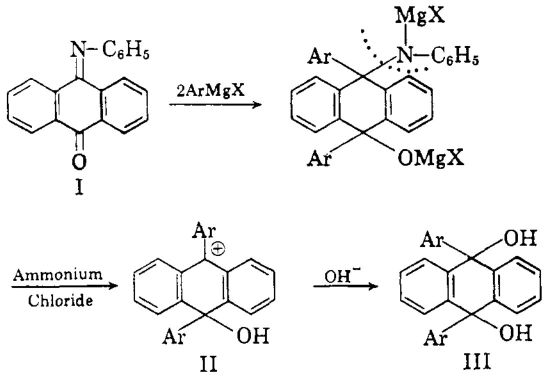

I II III

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.

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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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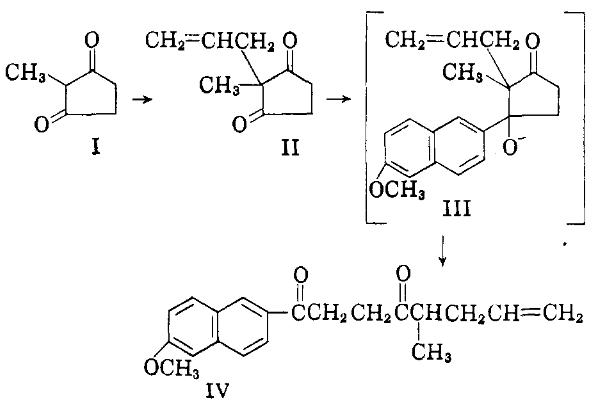
The availability of 2-methyl-1,3-cyclopentanedione,[3] I, prompted further attempts at modified steroid syntheses.[4] It was hoped that allylation of I to 2-allyl-2-methyl-1,3-cyclopentanedione, II, followed by condensation of II with an organometallic reagent prepared from 2-bromo-6-methoxynaphthalene 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.

The structure, IV, was confirmed by elemental analysis, infrared spectral data NMR analysis,[6] and chemical behavior.

Because of the unpromising nature of the reaction by which IV was produced we have abandoned this line of attack.

EXPERIMENTAL[7]

2-Methyl-1,3-cyclopentanedione, I. This compound was prepared essentially as described.[3] However, on a scale which afforded 10–40 g. of pure I, m.p. 205–209° dec., we obtained yields in the 50–54% region or less when certain modifications were tried.[8]

2-Allyl-2-methyl-1,3-cyclopentanedione, II. Conditions for high yields of II on allylation of I were not found. In a typical experiment a mixture of 8.6 g. of I, 75 ml. of 1 *M* sodium hydroxide and 9.1 g. of allyl bromide was stirred at room temperature for 4 hr. Suitable treatment of the neutral fraction yielded 3.9 g. (34%) of II, b.p. 63–70° at 1 mm. and 4.3 g. (50%) of I was recovered from alkaline extracts of the reaction mixture. Redistillation of crude II afforded pure II, b.p. 61–62° at 1 mm., m.p. 6.0–6.5° (time-temperature cooling curve).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.0; H, 8.0. Found[g]: C, 71.3; H, 7.9.

The bis-2,4-dinitrophenylhydrazone[9] of II melted at 248–252° dec., and was formed in 76% yield.

Anal. Calcd. for $C_{21}H_{20}N_8O_8$: C, 49.2; H, 3.9; N, 21.9. Found[s]: C, 49.2; 49.2; H, 4.0, 4.1; N, 22.0, 22.1.

1-(2-Methoxy-6-naphthyl)-5-methyl-7-octene-1,4-dione, IV. To a solution of 15.2 g. of II in 100 ml. of ether at −10° was added an equivalent of titrated[4] 2-methoxy-6-naphthyllithium, the mixture was stirred at −10 to 0° for 1 hr., and then added slowly to 200 ml. of cold dilute hydrochloric acid. Steam distillation of 10 g. of the resulting dark oily product (29.5 g.) yielded 3 g. of 2-methoxynaphthalene and 1 g. of II. Chromatography of the residue on alumina yielded a total of 2.1 g. (7% based on starting II) of IV,[6] m.p. 78.4–78.8°, infrared absorption at 5.82, 5.94, 7.90, 9.72, 10.15, and 10.90 *μ*.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.4; H, 7.2. Found[g]: C, 77.7, 77.8; H, 7.3, 7.5.

A solution containing 0.033 mole of the Grignard reagent from 2-methoxy-6-bromonaphthalene in tetrahydrofuran was added to a solution of 5.0 g. of II in 25 ml. of tetrahydrofuran at 0°. After 15 min. a negative Gilman color test showed the absence of Grignard reagent. From the neutral portion of the products 4.3 g. (0.027 mole) of 2-methoxynaphthalene, m.p. 68–70°, not depressed by mixing with authentic 2-methoxynaphthalene, m.p. 71–72°. This indicates that II reacts in the Grignard reaction mainly by the enolization mechanism.[10]

1-(2-Methoxy-6-naphthyl)-5-methyl-1,4-octanedione, V. A solution of 0.37 g. of IV in alcohol was catalytically reduced over platinum until 1 equivalent of hydrogen had been absorbed (30 min.). By recrystallization from ether-petroleum ether (b.p. 30–60°) there was obtained 0.32 g. (86%) of V,[5] m.p. 87.0–88.0°. The infrared spectrum was almost identical to that of IV, except for the bands at 10.15 and 10.90 *μ* (terminal methylene) which were absent.

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.9; H, 7.7. Found[s]: C, 76.8; H, 7.8.

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[6] We are indebted to Dr. G. V. D. Tiers, Minnesota Mining and Manufacturing Company, Minneapolis, Minn., for the NMR analysis and interpretation thereof.

[7] Analyses marked g by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and s by Schwartzkopf Microanalytical Laboratories, Woodside 77, N. Y. All melting points are uncorrected.

[8] C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2022 (1959) report a 51% average yield in thispreparation.

[9] Prepared using Johnson's procedure. G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

[10] We are indebted to Mr. N. Venkateswaran for this experiment.

Reaction of Ivanov and Ivanov-Like Reagents with Iodine

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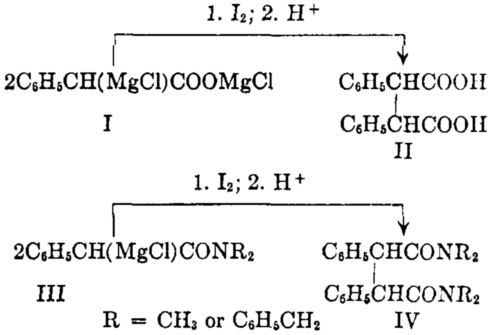
It has been found that the Ivanov reagent (I), prepared from phenylacetic acid, and the Ivanov-like reagents (III), obtained from *N,N*-dimethyl- and *N,N*-dibenzylphenylacetamide, respectively, reacted with iodine in the manner indicated below. The reaction products were *meso-α,α'*-diphenylsuccinic acid (II) (55% yield), *N,N,N',N'*-tetramethyl-(II), and *N,N,N',N'*-tetrabenzyl-*α,α'*-diphenylsuccindiamide (IV).



$$2C_6H_5CH(MgCl)COOMgCl \xrightarrow{1.\ I_2;\ 2.\ H^+} \begin{array}{l} C_6H_5CHCOOH \\ | \\ C_6H_5CHCOOH \end{array}$$

I II

$$2C_6H_5CH(MgCl)CONR_2 \xrightarrow{1.\ I_2;\ 2.\ H^+} \begin{array}{l} C_6H_5CHCONR_2 \\ | \\ C_6H_5CHCONR_2 \end{array}$$

III IV

$R = CH_3$ or $C_6H_5CH_2$

Ivanov and Spasov[1] found that sodium *α*-chloromagnesiumphenylacetate reacted with bromine to form *meso-α,α'*-diphenylsuccinic acid in 22% yield; phenylbromoacetic acid was obtained as a byproduct. Recently, Panaiotov[2] treated the same Ivanov reagent with iodine and isolated *meso-α,α'*-diphenylsuccinic acid in 17% yield.

meso-α,α'-Diphenylsuccinic acid was treated with lithium aluminum hydride to produce 2,3-diphenyl-1,4-butanediol. It was expected that the diol might react with bromoacetal to form 2-bromomethyl-5,6-diphenyl-1,3-dioxalane. However, instead of this substance, a product was obtained in 39% yield which, based on analytical data, was 3,4-diphenyltetrahydrofuran.

EXPERIMENTAL

meso-α,α'-Diphenylsuccinic acid. Phenylacetic acid (136.1 g., 1.0 mole), dissolved in 500 ml. of benzene, was added,

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[1] D. Ivanov and A. Spassov, *Archiv hem. i. farm.*, **8**, 8 (1934); *Chem. Abstr.*, **28**, 6711 (1934).