TABLE I

METHANE LIBERATED ON TREATMENT OF WATER WITH EXCESS METHYLMAGNESIUM IODIDE AT ROOM TEMPERATURE

Run	Water, G.	Time from Start	Methane Liberated Standard Conditions, Ml.	Theory for One H, Ml.	%, Theory
1[a]	0.0177	30 min.	11.5	22.0	52.3
		1 hr.	12.5		56.9
		6 days	13.9		63.2
2[a]	0.0199	1.5 hr.	15.8	24.7	64.0
		12 hr.	17.8		72.2
		4 days	19.7		79.8
		7 days	23.7		96.0
		2 weeks	24.9		101
		4 weeks	25.0		101
3[b]	0.0182	4 min.	16.6	22.6	73.5
		7 min.	20.1		89.0
		30 min.	22.3		98.6
		1 hr.	23.5		104
		13 hr.	25.6		113

[a] Anhydrous pyridine used as solvent; pyridine treated with Grignard reagent before bulb broken. [b] No solvent used.

used in the reaction vessel to allow agitation of the reactants and to break the glass bulb containing the sample of water. Methylmagnesium iodide was purchased as a 1.0N solution in purified n-butyl ether.[14] Four-bed deionized and distilled water of 700,000 ohm-cm. volume resistivity was used for each run. Pyridine solvent, Eastman white label, was dried by distillation from barium oxide.

The general procedure for each experiment was as follows. A thin, dry, tared glass bulb was filled with the sample of water, sealed, cooled, and weighed. The bulb was then placed in one neck of the reaction vessel which had previously been dried in an oven overnight at 110°. The glass ball, also oven-dried, was placed in the other neck of the vessel with 5 ml. of pyridine (runs 1 and 2), and the unit was attached to the apparatus. The apparatus was swept with dry nitrogen for 15 min. and then 10 ml. of methylmagnesium iodide solution was introduced into the neck containing the glass ball and pyridine. The reagent and solvent were allowed to stand for 10 min. to eliminate any error because of traces of moisture in the solvent, and then the entire reaction vessel was brought to room temperature by external cooling in a large beaker of water. The apparatus was again adjusted to atmospheric pressure to compensate for any gas given off on mixing the reagent and solvent, and the determination was then made in the usual manner.[15] The reactants were agitated periodically. The apparatus was tested for leakage during each experiment by application of a positive pressure with the leveling reservoir. No leakage was detected. That an excess of methylmagnesium iodide had been used was determined after each run by observation of gas evolution on addition of water.

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[14] Arapahoe Special Products, Inc., Boulder, Col.

[15] Ref. 3, p. 181.

Studies of Quinoid Structures. VI. A Note on the Action of Arylmagnesium Halides on Anthraquinone Monoanil at Elevated Temperature

W. I. AWAD, A. K. FATEEN, AND M. A. ZAYED

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It has been found in these laboratories[1–4] that Grignard reagents add preferentially to the carbonyl group of phenanthrenequinonimine, chrysenequinonimine, phenanthrenequinone monoxime, chrysenequinone monoxime, phenanthrenequinone and chrysenequinone monosemicarbazones, benzil monosemicarbazone, as well as anthraquinone monoanil. We have now allowed anthraquinone monoanil (I) to react with phenyl- and anisylmagnesium bromides in boiling toluene, where both the carbonyl group and the $>C{=}N{-}$ group are attacked by the Grignard reagent, with the ultimate formation of 9,10-diphenyl-9,10-dihydroanthracene-9,10-diol and 9,10-di-(p-methoxyphenyl)-9,10-dihydroanthracene-9,10-diol, respectively, according to the following scheme.

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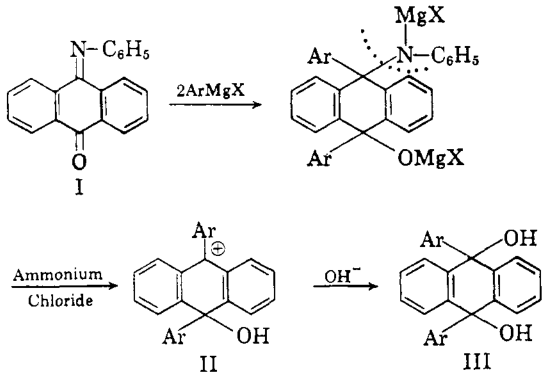
[1] W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **22**, 881 (1957).

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

[3] W. I. Awad, A. R. A. Raouf, and Miss A. M. Kamel, *J. Org. Chem.*, **24**, 1777 (1959).

[4] W. I. Awad, A. K. Fateen, and M. A. Zayed, *J. Org Chem.*, **25**, 358 (1960).



I II III

IIIa. Ar = C_6H_5; IIIb, Ar = p-$CH_3OC_6H_4$

The isolation of these compounds as the main product indicates that the Grignard complex undergoes C—N cleavage during the hydrolysis. The carbonium ion (II) is stabilized *via* resonance.

It is to be noticed that acetone and acetophenone anils undergo some cleavage identified only by the presence of aniline among the products.[5] Similar cleavage has occurred in the case of phenanthrenequinone benzophenone azine when treated with excess Grignard reagents.[6] The constitution of the products was proved by mixture melting point with authentic specimens (*cf.* Experimental part).

EXPERIMENTAL

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

Action of phenylmagnesium bromide on anthraquinonmonoanil,[7] *in boiling toluene.* A solution of I (5.6 g.) in hot dry toluene (200 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 6.3 g., and 1 g. of magnesium) and the reaction mixture was heated to get rid of the ether, then boiled under reflux for 2 hr. The reaction mixture was cooled, then hydrolyzed with saturated solution of ammonium chloride, and the toluene layer was separated, dried over anhydrous sodium sulfate, filtered, and the solvent was distilled off. IIIa was crystallized from benzene to give 0.5 g. of colorless crystals m.p. 254–255°,[8] undepressed on admixture with an authentic specimen.[9] Both samples gave an indigo color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.71; H, 5.49. Found: C, 85.95; H, 5.54.

Action of anisylmagnesium bromide on anthraquinone monoanil in boiling toluene. A solution of I (5.6 g.) in hot dry toluene (200 ml.) was added to an ethereal solution of p-anisylmagnesium bromide (from p-bromoanisole, 7.4 g., and 1 g. of magnesium) and the reaction mixture was treated as before. IIIb was crystallized from benzene to give 0.8 g. of colorless crystals m.p. 257–258°,[8] undepressed on admixture with an authentic specimen.[10] Both samples gave a blood red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.26; H, 5.65. Found: C, 79.36; H, 5.91.

CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
A'IN SHAMS UNIVERSITY
ABBASSIA, CAIRO, EGYPT, U.A.R.

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(5) Compare Kharasch and Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, p. 1209.

(6) W. I. Awad and Miss A. M. Kamel, *J. Org. Chem.*, **25**, 947 (1960).

(7) L. Sander, *Ber.*, **58**, 824 (1925).

(8) We were unable to raise the melting point of the sample by repeated crystallization up to that mentioned in the reference.

(9) Elsvier's *Encyclopaedia of Organic Chemistry*, **Vol. 13**, p. 307 (1946).

(10) Elsvier's *Encyclopaedia of Organic Chemistry*, **Vol. 13**, p. 308 (1946).

A Ring Cleavage Product Resulting from Reaction of 6-Methoxy-2-naphthyllithium with 2-Allyl-2-methyl-1,3-cyclopentanedione[1]

MELVIN S. NEWMAN AND JOSEPH H. MANHART[2]

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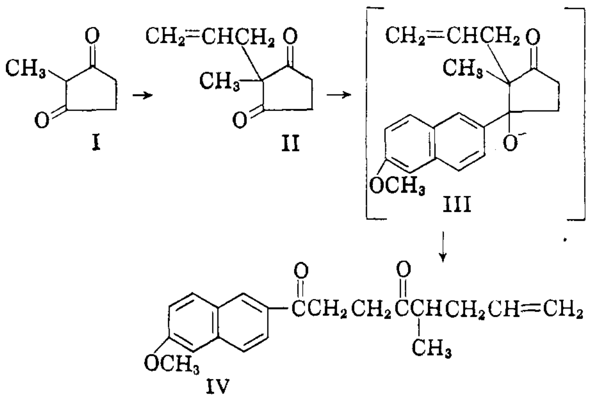
The availability of 2-methyl-1,3-cyclopentanedione,[3] I, prompted further attempts at modified steroid syntheses.[4] It was hoped that allylation of I to 2-allyl-2-methyl-1,3-cyclopentanedione, II, followed by condensation of II with an organometallic reagent prepared from 2-bromo-6-methoxynaphthalene would lead to an intermediate capable of being transformed into a 11,17-diketoequilenane derivative. Although the synthesis of II was successful, all attempts at condensation led to reaction mixtures from which the only recognizable condensation product, 1-(2-methoxy-6-naphthyl)-5-methyl-7-octene-1,4-dione, IV, was produced by ring cleavage of the initial condensation product, III. This cleavage reaction is similar to that of β-hydroxy esters encountered in earlier synthetic work.[5]



I II III IV

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(1) This work was supported by Grant CY-3184 from the National Institutes of Health.

(2) Taken from the Ph.D. thesis presented by J. H. M., 1960.

(3) J. J. Panouse and C. Sannie, *Bull. Soc. chim.*, 1036 (1955).

(4) G. Eglinton, J. C. Nevenzel, A. I. Scott, and M. S. Newman, *J. Am. Chem. Soc.*, **78**, 2331 (1956).

(5) See M. S. Newman, G. Eglinton, and H. M. Grotta, *J. Am. Chem. Soc.*, **75**, 349 (1953) and Ref. 4 above.