stirring the slurry, 19 g. of thionyl chloride was added and the mixture was refluxed for 0.5 hr. A further addition of 3 g. of thionyl chloride was added and refluxing was continued for 2.5 hr. Complete removal of volatile solvents *in vacuo* at room temperature left the hygroscopic crystalline hydrochloride which could be used without further purification. Recrystallization of this salt separated about 5% impurities.

Conversion of this hydrochloride to the free base, 1-formyl-4-(3-chloropropyl)piperazine, was accomplished with potassium hydroxide. Benzene extracts were distilled; approximately 60% yields were obtained of a pale yellow oil; b.p. 144.5–148.5°/0.4 mm; $n_{\mathrm{D}}^{25°}$ = 1.5053, which was not further characterized.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, AIN SHAMS UNIVERSITY]

Studies of Quinoid Structures. V. Action of Grignard Reagents on Phenanthrenequinone Benzophenone Azine

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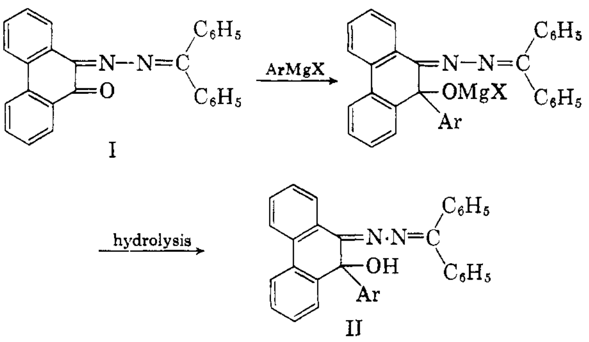
Arylmagnesium halides add preferentially to the carbonyl group of phenanthrenequinone benzophenone azine (I). When excess Grignard reagent is used, cleavage-condensation reaction takes place with the formation of 9,10-diarylphenanthrene.

In continuation of the previous study[1,2,3,4] of the action of Grignard reagents on derivatives of *ortho*-quinoid structures, the authors have now investigated the action of Grignard reagents on phenanthrenequinone benzophenone azine (I). In molecular proportion or slight excess, Grignard reagents add preferentially to the carbonyl group as it has been previously stated[1,2,3,4] (*cf.* Scheme A).

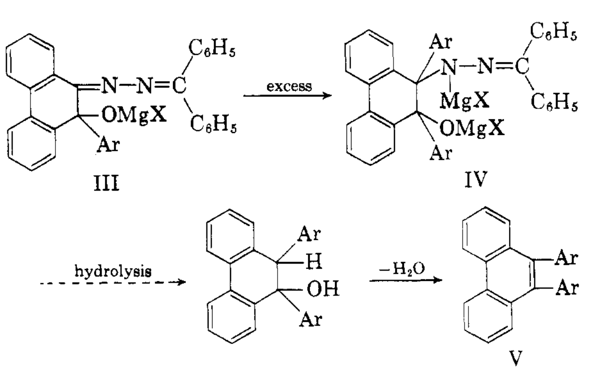


IIa. Ar = C_6H_5, IIb. Ar = $C_{10}H_7$-(α)
Scheme A

The constitution of II is based on 1) the preferential addition to the carbonyl group,[1,2,3,4,5,6a] 2) the carbonyl stretching frequency[6b] (at 1661 cm.$^{-1}$),[7] which is present in the infrared spectrum of the azine, is absent from the spectra of IIa and IIb, 3) an —OH stretching frequency at 3508 cm.$^{-1}$ appeared which was not present in the infrared spectrum of the starting material, and 4) elemental analysis.

However, excess of phenyl or anisylmagnesium bromide gave, in good yield, as a final product 9,10-diphenyl or 9,10-dianisylphenanthrene respectively as proved by 1) mixture melting point with an authentic sample of 9,10-diphenylphenanthrene,[8] and 2) elemental analysis.

It is to be noticed that the cleavage-condensation reaction takes place when acetone anil or acetophenone anil is treated with some Grignard reagents.[9] A possible series of steps for the reaction is:



Va. Ar = C_6H_5, Vb. Ar = C_6H_4—OCH_3(p)
Scheme B

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

(2) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **23**, 282 (1958).

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

(6) (a) O. Diels and J. M. Johlin, *Ber.*, **44**, 403 (1911). (b) The infrared measurements were carried out on Perkin-Elmer infracord, model 137 in nujol mulls.

(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 114.

(8) A. Werner and A. Grob., *Ber.*, **37**, 2887 (1904).

V might have been formed during the hydrolysis of IV or by loss of water after hydrolysis. As a fact the final product is the hydrocarbon V.

IIa on treatment with phenylmagnesium bromide yields Va in poor yield. This indicates that the halomagnesium complex of II may be the intermediate product in the formation of V.

During the preparation of phenanthrenequinone benzophenone azine[10a] (red), a yellow, highly crystalline product is formed if excess benzophenone hydrazone is used. We believe that it may be phenanthrenequinone diazine. This compound gave concordant nitrogen analysis for such a formula, but its carbon content showed less carbon than the theoretical value. The constitution of this product is under investigation.

EXPERIMENTAL[10b]

Action of phenylmagnesium bromide on phenanthrenequinone benzophenone azine. A solution of phenanthrenequinone benzophenone azine (3.8 g.) in dry benzene (100 ml.) was added to an ethereal solution of phenylmagnesium bromide (from 1.6 g. bromobenzene, 0.23 g. magnesium) and the reaction mixture was heated under reflux for 2 hr. and left overnight. The reaction mixture was hydrolyzed with a saturated solution of ammonium chloride and the ether-benzene layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was precipitated by addition of methyl alcohol and was recrystallized from benzene-methyl alcohol to give 2.5 g. of IIa as yellow crystals, m.p. 178–180°.

Anal. Calcd. for $C_{33}H_{24}ON_2$: C, 85.32; H, 5.21; N, 6.03. Found: C, 84.80; H, 5.38; N, 5.91.

The product gave a brownish-yellow color with concd. sulfuric acid.

Action of naphthylmagnesium bromide on phenanthrenequinone benzophenone azine. A solution of phenanthrenequinone benzophenone azine (3.8 g.) in dry benzene (100 ml.) was added to an ethereal solution of naphthylmagnesium bromide (from 2.1 g. α-bromonaphthalene and 0.23 g. magnesium) and the reaction mixture was heated under reflux for 2 hr. and left overnight. The reaction mixture was worked up as before. The product was recrystallized from benzene-methyl alcohol mixture to give 2.9 g. of IIb as yellow crystals, m.p. 208–210°.

Anal. Calcd. for $C_{37}H_{26}ON_2$: C, 86.38; H, 5.05; N, 5.44. Found: C, 86.74; H, 5.25; N, 5.13.

The product gave a brownish coloration with concd. sulfuric acid.

Action of excess phenylmagnesium bromide on phenanthrenequinone benzophenone azine. A solution of phenanthrenequinone benzophenone azine (1 g.) in dry benzene (25 ml.) was added to an ethereal solution of phenylmagnesium bromide (from 6.3 g. bromobenzene and 0.9 g. magnesium) and the reaction was completed as before. The product was precipitated on addition of methyl alcohol and recrystallized from benzene-methyl alcohol mixture to give 0.8 g. of Va as colorless needles, m.p. 231–233°.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 93.67; H, 5.36.

It gave no depression on admixture with an authentic specimen of 9,10-diphenylphenanthrene.

Action of excess anisylmagnesium bromide on phenanthrenequinone benzophenone azine. A solution of phenanthrenequinone benzophenone azine (1 g.) in dry benzene (25 ml.) was added to an ethereal solution of anisylmagnesium bromide (from 9.3 g. *p*-bromoanisole and 0.9 g. magnesium) and the reaction was completed as before. The product was precipitated by the addition of methyl alcohol and recrystallized from benzene-methyl alcohol mixture to give 0.85 g. of Vb as colorless needles, m.p. 250–251°.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 85.81; H, 5.64.

Action of phenylmagnesium bromide on IIa. A solution of IIa (1.1 g.) in dry benzene (25 ml.) was added to an ethereal solution of phenylmagnesium bromide (from 1.5 g. bromobenzene and 0.5 g. magnesium) and the reaction was completed as before. On addition of methyl alcohol, two products were precipitated. On extraction with cold benzene and concentration of the benzene solution, a colorless product was obtained. Recrystallization from benzene-methyl alcohol mixture gave colorless needles in poor yield. It proved to be 9,10-diphenylphenanthrene Va by melting point and mixture melting point. The product which was insoluble in cold benzene was recrystallized from hot benzene-methyl alcohol mixture and proved to be the starting material.

Action of excess benzophenone hydrazone on phenanthrenequinone. Phenanthrenequinone (2 g.) and benzophenone hydrazone (5 g.) in dry benzene (50 ml.) were heated under reflux on the water bath for 20 min. The solution acquired a reddish coloration. On addition of methyl alcohol a yellow product was obtained (2 g.). Recrystallization from benzene-methyl alcohol mixture gave a product with yellow crystals, m.p. 160–162°.

Anal. Calcd. for $C_{40}H_{28}N_4$: N, 9.92. Found: N, 9.77.

The product gave a yellowish-brown coloration with concd. sulfuric acid.

ABBASSIA, CAIRO, EGYPT, U.A.R.

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(9) M. S. Kharasch and Otto Reimuth, *Grignard Reactions of Nonmetallic Substances*. New York, Prentice-Hall, Inc., 1954, p. 1209.

(10) (a) O. Gerhardt, *Monatsh. Chem.*, **42**, 63 (1921); *Chem. Abstr.*, **15**, 3834 (1921). (b) Melting points are not corrected. Microanalyses were carried out by Alfred Bernhardt, in the Max-Planck Institut, Mülheim (Ruhr), Germany.