.

5,5a,6,11,11a,12-Hexahydro-5,11-diketonaphthacene (V). Dibenzylsuccinic acid (1 g.) and concentrated sulfuric acid (50 cc.) were heated on the water-bath for 1 hour; the mixture was then poured onto ice and the solid product collected (yield, 0.6 g.). From butyl alcohol, fine, white needles, m.p. 220–222°.

Anal. Calc'd for $C_{18}H_{14}O_2$: C, 82.5; H, 5.3.
Found: C, 82.5; H, 5.3.

Peroxide (VIII). The foregoing diketone (V, 1 g.) was added to an ethereal solution of phenyllithium (from 6 g. of bromobenzene and 0.6 g. of lithium shavings) in a Schlenk-tube under nitrogen in the usual manner. After 48 hours, the tube was opened and the reaction mixture decomposed with ice-cold dilute sulfuric acid. The ether residue was triturated with methyl alcohol and recrystallized from butyl alcohol; reddish, long needles, m.p. 295–298°, which liberate iodine from a solution of potassium iodide in glacial acetic acid.

Anal. Calc'd for $C_{24}H_{16}O_3$: C, 81.8; H, 4.5.
Found: C, 81.9, 82.0; H, 4.1, 4.3.

6,11-Di-(2'-methoxy-5'-bromophenyl)-5-keto-5,5a,6,11,11a,12-hexahydronaphthacene (XII). To the filtered organometallic solution (from 0.26 g. of lithium metal and 6.7 g. of *p*-bromoanisole in anhydrous ether), the diketone (V, 0.5 g.) was added. The color turned to a fluorescent green, then to brown-red, while the diketone dissolved. After one day in the sealed Schlenk-tube, the reaction product was treated with dilute sulfuric acid and the ether dried and evaporated. The residue was triturated with methyl alcohol and recrystallized from benzene; colorless, hexagonal prisms, m.p. 278°; yield, 0.33 g.

Anal. Calc'd for $C_{32}H_{26}Br_2O_3$: C, 62.1; H, 4.2; Br, 25.9.
Found: C, 62.5; H, 4.3; Br, 25.3.

The substance contains methoxyl and is resistant to prolonged treatment with boiling acetyl chloride.

5,11-Di-p-tolylnaphthacene (XIII). In the analogous reaction of (V) with *p*-tolyllithium, the reaction mixture turned first red, then brown. The reaction product was triturated with methyl alcohol and recrystallized from pyridine; deep yellow, rhombic crystals, m.p. 335–336°. The analysis (Found: C, 93.6; H, 6.4) is perhaps in better accord with the formula $C_{32}H_{26}$ than with the expected $C_{32}H_{24}$ (Calc'd: C, 94.1; H, 5.9), but $C_{32}H_{26}$ appears to be unlikely, all the properties of the material pointing to a purely naphthacenic structure. In addition, the analysis of hydrocarbons of this series is not always easy.

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