

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

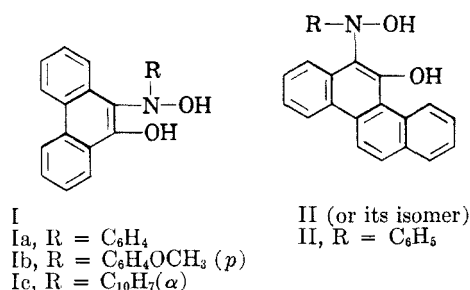
Studies of Quinoid Structures. II.¹ Action of Grignard Reagents on Phenanthrenequinone Monoxime, Chrysenequinone Monoxime and Chrysenequinonimine

WILLIAM IBRAHIM AWAD AND ABDEL REHIM ABDEL RAOUF

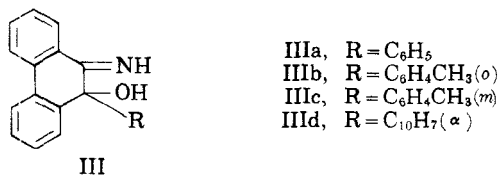
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Alkyl- and arylmagnesium halides react with phenanthrenequinone monoxime and chrysenequinone monoxime by 1,2-addition to the carbonyl group and not by 1,4-addition as previously described.² The constitution of the products is discussed.

Mustafa and Kamel² claimed that when arylmagnesium halides are allowed to react with phenanthrenequinone monoxime and chrysenequinone monoxime, an addition occurs which they formulated as (I) and (II), 1,4-additions.



The main line of evidence upon which these authors assigned the above structures is the reduction by lithium aluminum hydride of the compound thought to be 10-phenylhydroxylamino-9-hydroxyphenanthrene (Ia) to give the same product obtained by the action of phenylmagnesium bromide on phenanthrenequinonimine. Unfortunately, the previous workers thought the phenylmagnesium bromide-phenanthrenequinonimine reaction product was 10-phenylamino-9-hydroxyphenanthrene;¹ in reality, as we proved in our previous publication,¹ this reaction product is 9-phenyl-9,10-dihydro-10-imino-10-phenanthrol (IIIa). The correctness of this structure was established by conversion to 10-hydroxy-10-phenyl-9(10H)phenanthrone by acid hydrolysis; our phenanthrone had the same melting point as that recently reported by Shriner and Geipel.³



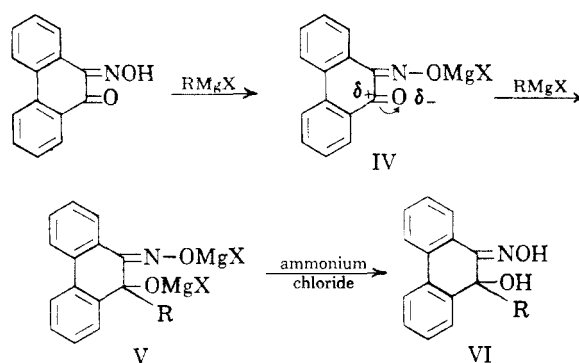
(1) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **22**, 881 (1957).

(2) A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, **76**, 124 (1954).

(3) R. L. Shriner and L. Geipel, *J. Am. Chem. Soc.*, **79**, 227 (1957).

In addition, the preferential addition of Grignard reagents to the carbonyl group has been reported by Diels, *et al.*^{4,5} to take place in the case of *N*-methyl biacetyl phenylhydrazone.

The present investigation deals with the action of alkyl and arylmagnesium halides on phenanthrenequinone monoxime. The reaction appears to proceed according to scheme A.



VIa, R = CH₃; VIb, R = C₂H₅; VIc, R = C₃H₇(*n*); VIId, R = C₄H₉(*iso*)
VIe, R = C₆H₅; VI f, R = C₆H₄OCH₃(*p*); VIg, R = C₆H₄CH₃(*o*)
VIh, R = C₆H₄CH₃(*m*); VIi, R = C₆H₄CH₃(*p*); VIj, R = C₁₀H₇(α)

It should be noticed that oximes do not normally react readily with Grignard reagents except as "active hydrogen" compounds.⁶ All other reactions reported have been carried out under more or less drastic conditions.^{6,7}

Since, on steric grounds, chrysenequinone monoxime was assigned by Awad and Raouf⁸ structure VII, the product of its interaction with alkyl and arylmagnesium halides is more likely represented by VIII.

(4) O. Diels and F. ter Meer, *Ber.*, **42**, 1940 (1909).

(5) O. Diels and J. M. Johlin, *Ber.*, **44**, 403 (1911).

(6) Kharasch and Reinmuth, *Grignard Reactions of Non-metallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 1217.

(7) M. Busch and R. Hobein, *Ber.*, **40**, 2096 (1907).

(8) W. I. Awad and A. R. A. Raouf, *J. Am. Chem. Soc.*, **77**, 3913 (1955).

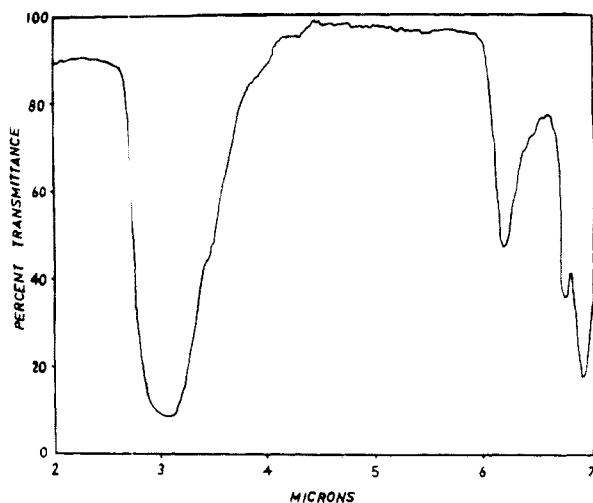
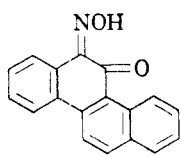
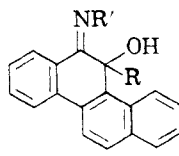


FIG. 1. 9-*o*-TOLYL-9,10-DIHYDRO-10-OXIMINO-9-PHENANTHROL (VIg) (potassium bromide wafer technique).



VII



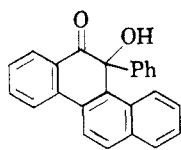
VIII

VIIIa, R' = OH, R = CH₃; VIIIb, R' = OH, R = C₂H₅; VIIIc, R' = OH, R = C₄H₉(*iso*); VIII d, R' = OH, R = C₆H₅; VIIIe, R' = OH, R = C₆H₄OCH₃(*p*).

The constitution of the Grignard products is based upon the following: (i) the preferential addition of the Grignard reagent to the carbonyl group,^{1,3,4} (ii) the reduction of (VIe) and (VIh) to the same products obtained by the action of phenyl- and *m*-tolylmagnesium halides on phenanthrenequinonimine, respectively.

Products (VI) are stable to hydrolysis in contrast to the corresponding imino compounds (III).¹

However, we find that when chrysenequinonimine is allowed to react with phenylmagnesium bromide, a nitrogen free keto compound (IX) is obtained directly instead of the expected compound VIII, (R' = H).



IX

It is suggested that this compound IX results from the direct hydrolysis of the imino compound on decomposition of the Grignard product. The constitution of IX is established by its identity with the ketone obtained by the hydrolysis of (VIII d). Similar keto compounds are obtained by the acid hydrolysis of III.¹

This shows that the products in the chrysenequinonimine series are more readily hydrolyzed than those in the phenanthrenequinonimine series.

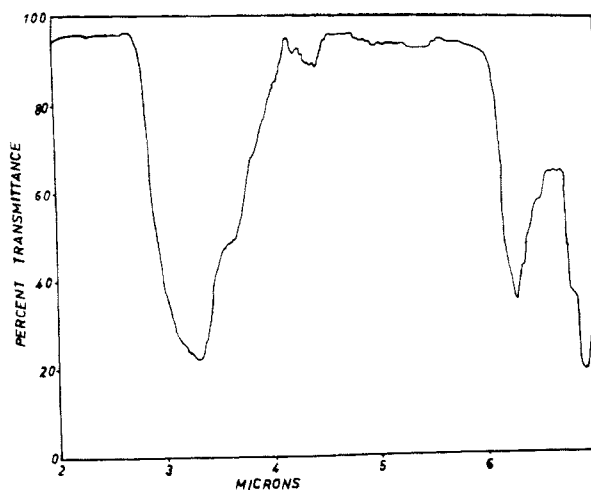
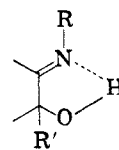


FIG. 2. 9-*o*-TOLYL-9,10-DIHYDRO-10-IMINO-9-PHENANTHROL (potassium bromide wafer technique).

The ease of hydrolysis of the products of chrysenequinonimine (VIII, R' = H) is also manifested by the hydrolysis of VIII d and the failure of the corresponding phenanthrene derivatives (VIe) to do so.

Comparison of the infrared curves of VIg and its corresponding imino compound (*cf.* Figs. 1 and 2

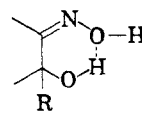
respectively) shows conjugated C=N stretching frequency⁹ at 6.2–6.3 microns. This is in favor of the structure assigned to these compounds. The curves also show stretching frequencies in the intramolecular hydrogen bridge¹⁰ (3.1–3.3 microns) which suggests the chelated structure (X).



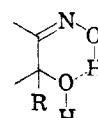
X

R = H or OH
R' = C₆H₄CH₃(*o*)

Similarly the absence of a free OH stretching frequency at 2.7–2.8 microns¹⁰ in the case of oximino products (VIg) (*cf.* Fig. 1) may be attributed to chelated structures (XI and XII).



XI



XII

The ultraviolet spectra of VIe (Fig. 3) and VIg (Fig. 4) and their imino analogs show a great similarity between the oximino- and imino-compounds.

(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen; London, 1956, p. 223.

(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen; London, 1956, p. 84.

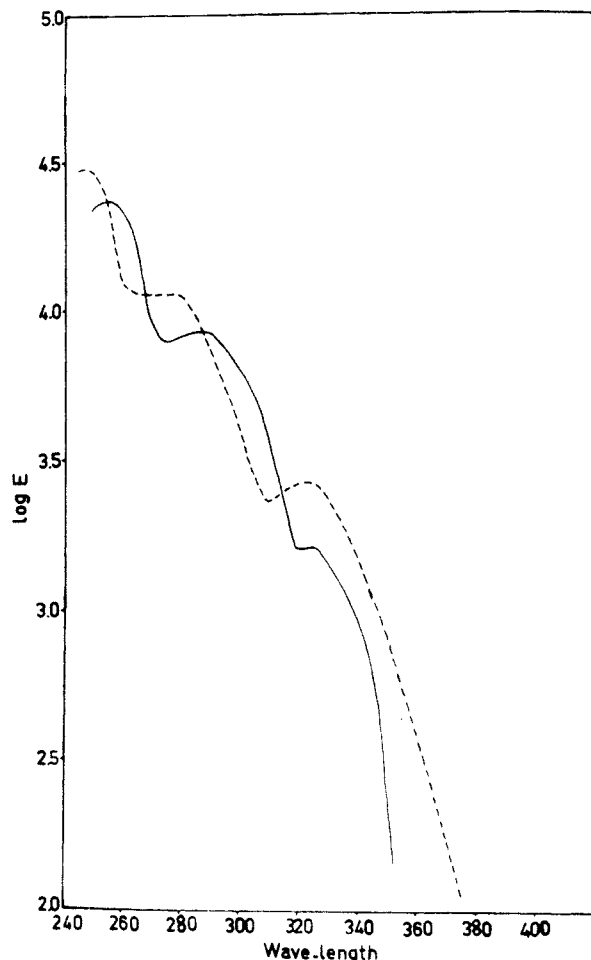


FIG. 3. ULTRAVIOLET SPECTRA. — VIe in chloroform; ---- imino analog in chloroform.

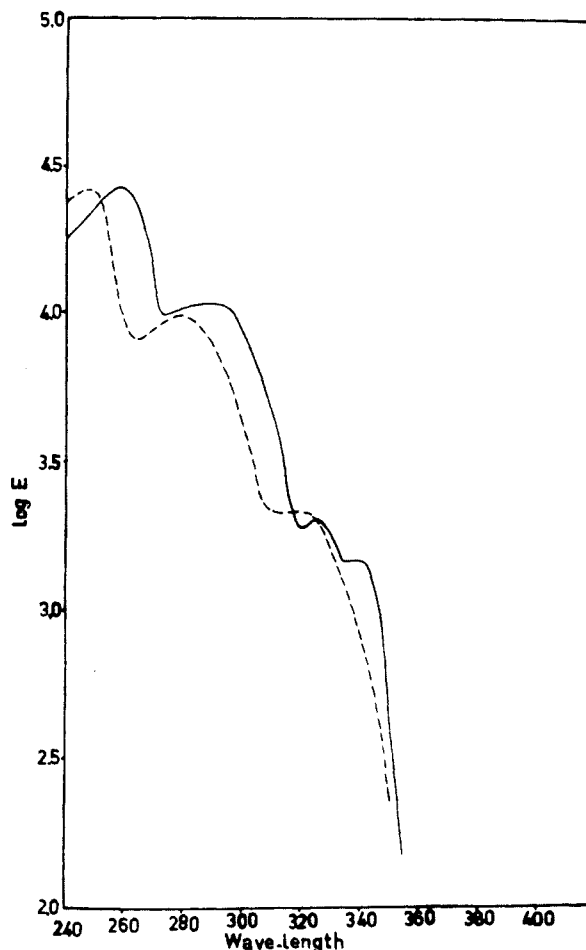


FIG. 4. ULTRAVIOLET SPECTRA. — VIg in chloroform; ---- imino analog in chloroform.

EXPERIMENTAL¹¹

Reaction of phenanthrenequinone monoxime with methylmagnesium iodide. A solution of phenanthrenequinone monoxime (2 g.) in hot dry benzene (100 ml.) was added to an ethereal solution of methylmagnesium iodide (from methyl iodide, 7.5 g. and magnesium, 1.2 g.) and the reaction mixture was heated under reflux for 2 hr. After cooling, it was poured slowly into 200 ml. of saturated aqueous ammonium chloride solution, and the ether-benzene layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was precipitated by the addition of petroleum ether (40–60°) and was recrystallized from benzene to give VIa as colorless crystals, m.p. 165°, yield 57%. It gave a brown color with concentrated sulfuric acid and the color then turned to yellowish green.

Anal. Calcd. for $C_{15}H_{13}O_2N$: C, 75.3; H, 5.5; N, 5.9. Found: C, 75.2; H, 5.8; N, 5.96.

Reaction of phenanthrenequinone monoxime with alkyl and arylmagnesium halides. The reaction was carried out as in the case of methylmagnesium iodide. The products are listed in Table I.

Reduction of VIe with lithium aluminum hydride. Dry ether (60 ml.) was added to pulverized lithium aluminum hydride (0.8 g.) and left for 15 min. A solution of VIe (1 g.) in dry benzene (100 ml.) was then added to the above mixture, refluxed for 3 hr., and then set aside overnight at room temperature. After treatment with cold aqueous ammonium

chloride solution, the ethereal solution was dried over anhydrous sodium sulfate, and evaporated (blue violet fluorescence). The residue left was crystallized from benzene to give IIIa, identified by m.p. and mixed m.p. determinations, yield 66%. The substance gave an olive green color with concentrated sulfuric acid and changed to reddish brown and finally to brown on adding a crystal of potassium nitrate or a drop of nitric acid.

Hydrolysis of VIe. The compound was recovered unchanged on trying to hydrolyze it either with alcoholic hydrochloric acid or alcoholic potash.

Reduction of VIh with lithium aluminum hydride. Dry ether (60 ml.) was added to pulverized lithium aluminum hydride (0.8 g.) and left for 15 min. A solution of VIh (1 g.) in dry benzene (100 ml.) was added to the above mixture, refluxed for 3 hr. and then set aside overnight at room temperature. After treatment with cold aqueous ammonium chloride solution, the ethereal solution was dried over anhydrous sodium sulfate, and evaporated. The product came down during concentration, filtered, and crystallized from benzene to give IIIe identified by m.p. and mixed m.p. determinations, yield 55%.

*Reaction of phenanthrenequinonimine with *o*-tolylmagnesium bromide.* A solution of phenanthrenequinonimine (1 g.) in hot dry benzene (50 ml.) was added to an ethereal solution of *o*-tolylmagnesium bromide (from *o*-bromotoluene, 6 g. and magnesium, 0.6 g.) and the reaction mixture was refluxed for 3 hr., hydrolyzed with ammonium chloride solution, the ether-benzene layer separated, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was precipitated by the addition of petroleum ether (40–60°)

(11) Microanalyses were carried out by Alfred Bernhardt, Germany. Melting points are not corrected.

TABLE I

Com- pound	Solvent of Crystalli- zation ^a	M.P., °C.	Yield, ^b %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Color with Concd. Sulfuric Acid
					Calcd.	Found	Calcd.	Found	Calcd.	Found	
VIb	A	147	41	C ₁₆ H ₁₅ O ₂ N	75.9	75.3	5.97	5.5	5.5	5.8	Light green
VIc	A	141	30	C ₁₇ H ₁₇ O ₂ N	76.4	76.1	6.4	6.4	5.2	5.2	Light green
VIId	B	194	56	C ₁₈ H ₁₉ O ₂ N	76.8	76.8	6.8	7.05	4.98	4.97	Lemon yellow
VIe	B	162	44	C ₂₀ H ₁₅ O ₂ N	79.7	79.8	5.0	5.4	4.7	4.3	Blue turned to purple
VIIf	B	178	28	C ₂₁ H ₁₇ O ₃ N	76.1	75.6	5.2	5.1	4.2	4.1	Prussian blue
VIg	B	162	66	C ₂₁ H ₁₇ O ₂ N	80.0	80.3	5.4	5.4	4.4	4.4	Reddish brown ^c
VIh	B	188	57	C ₂₁ H ₁₇ O ₂ N	80.0	80.5	5.4	5.99	4.4	4.2	Green turned to blue
VIi	B	185	35	C ₂₁ H ₁₇ O ₂ N	80.0	79.9	5.4	5.8	4.4	4.2	Prussian blue turned to green blue
VIj	B	192 ^d	20	C ₂₄ H ₁₆ O ₂ N	82.0	82.55	4.9	5.1	3.99	3.9	Dark green

^a A, benzene-petroleum ether (40–60°); B, benzene. ^b Yield is calculated for pure material. ^c Turned to brown on adding a crystal of KNO₃. ^d Brown melt.

TABLE II

Com- pound	Solvent of Crystalli- zation ^a	M.p., °C.	Yield, ^b %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Color with Concd. Sulfuric Acid
					Calcd.	Found	Calcd.	Found	Calcd.	Found	
VIIIb	A	173	36	C ₂₀ H ₁₇ O ₂ N					4.6	4.5	Prussian blue turned to green ^c
VIIIc	A	178	42	C ₂₂ H ₂₁ O ₂ N	79.7	79.7	6.4	6.5	4.2	4.1	Prussian blue turned to green ^d
VIIIId	B	202 ^e	42	C ₂₄ H ₁₇ O ₂ N ^f							Violet blue turned to green blue
VIIIe	C	236 ^e	62	C ₂₈ H ₁₉ O ₃ N	78.7	79.1	5.0	5.4	3.7	3.98	Olive green ^f

^a A, benzene-petroleum ether (40–60°); B, benzene; C, ethyl alcohol. ^b Yield is calculated for pure material. ^c Turned to wine-red on adding one drop of concd. HNO₃. ^d Turned to pink on adding one drop of concd. HNO₃. ^e Brown melt. ^f Reported in Ref. 2. ^g Turned to blue on adding one drop of concd. HNO₃.

and was recrystallized from benzene to give IIIb as pale yellow crystals, m.p. 176°, yield 28%. It gave a green color with concentrated sulfuric acid and the color turned to blue on adding one crystal of potassium nitrate.

Anal. Calcd. for C₂₁H₁₇ON: C, 84.3; H, 5.7; N, 4.7. Found: C, 84.0; H, 5.9; N, 4.6.

Reaction of chrysenequinone monoxime with methylmagnesium iodide. A solution of chrysenequinone monoxime (2.5 g.) in hot dry benzene (100 ml.) was added to an ethereal solution of methylmagnesium iodide (from methyl iodide, 7.5 g. and magnesium, 1.2 g.) and the reaction mixture was refluxed for 3 hr., hydrolyzed with ammonium chloride solution, the ether-benzene layer separated, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was precipitated by the addition of petroleum ether (40–60°) and was recrystallized from benzene to give VIIIa as pale yellow crystals, m.p. 176°, yield 50%. It gave a Prussian blue color with concentrated sulfuric acid, turned gradually to green. On adding one drop of concentrated nitric acid, the color changed to pink and finally to brown.

Anal. Calcd. for C₁₉H₁₅O₂N: C, 78.9; H, 5.2; N, 4.8. Found: C, 79.1; H, 5.4; N, 4.7.

Reaction of chrysenequinone monoxime with alkyl and arylmagnesium halides. The reaction was carried out as in the case of methylmagnesium iodide. The products are listed in Table II.

Hydrolysis of VIIIId. A solution of 0.3 g. of VIIIId in ethyl alcohol (100 ml.) and concentrated hydrochloric acid (3 ml.) was refluxed for 2 hr. on the steam bath. The compound dissolved gradually in the reaction mixture and the color of the

solution changed from colorless to red brown with slight violet fluorescence. The product came down after concentration and cooling and was recrystallized from benzene-petroleum ether (40–60°) to give the nitrogen free ketocompound as colorless crystals, m.p. 172°, undepressed on admixture with IX; yield 30%. It gave a dark brown color with concentrated sulfuric acid.

Reaction of chrysenequinonimine with phenylmagnesium bromide. A solution of chrysenequinonimine (1 g.) in hot dry benzene (50 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 8 g. and magnesium, 1 g.) and the reaction mixture was refluxed for 3 hr., hydrolyzed with ammonium chloride solution, the ether-benzene layer separated, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was precipitated by the addition of petroleum ether (40–60°) and was recrystallized from benzene-petroleum ether (40–60°) (after allowing the solution to evaporate slowly by standing for several days) to give IX as colorless crystals, m.p. 172°, yield 31%. It gave a dark brown color with concentrated sulfuric acid.

Anal. Calcd. for C₂₄H₁₆O₂: C, 85.7; H, 4.8. Found: C, 85.2; H, 4.9.

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ABBASSIA, CAIRO, EGYPT