Anal. Calcd. for $C_{22}H_{17}NO$: C, 4.50. Found: N, 4.32.

Oxidation of N-acetyldinaphthylamines. The procedure with *N*-acetyl-2,2′-dinaphthylamine was typical. One-half gram of the amide was dissolved in acetone (50 ml. distilled from permanganate). After cooling in an ice bath, 0.08 g. $KMnO_4$ was added. The oxidizing agent was not decolorized on standing at 0° for 1 hr. or overnight at room temperature. Since no decolorization had taken place, additional permanganate was not added. The pink color of the solution was then discharged by the addition of ethanol (5 ml.) and gentle warming. It was filtered and concentrated. Dilution of the concentrate with ice water regenerated the starting material in nearly quantitative yield. A similar result was obtained on oxidation of *N*-acetyl-1,1′-dinaphthylamine.

CHICAGO 14, ILL.

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

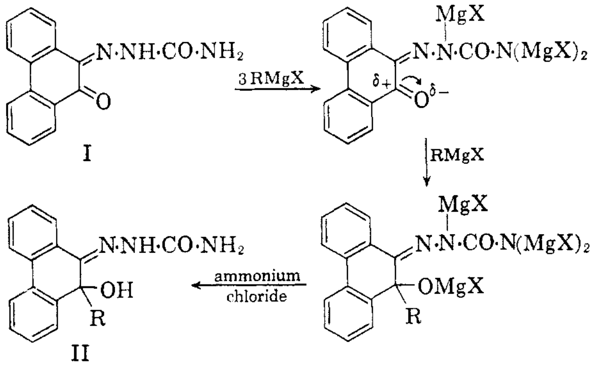
Studies of Quinoid Structures. III.[1] Action of Grignard Reagents on Phenanthrenequinone Monosemicarbazone, Chrysenequinone Monosemicarbazone, and Benzil Monosemicarbazone

WILLIAM IBRAHIM AWAD, ABDEL REHIM ABDEL RAOUF, AND AIDA MOUSTAFA KAMEL

Received April 17, 1959

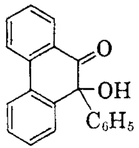
The preferential addition of alkyl and arylmagnesium halides to the carbonyl group of phenanthrenequinone monosemicarbazone, chrysenequinone monosemicarbazone, and benzil monosemicarbazone is described. The constitution of the products is discussed. Infrared data are given for these monosemicarbazones and some of their Grignard products.

Awad and Raouf[1,2] found that Grignard reagents add preferentially to the carbonyl group of phenanthrenequinonimine, chrysenequinonimine, phenanthrenequinone monoxime, and chrysenequinone monoxime. This investigation is now extended to phenanthrenequinone monosemicarbazone, chrysenequinone monosemicarbazone, and benzil monosemicarbazone. The reaction seems to proceed according to scheme A.



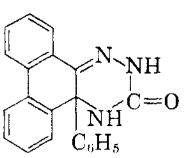
IIa. R = CH_3; IIb. R = C_2H_5; IIc. R = C_6H_5; IId. R = $C_{10}H_7(\alpha)$
Scheme A

The constitution of the Grignard products is based upon the following: (1) the preferential addition of the Grignard reagent to the carbonyl group,[1-4] (2) the action of acetic acid on (IIc) to yield the ketone (III),[1,2] (3) the infrared spectral study (inter-alia), (4) elemental analysis, (5) the inactivity of acetophenone semicarbazone towards Grignard reagent under the conditions of the experiment.

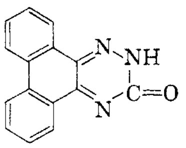


III

When (IIc) was heated with alcoholic hydrochloric acid, water is lost to give (IV). The constitution of (IV) is based upon: (1) elemental analysis, and (2) a comparative study of its infrared spectra with that of (V).[5]



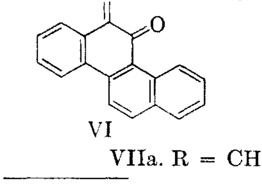
IV



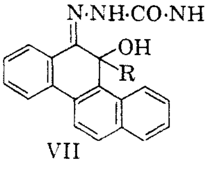
V

(or its enol form).

Similarly, chrysenequinone monosemicarbazone for which structure (VI) was assigned on steric grounds[1,6] reacted with Grignard reagents to give compounds for which structure (VII) was given.



VI



VII

VIIa. R = CH_3; VIIb. R = $C_{10}H_7(\alpha)$

---

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

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

[3] O. Diels and F. ter Meer, *Ber.*, **42**, 1940 (1909).

[4] O. Diels and J. M. Johlin, *Ber.*, **44**, 403 (1911).

[5] Schmidt, Schairer, and Glatz, *Ber.*, **44**, 276 (1911).

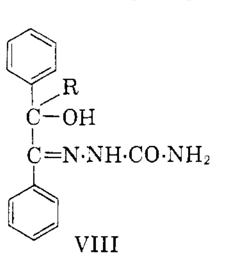
[6] W. I. Awad and A. R. A. Raouf, *J. Am. Chem. Soc.*, **77**, 3913 (1955).

TABLE I

	ν (NH) Unbonded	Amide I	ν(C=O)	Amide II	δ (NH) Unbonded (Rocking Modes)
Acetophenone semicarbazone	3485[a] 3571[b]	1750 [a] 1754[b]		1590[a] 1587[b]	772[a] 763[b]
Benzil monosemicarbazone	3636	1724	1695	1587	776
Phenanthrenequinone monosemicarbazone	3571	1724	1695	1639 (1600)	763
Chrysenequinone monosemicarbazone	3636	1754	1709	1600	758 w.[c]
IIc	3571	1681		1587	769
IV	3571	1695		1612	NA[d]
V		1754	1681	1612	758
VIIa	3508	1696		1612	745
VIII	3571	1695		1587	769

[a] These values are quoted from ref. (7). [b] Obtained in the present investigation. [c] w, weak band. [d] NA, not assigned.

When benzil monosemicarbazone was similarly treated with Grignard reagents, compounds of the structure (VIII) were analogously obtained.



VIII

VIIIa. R = CH_3; VIIIb. R = C_2H_5; VIIIc. R = C_6H_5; VIIId. R = $C_{10}H_7(\alpha)$

The infrared spectra[7] of the different semicarbazones used in this work (see Table I) were similar to those of the semicarbazones of the different aldehydes and ketones investigated by Davidson and Christie.[8] The stretching frequencies for amide I showed similar shifts to those observed by Davidson and Christie[8] in the case of the semicarbazones of aromatic carbonyl compounds. The stretching frequency of the carbonyl group does not exist in the spectra of the products of interaction of Grignard reagents with the monosemicarbazones.

EXPERIMENTAL[9]

Reaction of phenanthrenequinone monosemicarbazone with methylmagnesium iodide. A solution of methylmagnesium iodide (from methyl iodide, 7 g. and magnesium, 1 g.) was prepared in the usual way. A suspension of phenanthrenequinone monosemicarbazone[5] (1 g.) in dry benzene (40 ml.) was added to the above solution. The reaction mixture was refluxed for 2 hr. on a boiling water bath and left overnight at room temperature. The Grignard product was hydrolyzed with 100 ml. of a saturated solution of ammonium chloride. The ether-benzene layer was separated, washed with water, and dried (Na_2SO_4). The product was precipitated by the addition of petroleum ether (40–60°) and was recrystallized from a large bulk of benzene to give IIa as colorless crystals, m.p. 205°, yield 47%. The product gave a dichromate color with concentrated sulfuric acid.

TABLE II

Compound	Solvent of Crystallization	M.P., °C.	Yield,[a] %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Color with Concd. Sulfuric Acid
					Calcd.	Found	Calcd.	Found	Calcd.	Found	
IIb	A	194	45	$C_{17}H_{17}O_2N_3$	69.1	69.2	5.8	5.99	14.2	14.3	Dichromate
IIc	A	218	46	$C_{21}H_{17}O_2N_3$	73.5	73.4	5.0	5.0	12.2	12.3	Green
IId	A	225	40	$C_{25}H_{19}O_2N_3$	76.32	76.65	4.9	4.8	10.7	10.7	Brownish-green[b]
VIIa	A	216–217	47	$C_{20}H_{17}O_2N_3$	72.5	72.5	5.2	5.2	12.7	12.7	Violet[b]
VIIb	A	198–200	50	$C_{29}H_{21}O_2N_3$	78.6	78.8	4.8	5.1	9.48	8.93	Dark green
VIIIa	A	198–200	57	$C_{16}H_{17}O_2N_3$	67.8	67.7	6.4	6.3	14.84	15.39	
VIIIb	A	200–202	54	$C_{17}H_{19}O_2N_3$	68.7	68.9	6.1	6.3	14.1	14.0	Pale yellow
VIIIc	A	215–216	46	$C_{21}H_{19}O_2N_3$	73.0	72.7	5.6	5.6	12.2	12.0	Greenish-brown
VIIId	A	215–216	47	$C_{25}H_{21}O_2N_3$	75.9	76.2	5.4	5.3	10.6	10.4	Reddish-brown

A, benzene. [a] Yield is calculated for pure material. [b] Turned to brown.

Anal. Calcd. for $C_{16}H_{15}O_2N_3$: C, 68.3; H, 5.4; N, 14.94. Found: C, 68.5; H, 5.4; N, 15.09.

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

Action of glacial acetic acid on IIc. IIc (1 g.) in glacial acetic acid (30 ml.) was refluxed for 2 hr. The colorless solution became orange-brown. The cold solution was poured on ice. The precipitated product, which was found to be a mixture containing mostly the starting material, was fractionally crystallized from methyl alcohol to give 9-hydroxy-9-phenyl-9(10H)-phenanthrone, III, as colorless crystals, m.p. 117°, not depressed on admixture with an authentic sample,[2] yield 12%. It gave a brown color with concentrated sulfuric acid, which turned to violet.

Action of alcoholic hydrochloric acid on IIc. A mixture of IIc (0.2 g.), ethyl alcohol (30 ml.), and concentrated hydrochloric acid (4 ml.) was refluxed for 2 hr. on the water bath. The product which was precipitated on concentration and cooling, was crystallized from ethyl alcohol to give IV as colorless crystals, m.p. 304°, yield 95%.

Anal. Calcd. for $C_{21}H_{15}ON_3$: C, 77.5; H, 4.7; N, 12.9. Found: C, 77.7; H, 5.2; N, 12.9.

---

[7] The infrared measurements were carried out on a Perkin-Elmer Infracord Model 137, in Nujol medium.

[8] W. H. T. Davidson and P. E. Christie, *J. Chem. Soc.*, 3389 (1955).

[9] Microanalyses were carried out by Alfred Bernhardt, in Max-Planck-Institut, Mülheim (Ruhr), Germany. Melting points are not corrected.

Reaction of acetophenone semicarbazone with phenylmagnesium bromide. The substance was recovered unchanged when allowed to react with phenylmagnesium bromide under the same previous conditions. This was proved by melting point and mixture melting point determinations.

Preparation of chrysenequinone monosemicarbazone. A solution of chrysenequinone (2 g.) in ethyl alcohol (800 ml.) was treated with a solution of semicarbazide hydrochloride (1 g.) in the least amount of water and refluxed for 15 min. on the water bath. The product began to separate after 5 min. reflux as yellow crystals, and completely precipitated on cooling, dried by heating at 150° under reduced pressure, m.p. 256–258°, yield almost quantitative. It gave a brownish-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{13}O_2N_3$: N, 13.3. Found: N, 13.6.

Reaction of chrysenequinone monosemicarbazone with Grignard reagents. The reaction was carried out as in the case of phenanthrenequinone monosemicarbazone. The products are listed in Table II.

Reaction of benzil monosemicarbazone with Grignard reagents. The reaction was carried out as in the case of phenanthrenequinone monosemicarbazone. The products are listed in Table II.

ABBASSIA, CAIRO, UNITED ARAB REPUBLIC