

much salt. In this way one could deal with a twenty-five-fold increase in solubility, which must be regarded as exceptional. Alternatively, five times as much solvent may be used at one filling without sacrifice of accuracy, if the lower end of the measuring tube is increased stepwise in volume by blowing a few bulbs separated by graduated necks. (b) **Low Solubilities.**—If we take 0.1 mg. as the limit of visibility for illuminated crystals, then 1% accuracy demands 0.01 g. of solute. Using 5 g. of solvent, a solubility as low as one part in 500 might thus be measured with 1% accuracy. (c) **Higher Temperatures.**—Kracek reports⁷ that his Pyrex tubes of 11 mm. outside diameter and 1.2 mm. wall thickness were not attacked by water nor fractured up to 250°.

Economy of Solvent.—After the desired temperature range has been covered for one solute, the solvent may be distilled back into the gradu-

ated tube. After closing the trap, a fresh container with a new solute may be sealed on in readiness for some other study. Provision for exhaustion and desiccation may be furnished by a small side-tube, which is later sealed off.

Summary

1. A modification of the synthetic method has been described which permits solubilities of non-volatile solids in volatile liquids to be measured with accuracy better than 1% over a wide temperature range, with complete recovery of the single cubic centimeter of solvent utilized.

2. This is illustrated by the determination of solubility curves in the system strontium chloride-water in the range 20–200° with accuracy better than 1% using 1.097 g. of water. The solubilities are tabulated for each 5° interval of temperature, and two transition temperatures are reported.

PRINCETON, N. J.

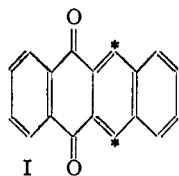
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

A Synthesis of Rubrene

BY C. F. H. ALLEN AND LUCIUS GILMAN

In continuation of the investigation of the behavior of polynuclear ketones with the Grignard reagent¹ naphthacenequinone was selected for study. According to Fieser² this substance has the bond structure shown in I. In view of our



previous work, in which it was shown that 1,4-addition to benzanthrones occurred, it seemed reasonable to expect that phenylmagnesium bromide should add to naphthacenequinone in a similar manner, the phenyl groups

appearing in the starred positions. This was, indeed, found to be the case, as two stereoisomeric tetrahydroquinones II were obtained. In alkaline solution they were both easily dehydrogenated by atmospheric oxygen to give 6,11-diphenyl-5,12-naphthacenequinone III. The new quinone does not form a vat, in agreement with Fieser's observation³ on naphthacenequinone; this behavior is also in accord with the effect of α, α' -substitution in the anthraquinone series.

(1) Allen and Overbaugh. *THIS JOURNAL*, **57**, 740, 1322 (1935).

(2) Fieser, *ibid.*, **53**, 2329 (1931); Fieser and Martin, *ibid.*, **57**, 1844 (1935).

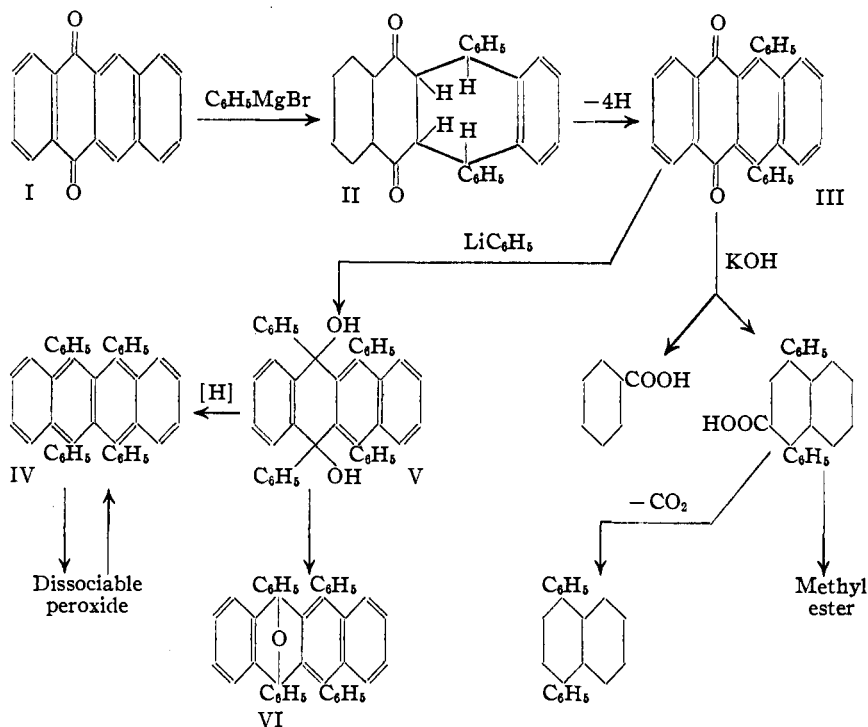
(3) Fieser, *ibid.*, **57**, 1846 (1935).

The location of the phenyl groups in III was shown by the production of 1,4-diphenylnaphthalene-2-carboxylic and benzoic acids and 1,4-diphenylnaphthalene on alkaline fusion. The former acid was converted into the methyl ester and silver salt. The physical constants of all these substances agreed with those described in the literature.

The production of the diketones II and III affords experimental evidence of the correctness of Fieser's bond structure for naphthacenequinone. It also indicates that in the case of benzanthrone and other substances to which 1,4-addition involving a benzene ring takes place¹ the mechanism is exactly analogous to that observed with open chain conjugated systems of double bonds. The primary product is a saturated ketone, but since it is a dihydrobenzene it is easily dehydrogenated to the aromatic condition. In the case of naphthacenequinone, this intermediate is a tetrahydrobenzene and thus possible of isolation.

In October, 1935,⁴ a short note appeared in which Dufraisse was recorded as being of the

(4) Dufraisse, Velluz, Horclois, Étienne and Gerard, *Bull. soc. chim.*, [5] **2**, 1546 (1935).



opinion that the hydrocarbon formerly known as rubrene was in reality 5,6,11,12-tetraphenyl-naphthalene IV, but in two later papers⁵ the diindenyl structures were still used. It was therefore decided to synthesize this hydrocarbon from the diphenylnaphthacenequinone III. To our surprise it was recovered unchanged after three hours of treatment with phenylmagnesium bromide under "forced conditions." However, on using phenyllithium, which has been shown to add when the Grignard reagent will not,⁶ a dicarbinol V resulted; this substance was found to be identical with the dihydroxyrubrene of Dufraisse and Badoche.⁷ Hence it was only necessary to carry out a reduction by iron and acetic acid to obtain the hydrocarbon, rubrene III.⁸ Its identity was assured on comparison with an authentic specimen,⁹ having identical absorption spectra, reversible autoxidation, and yellow fluorescence.

Unfortunately, we had missed a paper¹⁰ in which Dufraisse announced the synthesis of rubrene from dihydroxynaphthacenequinone and phenylmagnesium bromide, so our results, obtained independ-

(5) Dufraisse and Rocher, *Bull. soc. chim.*, [5] 2, 2236 (1935); Dufraisse and Velluz, *ibid.*, 3, 254 (1936).

(6) Wittig, *Ber.*, 64, 2405 (1931); 63, 924 (1935).

(7) Dufraisse and Badoche, *Compt. rend.*, 193, 63 (1931).

(8) Moureu, Dufraisse and Dean, *ibid.*, 182, 1440 (1926); Dufraisse, *Bull. soc. chim.*, [4] 53, 789 (1933).

(9) We are indebted to Dr. C. S. Marvel, University of Illinois, for a very pure sample.

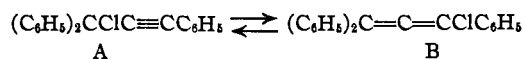
(10) Dufraisse and Velluz, *Compt. rend.*, 201, 1394 (1935).

ently and in a somewhat different yet unambiguous manner, confirm his conclusions as to the correct structure of rubrene. Since the diphenylnaphthacenequinone III does not react with phenylmagnesium bromide it cannot have been an intermediate product in Dufraisse's synthesis; this fact accounts for his isolation of it.

As the structure of the diol VI has been shown by the method of synthesis, the oxide (metrubrene) undoubtedly has the structure VI. Enderlin¹¹ has reached a similar conclusion, based on other evidence.

With the acceptance of the naphthalene formula for the rubrenes, the question arises as to the mechanism of their formation from the acetylenic carbinols or their derivatives. Since the reaction is observed in the presence or absence of all substances ordinarily considered as catalysts, and takes place even on standing at room temperature,¹² the formation of the cyclic compounds must be extraordinarily easy. The reaction that best meets the situation is the diene synthesis. If this hypothesis is adopted, the closing of the middle bond which divides the molecule into two naphthalene residues becomes obvious; this is otherwise difficult to explain in a plausible manner.

Using the chloride A in illustration it is only necessary to assume that an isomeric chloroallene B is formed by α, γ -rearrangement.



This shift was originally suggested by Willemart¹³ and adopted by Dufraisse¹⁴ to explain the formation of the rubrenes using the old diindenyl formula. The allenic structure contains a conjugated system involving a benzene ring. To this

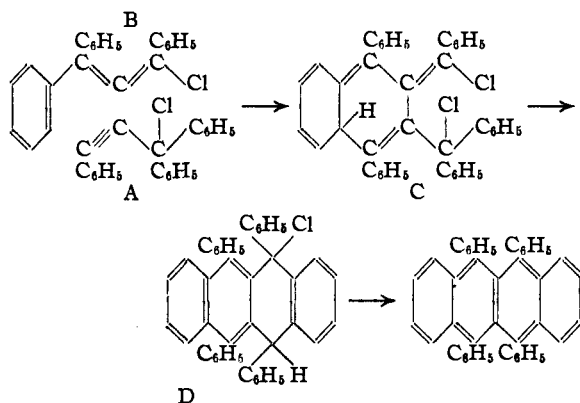
(11) Enderlin, *ibid.*, 202, 669 (1936).

(12) Robin, *Ann. chim.*, 16, 421 (1931).

(13) Willemart, *ibid.*, 12, 345 (1929); *Compt. rend.*, 187, 385 (1928).

(14) Moureu, Dufraisse and Enderlin, *ibid.*, 187, 406 (1928).

system a molecule of the acetylenic form of the chloride adds in the manner of the diene synthesis, resulting in an intermediate C; this loses hydrogen chloride, either at once or after a second ring closure, to form a monochloride D. It has been shown that an intermediate chloride $C_{42}H_{29}Cl$ can be isolated¹⁵ and, by the suggested mechanism, its structure is indicated to be D. Robin¹² found that this intermediate chloride had a chlorine atom sufficiently active to be replaced by C_2H_5O , thus resembling triarylmethyl chlorides.



The adoption of this mechanism enables one to predict the structures of any rubene formed from an acetylenic carbinol $R_2C(OH)C\equiv CR'$ or beta-arylated chalcone $R_2C=CHCOR'$, in which the radicals R are alike; if unlike, three isomers would be expected, and have been obtained in a specific instance.¹⁶ In either case, the group R' will appear in the 5,11 (6,12) positions in the rubene. Unfortunately, by the synthesis described in this paper only the 5,12 (6,11) homologs can be prepared.

Experimental

6,11-Diphenyl-5,12-naphthacenequinone, III.—To the filtered solution of phenylmagnesium bromide (6 equivalents; prepared from 45 g. of magnesium, 292 g. of bromobenzene and 400 cc. of dry ether) from which 150 cc. of ether had been distilled were added 200 cc. of dry *n*-butyl ether and then 40 g. of 5,12-naphthacenequinone² in small portions over a five-minute period, allowing the moderate reaction to subside slightly between each portion. The whole was stirred and heated (internal temperature 85–90°) on a steam-bath for two hours. An excess of Grignard reagent was shown by Gilman's test. After decomposing by ice and acetic acid, the organic material was transferred to a flask and steam distilled for twenty hours; 8 g. of diphenyl was collected after the solvent had been removed. The brownish resinous substance left weighed 69 g. It was triturated, first with a 100-cc. and then a

50-cc. portion of ether, followed by 20 cc. of cold acetone; 15 g. of a greenish-yellow residue was thus obtained. This is a mixture of the tetrahydroquinones, the separation of which (described below) is unnecessary for the next step.

A portion (9.2 g.) of this residue was mixed with 150 cc. of alcoholic potash; it became dark blue almost immediately and yellow crystals slowly separated. After three days the blue color had disappeared, so the solid was filtered from the alkaline solution, dissolved in chloroform, and a small amount of gray, insoluble material filtered. On evaporation of the solvent, 8 g. (20.4%) of bright yellow prisms remained. The best solvent for recrystallization was found to be a 1:1 mixture of *p*-cymene and *o*-dichlorobenzene. The melting point was 284°, and a mixed melting point with naphthacenequinone, which also has a melting point of 283–284° was depressed to 255–260°.

Anal. Calcd. for $C_{30}H_{18}O_2$: C, 87.8; H, 4.4. Found: C, 87.5; H, 4.5.

The Tetrahydroquinones, II.—The greenish-yellow residue (4 g.) was refluxed for a half hour with 60 cc. of glacial acetic acid and filtered hot; the 0.4 g. of crystalline residue was recrystallized once from chlorobenzene and once from chloroform, and formed very fine needles, m. p. 293–297°.

The acid filtrate, on cooling, deposited yellowish needles, m. p. 215–220°; they were dissolved in a minimum of hot chloroform and methanol added until a solid began to appear. The solution was chilled to –5° and the solid filtered. A similar crystallization was carried out with dioxane and *n*-propyl alcohol, followed by a final one from acetic acid; the melting point was then constant at 224–225°.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 87.0; H, 5.3. Found: (293°) C, 87.2; H, 5.2; (224°) C, 87.1; H, 5.3.

Since both were oxidized by atmospheric oxygen in a blue alkaline solution to the diphenylquinone III, a property characteristic of partially reduced anthraquinones, it seems extremely likely that they are the reduced compounds indicated.

Alkaline Fusion of III.—A finely ground mixture of 2 g. of the diphenylquinone and 12 g. of potassium hydroxide was heated by means of a metal bath at 310° for ten minutes and at 290° for a further ten minutes. The cold melt was dissolved in water and extracted with chloroform; this removed 0.65 g. of 1,4-diphenylnaphthalene, m. p. 134–136° after one recrystallization. The literature¹⁷ gives 135–137°.

The aqueous alkaline solution was acidified, digested on the steam-bath for several hours and filtered; from the cooled filtrate benzoic acid was isolated by ether extraction and identified in the usual manner (m. p. and mixed m. p. 122°). The insoluble acid weighed 0.15 g.; repeated recrystallization yielded a product, m. p. 218–223°. Since the literature¹⁷ gave 223–225° the silver salt was prepared and analyzed, and the methyl ester prepared.

Anal. Calcd. for $C_{23}H_{15}O_2Ag$: Ag, 25.0. Found: Ag, 25.4.

The methyl ester had a melting point of 163–165°, agreeing with the value in the literature.¹⁷

5,6,11,12-Tetraphenyl-5,12-naphthacenediol, V (Dihydroxyrubrene).—To a solution of phenyllithium (from

(15) Moureu, Dufraise and Robin, *Compt. rend.*, **188**, 1582 (1929).

(16) Dufraise and Loury, *ibid.*, **194**, 1664, 1832 (1932).

(17) Weiss, Abeles and Knapp, *Monatsh.*, **61**, 162 (1932).

0.83 g. of lithium, 9.7 g. of bromobenzene and 200 cc. of dry ether; 6 equivalents) in the usual apparatus and swept by nitrogen, was added 1.5 g. of diphenylnaphthacenequinone. The mixture was refluxed for thirteen hours, at the end of which time it had become a reddish-brown and still gave a positive test (Gilman's) for organometallic compound. The cooled solution was decomposed by the cautious addition of small lumps of ice, and, after adding enough water to bring the volume up to approximately 200 cc., the ether was distilled, leaving sticky, orange lumps. The latter were filtered, dissolved in chloroform for convenience in handling, and then steam distilled to remove diphenyl. The residual organic material was again dissolved in chloroform, filtered from a trace of grayish solid and the solvent evaporated. The salmon colored residue was dissolved in 10 cc. of dioxane on the steam-bath, and, with continued heating, was diluted by the addition of 60 cc. of ligroin (b. p. 90-100°). After the solution had cooled to room temperature the crude diol was filtered and recrystallized from *n*-propyl alcohol. It melted at 308-310°; Dufraisse and Badoche⁷ give 307-308°. The total yield of pure diol was 0.7 g. (34%).

When treated with acetyl chloride it gave a different white solid, melting above 360° and characterized by sparing solubility in the usual solvents; a strong violet fluorescence was noted in the very dilute solutions. This substance is presumably the "white fluorescent" hydrocarbon, C₄₂H₂₄, obtained by an identical procedure in the literature, m. p. 440°. ^{7,18} The diphenylquinone forms a complex when treated with phenylmagnesium bromide, but on working it up by the usual procedure the quinone is recovered unchanged.

5,6,11,12-Tetraphenylnaphthacene, IV (Rubrene).—An intimate mixture of 0.1 g. of the diol and 1 g. of iron powder was suspended in 12.5 cc. of glacial acetic acid and the whole refluxed for an hour. After addition of 125 cc. of distilled water, the solid was filtered. The filtrate gave pink benzene extracts. The residual solid was extracted by portions of boiling benzene until no more colored material was removed, and the solvent distilled from the combined extracts. The crude resinous residue, presumably containing some dioxide, was transferred by use of a solvent to a large test-tube, the air replaced by carbon dioxide and the system evacuated. The tube and contents were then heated for two hours at 140° (oil-bath temperature) and 10 mm., and then for forty-four hours at 200°. During this time the hydrocarbon slowly sublimed to the

cooler portion of the tube and was deposited as a ruby-red resin.

Anal. Calcd. for C₄₂H₂₄: C, 94.7; H, 5.3. Found: C, 94.5; H, 5.4.

Benzene or carbon disulfide solutions of the hydrocarbon were orange if concentrated, but pink when dilute, showing a strong yellowish fluorescence. When a benzene solution was shaken with air in moderate sunlight it was rapidly decolorized; low temperature evaporation of the solvent left a white solid, which, on warming at 120°, rapidly lost oxygen and reformed the red hydrocarbon.

Benzene solutions of equal concentration of the hydrocarbon thus prepared and of a specimen obtained by Dufraisse's method gave indistinguishable absorption spectra.¹⁹

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

By the action of phenylmagnesium bromide on naphthacenequinone it has been possible to obtain products that (a) confirm the bond arrangement suggested by Fieser for this quinone, and (b) indicate that 1,4-addition involving an aromatic ring proceeds to the diphenylquinone by way of a substance with a reduced ketone structure.

The diphenylnaphthacenequinone does not react with phenylmagnesium bromide, but with phenyllithium gives a tetraphenyldihydroxynaphthacene, identical with a substance formerly known as dihydroxyrubrene.

The latter is easily reduced to the hydrocarbon, 5,6,11,12-tetraphenylnaphthacene, formerly known as rubrene. Since the course of the reaction is clearly shown, step by step, the structure of the hydrocarbon is certain, and this synthesis thus affords a confirmation of the structure assigned by Dufraisse.

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(18) Dufraisse and Enderlin, *Compt. rend.*, **194**, 133 (1932).

(19) These were examined by Dr. J. S. Foster, Physics Department, McGill University, to whom we express our indebtedness.