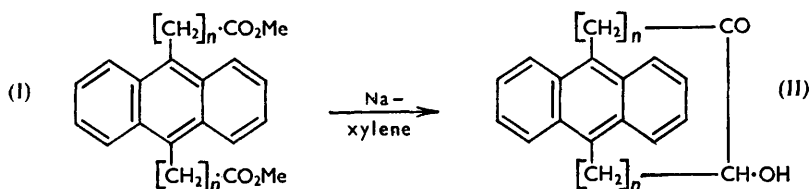


301. A New Method for the Preparation of 9 : 10-Disubstituted Anthracenes.

By K. JASPER CLARK.

9 : 10-Disubstituted 9 : 10-dihydro-9 : 10-dihydroxyanthracenes, obtained by the action of Grignard reagents upon anthraquinone, can be conveniently reduced by phenylhydrazine in acetic acid to 9 : 10-disubstituted anthracenes in good yield.

9 : 10-DI-(ω -CARBOXYALKYL)ANTHRACENES were required for attempted acyloin ring-closures of their dimethyl esters (I; $n > 3$), and the consequent production of bridges across the 9 : 10-positions of anthracene (II), but no general method for the synthesis of such acids has been published.



The reaction of 9 : 10-dihydro-9 : 10-disodioanthracene with ω -halogeno-esters failed to produce any hydrolysable material, possibly because of acylation of the disodio-compound analogous to that reported for ethyl benzoate.¹ Clearly, a halide is required which bears on the ω -position a relatively inert system which is capable of being converted into a carboxy-group. Allyl bromide has been employed successfully to give a 35% yield of 9 : 10-diallyl-9 : 10-dihydroanthracene. However, oxidation of this compound to 9 : 10-diallylanthracene, by the use of benzoquinone or chloranil, gave only very poor yields.

Accordingly, Grignard reagents bearing ω -olefinic and ω -ethereal groups, capable of further reaction, have been examined for activity towards anthraquinone, and a study made of the reduction of the 9 : 10-disubstituted 9 : 10-dihydro-9 : 10-dihydroxyanthracenes so obtained. The method of Cook *et al.*² for the reaction of anthraquinone with twice the calculated quantity of Grignard reagents gave reproducible yields of the desired diols. Hitherto, the most generally successful reduction of such diols has been to shake their dimethyl ethers with an alkali metal for several days.³ This method failed with 9 : 10-diallyl-9 : 10-diethoxy-9 : 10-dihydroanthracene, potassium or sodium being used, but it was found that such diols, or their ethereal derivatives, could be reduced smoothly by phenylhydrazine in acetic acid in $\frac{1}{2}$ hr. The yields of 9 : 10-disubstituted anthracenes (III) from diprimary alkylanthracenediols are of the order of 60%.

9 : 10-Diallyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene, prepared by Cook *et al.*² in unquoted yield, was obtained in 73% yield from allylmagnesium bromide, and found to exist in two isomeric forms, which were easily separated after methylation or ethylation. Both diethyl derivatives absorb at 10.09 μ and 10.95 μ (allyl), and at 9.4 μ (ethoxy). The mixture of diallylanthracenediols, and both dimethyl and diethyl ethers, reacted with phenylhydrazine in acetic acid to give a 65% yield of 9 : 10-diallylanthracene, absorbing at 10.09 μ and 10.95 μ (allyl), and identical with the product obtained from 9 : 10-dihydro-9 : 10-disodioanthracene. The best results were obtained by mixing the reactants in the cold, warming the solution rapidly until nitrogen was evolved, and finally refluxing for $\frac{1}{4}$ hr. Addition of the diol to a boiling solution of phenylhydrazine in acetic acid lowered the yield to 31%, and the major product was a yellow powder, m. p. 195°; the spectral and

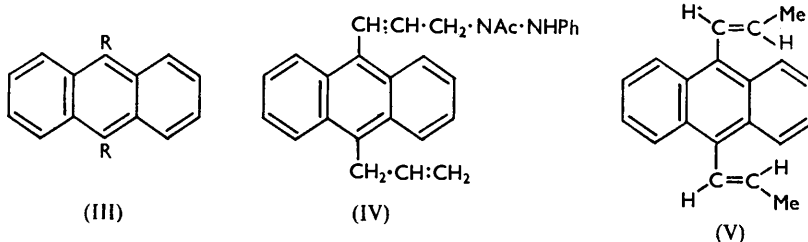
¹ Lerer, *Ann. Combustibles liquides*, 1933, **8**, 681.

² Cook, Dodds, and Lawson, *Proc. Roy. Soc.*, 1936—1937, *B*, **121**, 133.

³ Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583.

analytical evidence suggested that this material was 9-(3-*N*-acetyl-*N'*-phenylhydrazino-propenyl)-10-allylanthracene (IV), resulting from a 1:7-anionotropic rearrangement, during the reduction of the diallylanthracenediol.

9:10-Diallylanthracene was isomerised smoothly to the 9:10-dipropenyl compound, which absorbs at 10.33 μ and must therefore contain the most sterically probable *trans*-H configuration of the two double bonds (V). Bromination of both anthracenes, by either



bromine or *N*-bromosuccinimide, failed to yield identifiable products. However, hydrobromination of 9:10-diallylanthracene in acetic acid or benzene, in the presence of peroxide, gave a 90% yield of a dihydrobromide, which has an anthracene-type ultraviolet absorption and must therefore be a 9:10-bisbromopropylanthracene. It is hoped that this product is, in fact, the $\omega\omega'$ -dibrominated dipropylanthracene, which can be converted by standard reactions into 9:10-di-(4-carboxylbutyl)anthracene.

3-Ethoxypropylmagnesium bromide gave a 60% yield of 9:10-di-(3-ethoxypropyl)-9:10-dihydro-9:10-dihydroxyanthracene.

9:10-Dihydro-9:10-dihydroxy-9:10-diundecenylanthracene was prepared in 10% yield from undecenylmagnesium chloride, and gave a 67% yield of 9:10-diundecenylanthracene by the phenylhydrazine method. The three allyl absorption peaks of 5.42 μ , 10.09 μ , and 10.95 μ are all clearly shown in this anthracene.

3-Phenoxypropyl bromide and 4-phenoxybutyl bromide failed to yield recognizable addition products with anthraquinone in the Grignard reaction. The former reacted with magnesium in ether to give some gas, presumably *cyclopropane*,⁴ and phenoxymagnesium bromide. In addition, 1:6-diphenoxyhexane was isolated in small yield, after attempted reaction with anthraquinone. The liberation of phenoxymagnesium bromide did not take place in the preparation of 4-phenoxybutylmagnesium bromide, and a clear Grignard solution was obtained. This reagent has been reported to give a 30% yield of alcohol with benzophenone,⁵ but only 1:8-diphenoxyoctane was isolated after attempted reaction with anthraquinone.

Secondary alkylmagnesium halides gave poor or no yields of 9:10-dialkyl-9:10-dihydro-9:10-dihydroxyanthracenes. *iso*Propylmagnesium chloride gave only a 5% yield of the expected diol, and the bromide no yield. Reduction by phenylhydrazine gave a 29% yield of 9:10-di*iso*propylanthracene, absorbing at 7.35 μ . *cyclo*Hexylmagnesium bromide reacted with anthraquinone to give an unidentified oil, which would not distil, form solid ethers, or undergo reduction by phenylhydrazine. Steric effects, and the well-known reducing power of *cyclo*hexylmagnesium halides,⁶ undoubtedly complicate this reaction. Cook *et al.*,² however, report the isolation of 9:10-dihydro-9:10-dihydroxy-9:10-dicyclo-pentylanthracene by the Grignard method.

As a model preparation, 9:10-dimethylanthracene was prepared in 57% yield (overall) from anthraquinone by combination of the Grignard and the phenylhydrazine reduction method.

EXPERIMENTAL

9:10-Diallyl-9:10-dihydroanthracene.—A mixture of anthracene (50 g.), broken glass (20 g.), dry ether (600 ml.), and sodium powder (34.5 g.) was shaken under nitrogen for 3 days, and

⁴ Gragson, Greenlee, Derfer, and Boord, *ibid.*, 1955, **20**, 275.

⁵ Benoit, Delavigne, and Eliopoulo, *Ann. Pharm. franç.*, 1952, **10**, 181.

⁶ Sabatier and Mailhe, *Compt. rend.*, 1905, **141**, 298.

allyl bromide (72 g.) then added dropwise, with vigorous stirring and external cooling. Finally, the mixture was refluxed for 2 hr., cooled, and filtered, the residue being washed with dry ether (2 × 100 ml.). The combined ethereal solutions were washed with dilute hydrochloric acid, sodium carbonate solution, and water, dried (Na₂SO₄), and evaporated. The residual viscous oil was dissolved in light petroleum (b. p. 60—80°), and kept for 3 days. After filtration, the solution was distilled, and the pale yellow fraction, b. p. 160—170°/2—3 mm., collected (25.7 g., 35%). For analysis, this compound was redistilled at 110—112°/0.04 mm., and a small portion again distilled from a bulb (Found : C, 91.9; H, 7.6. C₂₀H₂₀ requires C, 92.3; H, 7.7%).

Oxidation of 9 : 10-Diallyl-9 : 10-dihydroanthracene.—This product (10.6 g.) and *p*-benzoquinone (8.8 g.) were refluxed for 3 hr. in dry xylene (100 ml.). After cooling overnight, the solution was filtered and evaporated to a tarry residue, which deposited a little solid during several days. This was crystallised repeatedly from alcohol (charcoal), to give light yellow needles of the *diallylanthracene*, m. p. 135.5°, strongly fluorescent in alcohol and benzene (Found : C, 92.8; H, 7.1. C₂₀H₁₈ requires C, 93.0; H, 7.0%). Light absorption : λ_{max}. 2600, 3400, 3580, 3750, and 4000 Å (ε 25,500, 2240, 4960, 7290, and 7480 respectively). Absorption also occurred at 10.09 μ and 10.95 μ (allyl).

No improvement in yield was found on lengthening the reaction time, or substituting chloranil for benzoquinone. A maleic anhydride adduct was prepared in xylene, and crystallised therefrom as white needles, m. p. 240° (decomp.) (Found : C, 81.1; H, 5.5. C₂₄H₂₀O₃ requires C, 80.9; H, 5.6%).

9 : 10-Diallyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene.—This compound was prepared, with certain modifications, according to the procedure of Cook *et al.*⁷ A solution of allylmagnesium bromide was prepared⁷ by adding allyl bromide (121 g.), in dry ether (500 ml.), dropwise to magnesium turnings (72 g.) and ether (300 ml.), with vigorous stirring. The rate of addition was adjusted to give a steady reflux (2—3 hr.). Stirring was continued for 2 hr., ether (500 ml.) added, and the ethereal solution decanted from excess of magnesium into a second flask. At 0°, and under vigorous stirring, anthraquinone (52 g.) was added in small portions (½ hr.). The stirring was continued for 3 hr., and the mixture stored overnight, a dark oil separating from the green ethereal solution. Decomposition was effected with concentrated ammonium chloride solution, with cooling, and the ethereal solution of the product was washed with water, and separated from any precipitated anthraquinone. On distillation, an oil remained, which crystallised on cooling. This was dissolved in hot benzene and shaken with boiling sodium hydrosulphite (dithionite) solution until the lower, aqueous layer was colourless. The benzene solution was dried (Na₂SO₄) and distilled, yielding a light yellow oil which crystallised on trituration with light petroleum (b. p. 60—80°). Recrystallisation from this solvent gave a mixture of the *cis*- and the *trans*-diol, m. p. 100—110° (53.3 g., 73%).

α- and β-9 : 10-Diallyl-9 : 10-dihydro-9 : 10-dimethoxyanthracene.—9 : 10-Diallyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene (5.4 g.) in dry methanol (20 ml.) was shaken with methanol (5 ml.) containing sulphuric acid (5 drops). A fine white solid was precipitated at once, and was filtered off and washed with aqueous ammonia and methanol. The *α*-dimethoxy-compound was insoluble in methanol, and was crystallised several times from benzene, forming fine white crystals (1.5 g.), m. p. 184° (Found : C, 82.7; H, 7.5. C₂₂H₂₄O₂ requires C, 82.5; H, 7.5%).

½ Hr. after deposition of the *α*-compound, macro-crystals began to be deposited, and this was allowed to proceed for ¼ hr. The *β*-compound was filtered off and washed as before; it crystallised from methanol as long white needles (2.3 g.), m. p. 92.5° (Found : C, 82.4; H, 7.6%).

α- and β-9 : 10-Diallyl-9 : 10-diethoxy-9 : 10-dihydroanthracene.—These two isomers were prepared, in the same manner as the methyl analogues, from ethanol, but reaction was slower. Deposition of the *α*-isomer occurred only after ¼ hr., and the fine white deposit was washed and crystallised from ethanol, small white crystals, m. p. 126°, being obtained (Found : C, 82.7; H, 8.1. C₂₄H₂₈O₂ requires C, 82.7; H, 8.0%). The *β*-form was deposited only after 2 hr., and crystallised from ethanol as long white needles, m. p. 76° (Found : C, 82.5; H, 8.0%). Light absorption : both isomers absorbed at 9.4 μ (ethoxy), and at 10.09 and 10.95 μ (allyl).

9 : 10-Diallylanthracene.—All four of the above dimethyl and diethyl ethers reacted, as the diol mixture below, to yield 9 : 10-diallylanthracene. The alkali-metal dealkoxylation⁹ failed in the one instance in which it was tried, *viz.*, on the *α*-diallyldiethoxy-compound. A mixture of 9 : 10-diallyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene (32.2 g.), phenylhydrazine (60 ml.), and glacial acetic acid (260 ml.) was heated on the water-bath until the evolution of nitrogen

⁷ Gilman and McGlumphy, *Bull. Soc. chim. France*, 1928, **43**, 1322.

⁸ Gensler, Behrmann, and Thomas, *J. Amer. Chem. Soc.*, 1951, **73**, 1071.

⁹ Anderson, Crawford, and Sherrill, *ibid.*, 1946, **68**, 1294.

ceased ($\frac{1}{4}$ hr.), and then refluxed for $\frac{1}{4}$ hr. Long yellow needles of 9 : 10-diallylanthracene crystallised from the mixture, and were washed with a little acetic acid and ethanol (18.7 g., 65.7%). For analysis, the compound was recrystallised from alcohol (charcoal) several times to give light yellow needles, m. p. 135.5° (Found : C, 92.9; H, 7.1. C₂₀H₁₈ requires C, 93.0; H, 7.0%).

Yields of 9 : 10-diallylanthracene were halved when the diallyl-diol was added, in small portions, to a boiling solution of phenylhydrazine in acetic acid. The main product was an amorphous yellow powder, which was recrystallised repeatedly from alcohol for analysis, m. p. 195°. Spectroscopic and analytical data indicated that it was 9-(3-N-acetyl-N'-phenylhydrazinopropenyl)-10-allylanthracene (Found : C, 83.0; H, 6.5; N, 6.75. C₂₈H₂₆ON₂ requires C, 82.75; H, 6.4; N, 6.8%). Light absorption : λ_{\max} . 2600, 3250, 3625, 3770, and 4000 Å (ϵ 30,000, 1290, 4400, 6600, and 6200, respectively). Absorption also occurred at 3.1 (NH), 6.01 (amide), 10.33 (*trans*-H), and 10.1 and 11.0 μ (allyl).

9 : 10-Dipropenylanthracene.—9 : 10-Diallylanthracene (3.35 g.) was heated at reflux temperature with ethanol (120 ml.) and potassium hydroxide (10 g.) for 12 hr. Green needles of the isomeric *propenyl compound* crystallised and were filtered off and washed with hot water (yield >90%). Recrystallisation from alcohol (charcoal) gave pale green needles, m. p. 166° (Found : C, 92.7; H, 6.9. C₂₀H₁₈ requires C, 93.0; H, 7.0%). Light absorption : λ_{\max} . 2550, 3850, and 4000 Å (ϵ 24,000, 10,200, and 9300, respectively). Absorption also occurred at 10.33 μ (*trans*-H).

9 : 10-Di-(*x*-bromopropyl)anthracene.—Glacial acetic acid (100 ml.) was saturated at below 10° with hydrobromic acid, from a tetralin generator, and phthalic acid (0.1 g.) added. 9 : 10-Diallylanthracene (5 g.) was added, and the mixture warmed. As the unsaturated compound dissolved, reaction took place, and finally the evolution of hydrobromic acid ceased as the solution refluxed. Dark green crystals were deposited when the mixture cooled, and these were separated and crystallised from alcohol (1 l.) (yield, 7.3 g., 90%). The *di(bromopropyl)-anthracene* was recrystallised several times for analysis, forming light green needles, m. p. 181.5° (Found : C, 57.0; H, 4.9; Br, 38.2. C₂₀H₂₀Br₂ requires C, 57.1; H, 4.8; Br, 38.1%). Light absorption : λ_{\max} . 2600, 3425, 3600, 3800, and 4000 Å (ϵ 34,300, 4480, 9330, 14,000, and 14,360, respectively).

9 : 10-Dihydro-9 : 10-dihydroxy-9 : 10-diundecenylanthracene. Undecenyl chloride⁸ (27 g.) in dry ether (70 ml.) was added dropwise to magnesium (3.4 g.) in ether (15 ml.). A small amount of allyl bromide was needed to initiate the reaction. The Grignard solution was then cooled to 0°, ether (150 ml.) added, and anthraquinone (7.42 g.) dropped in to the well-stirred solution at once. Stirring was continued at room temperature for 1 hr., and then under reflux for 3 hr. After the usual decomposition and extraction, an oil remained which crystallised from light petroleum (b. p. 60–80°) as white plates, m. p. 88° (1.85 g., 10%). A good analysis could not be obtained.

9 : 10-Dihydro-9 : 10-dimethoxy-9 : 10-diundecenylanthracene.—This *ether*, prepared as for the diallyl compound, crystallised from methanol; it had m. p. 77° (Found : C, 83.7; H, 10.3. C₃₈H₅₆O₂ requires C, 83.8; H, 10.3%).

9 : 10-Diundecenylanthracene.—The foregoing ether (0.8 g.) was treated with phenylhydrazine (1.5 ml.) and glacial acetic acid (6 ml.) in the manner described above. An oil separated during the refluxing period, but, on cooling, this solidified, and was separated and crystallised from ethanol, to give fine yellow-green needles (0.5 g., 67%), m. p. 70° (Found : C, 89.6; H, 10.5. C₃₆H₅₀ requires C, 89.6; H, 10.4%). Light absorption : λ_{\max} . 2600, 3425, 3600, 3800, and 4025 Å (ϵ 61,000, 3300, 7000, 11,900, and 11,200, respectively). Absorption also occurred at 5.42, 10.0, and 11.0 μ (allyl).

9 : 10-Di-(3-ethoxypropyl)-9 : 10-dihydro-9 : 10-dihydroxyanthracene.—3-Ethoxypropyl bromide⁹ (54.5 g.) in dry ether (160 ml.) was added dropwise to magnesium (7.8 g.) in ether (50 ml.), at such a rate that moderate refluxing was maintained. A crystal of iodine and warming were both necessary to initiate the reaction. After the dissolution of the metal, the solution was kept for $\frac{1}{2}$ hr., and then, with vigorous stirring at 0°, anthraquinone (16.9 g.) was added in small portions. A solid Grignard complex settled out. The solution was stirred for 3 hr., and finally refluxed for 2 hr. The usual procedure was followed for the isolation of the product, and, on treatment of the residual oil with light petroleum (b. p. 60–80°), the diol (17 g., 61%), m. p. 111–112° was precipitated, but could not be obtained analytically pure.

9 : 10-Di-(3-ethoxypropyl)-9 : 10-dihydro-9 : 10-dimethoxyanthracene.—This *ether* was obtained from the acid-catalysed reaction of methanol with the diol, in the usual manner; crystallised from methanol it had m. p. 153.5° (Found : C, 75.9; H, 8.6. C₂₆H₃₄O₄ requires C, 75.7; H, 8.7%).

9 : 10-*Diethoxy-9 : 10-di-(3-ethoxypropyl)-9 : 10-dihydroanthracene*.—The use of ethanol in the previous preparation gave the *diethoxy-ether*, m. p. 93.5° (Found : C, 76.1; H, 9.1. $C_{28}H_{40}O_4$ requires C, 76.4; H, 9.1%).

9 : 10-*Diisopropylantracene*.—*iso*Propyl chloride (39.25 g.) was treated with magnesium (12 g.) in ether (300 ml.). Anthraquinone (26 g.) was added in the usual manner, and the product isolated as before. Only 1.9 g. of 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-diisopropylantracene were obtained (5%). This was treated with phenylhydrazine (4 ml.) and acetic acid (12 ml.), to yield green-yellow crystals (0.5 g., 29%) of the *anthracene*. Recrystallisation from alcohol gave light green crystals, m. p. 172° (Found : C, 91.5; H, 8.2. $C_{20}H_{22}$ requires C, 91.6; H, 8.2%). Light absorption : λ_{max} . 2600, 3420, 3600, 3800, and 4000 Å (ϵ 25,600, 2500, 5370, 8300, and 9560, respectively). Absorption also occurred at 7.35 μ (*isopropyl*).

9 : 10-*Dimethylantracene*.—Methyl iodide (17.7 g.) was treated with magnesium (3 g.) in ether (75 ml.), and anthraquinone (5.2 g.) added. After isolation, the dimethylantracenediol was caused to react with phenylhydrazine (8 ml.) and acetic acid (35 ml.). From this reaction yellow crystals (2.9 g., 57% overall), m. p. 180°, were obtained.

Some analyses were performed by Mr. F. Hall. The author thanks Sir Robert Robinson for his interest and advice.

DYSON PERRINS LABORATORY, OXFORD.

[Received, October 17th, 1955.]
