mono- and diethanolamines, using various concentrations of boron trifluoride in acetic acid with ten milliequivalents of hydroxyl. Results obtained are shown in Table II.

TABLE II

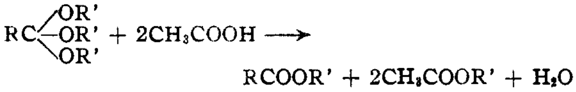
EFFECT OF CONCENTRATION OF BF_3 ON ESTERIFICATION OF ETHANOLAMINE

	—% Reaction of —OH group—		
	50 g. BF_3/l.	100 g. BF_3/l.	200 g./l.
Monoethanolamine	38	96	99.8
Diethanolamine	79	96	99.9

It is interesting to note that in the experiment using 50 g. of boron trifluoride per liter the reaction of diethanolamine was considerably greater than the monoethanolamine.

Interfering Substances.—The new hydroxyl procedure is unfavorably affected by aldehydes and ketones, acetals and ketals as indicated in an earlier publication.[5]

Orthoesters react quantitatively. The reaction apparently is general, probably following the equation



$$RC\begin{matrix}\diagup OR'\\ -OR'\\ \diagdown OR'\end{matrix} + 2CH_3COOH \longrightarrow RCOOR' + 2CH_3COOR' + H_2O$$

Five Eastman Kodak Co. orthoesters were mixed with the 100 g. of catalyst and heated for two hours at 60° and at 67°. Analytical results are summarized in Table III.

TABLE III

ANALYTICAL DATA ON ORTHOESTERS

Substance	Found, wt. %
Ethyl orthoformate	97.6 ± 0.4
Methyl orthoacetate	99.4 ± 0.3
Methyl orthopropionate	97.4 ± 0.0
Methyl ortho-*n*-butyrate	97.1 ± 0.0
Methyl ortho-*n*-valerate	92.2 ± 0.3

Summary

1. A specific quantitative method for the determination of hydroxyamines has been described. The method is based on quantitative esterification and subsequent titration of the water liberated with Karl Fischer reagent.
2. The method is applicable to the determination of hydroxyl in the presence of ammonia or amines.
3. Analytical results are reported for twelve amino alcohols.
4. The method is quantitative for samples containing a large excess of water.
5. Orthoesters react quantitatively with the acetic acid in the esterification reagent.

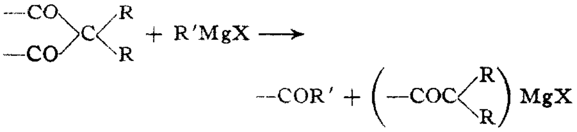
WILMINGTON, DELAWARE RECEIVED JANUARY 26, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Reaction between Cyclic β-Diketones and Grignard Reagents. II. 8,8-Dimethylperinaphthindandione-7,9[1]

BY T. A. GEISSMAN AND LESTER MORRIS

The reaction between cyclic β-diketones and Grignard reagents has been studied in a few cases only, and in none of these cases has the cleavage of the diketone been observed, normal addition of the reagent to the carbonyl groups having occurred.[2] This behavior is in marked contrast to that of many open-chain diketones, which are cleaved by the action of Grignard reagents according to the partial equation



$$\begin{matrix}-CO\\-CO\end{matrix}\!\!>C<\!\begin{matrix}R\\R\end{matrix} + R'MgX \longrightarrow -COR' + \left(-COC\begin{matrix}\diagup R\\ \diagdown R\end{matrix}\right)MgX$$

When the ketone represented by —COR' is capable of further reaction with the reagent a tertiary alcohol is the final product.

In the present work the study has been extended to include a diketone in which the diketonic function is a part of a six-membered ring: 8,8-dimethylperinaphthindandione-7,9 (I). The reaction of this compound with phenylmagnesium bromide has been carried out under a variety of conditions and three products have been isolated and characterized. None of these is the expected cleavage product.

8,8-Dimethylperinaphthindandione-7,9 was prepared by the methylation (in two steps) of perinaphthindandione-7,9.[3] It has been described by Freund and Fleischer,[4] who prepared it by the condensation of naphthalene with dimethylmalonyl chloride under the influence of aluminum chloride, followed by manual separation of the crystals of the three possible isomers, all of which were produced. An unsuccessful attempt was made in the present work to prepare the monomethyl derivative by the condensation of ethyl propionate with methyl 1,8-naphthalate; although the expected product was formed the yield was very low.

By a suitable control of the experimental con-

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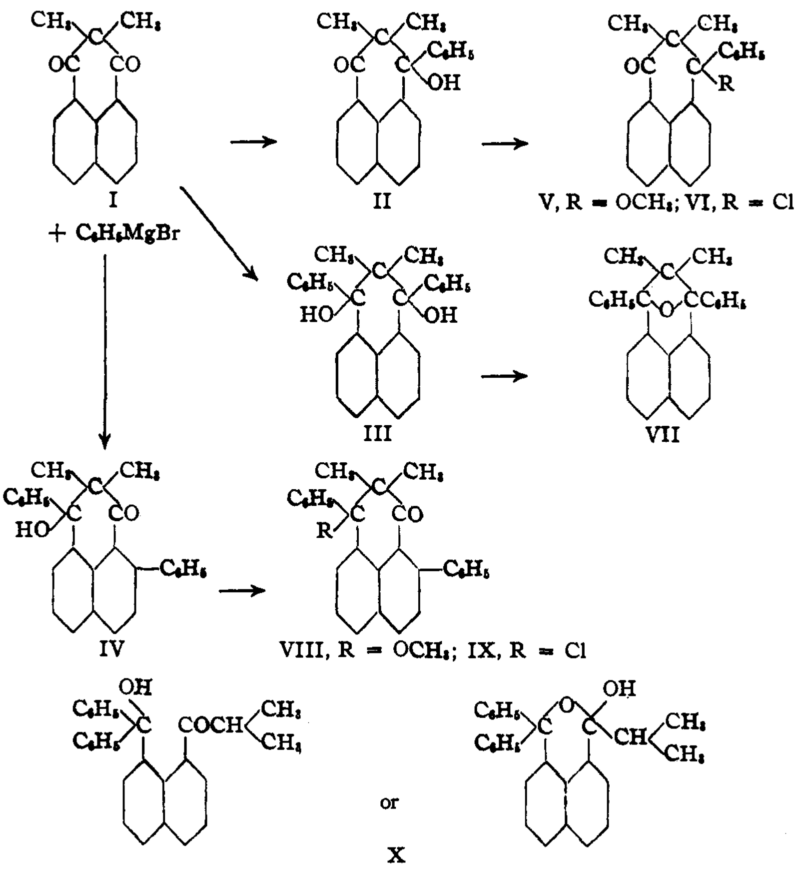
[1] Presented before the American Chemical Society, Fall Meeting, 1942, at Buffalo, N. Y.

[2] Geissman and Tulagin, THIS JOURNAL, **63**, 3352 (1941), and other references there cited.

[3] Errera, *Gazz. chim. ital.*, **41**, I, 190 (1911); *Chem. Centr.*, **82**, II, 1633 (1911).

[4] Freund and Fleischer, *Ann.*, **399**, 203 (1913).



ditions the reaction between the diketone (I) and phenylmagnesium bromide can be made to yield as the predominant product any of three substances. These are the normal monoaddition compound (II), the normal diaddition compound (III) and a compound which is formed by normal addition to one of the carbonyl groups followed by 1,4-addition (into the naphthalene ring) to the other (IV).

The monoaddition product (II) was formed when one mole of phenylmagnesium bromide was added at 0° to the diketone. The compound was converted into a methyl ether (V) and a monochloro compound (VI) when it was treated with hydrogen chloride in methanol and benzene, respectively.

The action of excess phenylmagnesium bromide upon the diketone at 25° led to the formation of the normal diaddition product (III). An attempt to convert this compound into the dimethyl ether by treating it with hydrogen chloride in methanol resulted in the formation of a substance to which has been assigned the structure of the endoxo compound VII, formed by transannular dehydration of the diol. The oxide (VII) liberated no gas and consumed no reagent when treated with methylmagnesium iodide in the "Grignard machine."

When an excess of phenylmagnesium bromide was added to the diketone at the temperature of boiling benzene, the principal product was a substance (IV) different from I and II. It formed a monomethyl ether (VIII) in acidic methanol, showed one active hydrogen and one carbonyl group in the "Grignard machine" and formed a monochloro compound (IX) when treated with anhydrous hydrogen chloride in benzene. These observations definitely exclude the possibility that it is the isomeric diaddition product corresponding to III, of which a *cis* and a *trans* form can exist. It was at first assumed, on the basis of carbon–hydrogen analyses, that IV was isomeric with III. Since IV is not the cleavage product (which has been synthesized independently[5]) and is not a glycol, the only reasonable assumption was that it was the product of 1,2- and 1,4-addition to the carbonyl groups. The product formed in such a way, however, would be a dihydronaphthalene derivative and would be expected to show considerable reactivity toward oxidizing agents and bromine. The compound (IV) is quite resistant to attack by such reagents and thus it appears that it has lost the two hydrogen atoms which would be present in the direct product of a 1,4-addition into the naphthalene nucleus. Such an aromatization, occurring either during the course of the initial reaction or in the isolation process, has been observed in analogous cases.[6]

The compound which would be expected if cleavage of the diketone had occurred (X) has been synthesized by an independent method.[5] It is not identical with any of the products obtained by the action of phenylmagnesium bromide on I.

8,8-Dimethylperinaphthindandione-7,9 is one more example of a cyclic β-diketone which does not undergo cleavage upon reaction with a Grignard reagent. Except for the reaction leading to the product IV its behavior parallels that of 2,2-dimethyl-1,3-diketohydrindene.[2] No observation made in the present work offers a basis for modifying or extending the discussion of the reaction of cyclic β-diketones and Grignard reagents, presented in the previous paper of this series.[2] The present results serve to emphasize the influence of the spatial disposition of the β-diketone function upon the course of its reaction with a Grignard reagent.

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(5) Geissman and Morris, THIS JOURNAL, 63, 1111 (1941).

(6) Fuson and Speck, *ibid.*, 64, 2446 (1942).

Experimental

Dimethyl 1,8-Naphthalate.[7]—A solution of 116 g. of naphthalic anhydride (recrystallized from concentrated nitric acid) in 670 ml. of a solution of 224 g. of potassium hydroxide in two liters of absolute methanol was placed in a 3-necked flask fitted with two dropping funnels. Into one of the dropping funnels was placed the remainder of the alcoholic potassium hydroxide solution and into the other was placed 373 ml. of dimethyl sulfate. The two reagents were run in simultaneously in a 4:1 ratio, with stirring and cooling of the flask contents. After all of the reagents had been added the potassium methyl sulfate was removed by filtration and the filtrate cooled in ice-salt. The product was collected and the filtrate diluted with water to precipitate the remainder. The second crop was recrystallized from methanol and combined with the first crop. The yield was 143 g. (89%), m. p. 102° (reported,[7] 25% yield, m. p. 102–103°).

The condensation of ethyl propionate with methyl 1,8-naphthalate in the presence of sodium resulted in the formation of a very small amount of 8-methylperinaphthindandione-7,9.

Perinaphthindandione-7,9.[3]—A mixture of 100 g. each of pulverized naphthalic anhydride, 100 g. of freshly fused zinc chloride and 200 g. of ethyl malonate was heated at 170–175° for four hours, with occasional stirring to break up a hard crust which formed around the edges of the mass. The mixture became yellow, then brown, and largely liquefied as the reaction progressed. The mixture was cooled and stirred with 500 ml. of 0.1 *N* hydrochloric acid, ground in a mortar with a fresh portion of acid and then shaken with two further portions. The resulting brown, granular material was stirred with 600 ml. of 4 *N* sodium hydroxide and the mixture filtered. The deep red filtrate was acidified, the bright yellow precipitate collected, redissolved in alkali and reprecipitated. Crystallization of the product from glacial acetic acid yielded 65 g. of brownish-yellow granular crystals, m. p. 247°, dec. Reported,[3] turns brown at 250°, melts toward 265°.

8-Methylperinaphthindandione-7,9.—To a solution of 2.5 g. of sodium in 150 ml. of absolute alcohol was added 14 g. of perinaphthindandione-7,9 and 14 ml. of methyl iodide. A heavy-walled bottle equipped with a pressure-tight closure was used. The bottle was heated before sealing and sealed when vapors of the contents began to escape. It was then heated at 100° for four hours. After cooling, the contents of the bottle were filtered. The filtrate was concentrated on the water-bath, cooled, and to the resulting solution eight volumes of 4 *N* sodium hydroxide were added. The undissolved solid (a mixture of O-methyl ether and dimethylated products) was removed and the filtrate acidified. The yellow precipitate was redissolved in alkali, reprecipitated, and recrystallized from ethanol. The yield of orange-yellow product, m. p. 183–185°, was 60%.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8. Found: C, 79.8; H, 4.8.

8,8-Dimethylperinaphthindandione-7,9 (I).—In a 500-ml., three-necked flask fitted with a reflux condenser, stirrer and dropping funnel were placed 30 ml. of anhydrous acetone, 8 ml. of methyl iodide and 12 g. of the monomethyl compound. A solution of 1.3 g. of sodium in the minimum quantity of absolute methanol was added over a period of three hours under reflux and with constant stirring. The final mixture was concentrated on the water-bath until most of the solvents had been removed and to the residue was added dilute sodium hydroxide solution. A crystalline material separated. This was removed and recrystallized from ligroin (b. p. 95–100°), affording long, light yellow needles of the dimethyl compound mixed with a small amount of tiny rosets of the O-methyl ether. The latter could be separated easily by shaking the dried crystals on a piece of wire gauze, the coarse needles of the desired product being retained and the fine needles of the impurity passing through. The yield of final material, m. p. 99–101°, was 30–40% (m. p. reported[4] 100–101°).

2,4-Dinitrophenylhydrazone of I.—A solution of the diketone and 2,4-dinitrophenylhydrazine in alcohol, containing a few drops of hydrochloric acid, was boiled for twenty minutes. On cooling a dark purple material separated. Recrystallization of this crude product from ethyl acetate–petroleum ether afforded brown-red crystals, m. p. 208–210°.

Anal. Calcd. for $C_{21}H_{16}O_5N_4$: C, 62.4; H, 4.0. Found: C, 62.3; H, 4.0.

The Reaction of the Diketone (I) with Phenylmagnesium Bromide. One Mole of C_6H_5MgBr at 0°: 7-Phenyl-7-hydroxy-8,8-dimethylperinaphthindanone-9 (II).—To a solution of 3.3 g. of the diketone (I) in a mixture of 50 ml. of benzene and 10 ml. of ether, cooled in an ice-bath, was slowly added exactly one equivalent of an ether solution of phenylmagnesium bromide. A deep purple complex separated. After two hours the mixture was hydrolyzed with iced ammonium chloride solution and subjected to steam distillation. The involatile residue was recrystallized from alcohol, yielding 1.3 g. of II and, from the mother liquors, 1.5 g. of unchanged I. In later runs it was found that extending the time of the reaction to six to eight hours gave better yields of II. The product formed colorless prisms, m. p. 190°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.2; H, 5.8.

The compound gave a cherry-red solution in concentrated sulfuric acid. Attempts to prepare a dinitrophenylhydrazone were not successful.

7-Phenyl-7-methoxy-8,8-dimethylperinaphthindanone-9 (V).—The conversion of II into its methyl ether was readily brought about by adding a drop of concd. hydrochloric acid to its solution in boiling methanol and allowing the solution to cool. The ether separated in iridescent needles, m. p. 214–216°.

Anal. Calcd. for $C_{22}H_{20}O_2$: OCH_3, 9.8. Found: OCH_3, 9.8.

7-Phenyl-7-chloro-8,8-dimethylperinaphthindanone-9 (VI).—Anhydrous hydrogen chloride was passed through a solution of 0.1 g. of II in 6 ml. of dry benzene for three hours. Evaporation of the solvent left a clear glass. This was dissolved in a little benzene and the solution allowed to evaporate slowly; large, cubical crystals were deposited. The compound melted at 156°, dec.

Anal. Calcd. for $C_{21}H_{17}OCl$: Cl, 11.1. Found: Cl, 10.9.

Excess C_6H_5MgBr at Room Temperature: 7,9-Diphenyl-7,9-dihydroxy-8,8-dimethylperinaphthindane (III).—To a solution of 3.2 g. of the diketone (I) in 100 ml. of benzene, cooled in an ice-bath, was added an ether solution of three equivalents of phenylmagnesium bromide. The purple complex which formed persisted after three hours, so the mixture was allowed to come to room temperature. The purple color disappeared and a clear red-violet solution resulted. After four hours the solution was decomposed with iced ammonium chloride and the mixture steam distilled. The residue was recrystallized from ligroin, forming colorless prisms, m. p. 168°.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.2; H, 6.4; active H, 2. Found: C, 85.2; H, 6.2; active H (Grignard machine), 2.0.

The glycol gives a deep blue-violet color in concd. sulfuric acid, forming a dark, resinous mass.

7,9-Diphenyl-7,9-endoxo-8,8-dimethylperinaphthindane (VII).—A solution of the glycol (III) in methanol containing a trace of hydrochloric acid was boiled for a short time and cooled. Colorless crystals separated, m. p. 134°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.5; H, 6.1. Found: C, 89.4; H, 5.9.

The compound liberated no gas in the Grignard machine.

Excess C_6H_5MgBr at 80°: 1,7-Diphenyl-7-hydroxyperinaphthindanone-9 (IV).—To a solution of 3.0 g. of the diketone (I) in 100 ml. of boiling benzene was slowly (two hours) added a solution of three equivalents of phenylmagnesium bromide in ether. A purple complex separated

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[7] Graebe, *Ann.*, **340**, 247 (1905).

at first but later disappeared with the formation of a clear, light red solution. The solution was cooled, decomposed with iced ammonium chloride and steam distilled. Recrystallization of the residue from alcohol yielded colorless needles, m. p. 238–239°. From the mother liquors was isolated a small amount of the glycol (III), identified by m. p. and conversion into VII.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.7; H, 5.9; active H, 1; carbonyl, 1. Found: C, 85.5; H, 6.1; active H, 0.96; carbonyl (addition), 1.05.

The compound gives a red-violet color in concd. sulfuric acid. It does not react with bromine in acetic acid or carbon tetrachloride nor with cold potassium permanganate solution in acetone. It is reduced by hydriodic acid (in boiling acetic acid) with the formation of a compound, m. p. 157°, which was obtained in small amounts only and was not further characterized.

1,7-Diphenyl-7-methoxy-8,8-dimethylperinaphthindanone-9 (VIII).—The ether was formed when a solution of IV in boiling methanol was treated with a trace of hydrochloric acid and allowed to cool. It formed colorless crystals, m. p. 224°.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.7; H, 6.2; OCH_3, 7.8. Found: C, 85.4; H, 6.3; OCH_3, 7.9.

1,7-Diphenyl-7-chloro-8,8-dimethylperinaphthindanone-9 (IX).—Anhydrous hydrogen chloride was passed into a solution of 0.2 g. of IV in warm, anhydrous benzene, containing a few granules of calcium chloride. Evaporation of the benzene left a colorless oil which crystallized slowly when dissolved in benzene–petroleum ether and allowed to stand. The chloro compound melted at 158–162°, dec.

Anal. Calcd. for $C_{27}H_{23}OCl$: C, 81.3; H, 5.8; Cl, 8.9. Found: C, 81.1; H, 5.7; Cl, 9.4.

Summary

A study has been made of the reaction between phenylmagnesium bromide and 8,8-dimethylperinaphthindandione-7,9. The diketonic function was not cleaved under any of the conditions used. Three products were obtained, two of which were the result of normal addition to either one or both of the carbonyl groups, the other being the result of 1,2-addition to one of the carbonyl groups and 1,4-addition to the other.

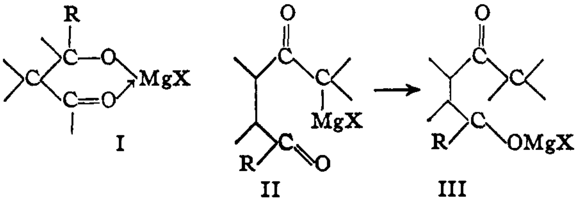
LOS ANGELES, CALIFORNIA RECEIVED JANUARY 6, 1944

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Reaction between Cyclic β-Diketones and Grignard Reagents. III. 2-Methyl-2-benzoylhydrindone

BY T. A. GEISSMAN AND VSEVOLOD TULAGIN

It has been shown in a number of instances that β-diketones in which the two carbonyl groups are members of a four-,[1] five-,[2] or six-membered[3] ring undergo normal addition when treated with Grignard reagents. This behavior is in contrast to that of many open-chain β-diketones, which are readily cleaved by alkyl- and arylmagnesium halides.[4] Among the possible explanations for this difference in behavior are[2] (1) that for cleavage to occur it must be necessary for a coördination complex such as I to form after the first mole of reagent adds, and (2) that the cleavage product (II) which would be expected in the case of a cyclic β-diketone is incapable of existence because of its readiness, for steric reasons, to reform the monoaddition product (III).

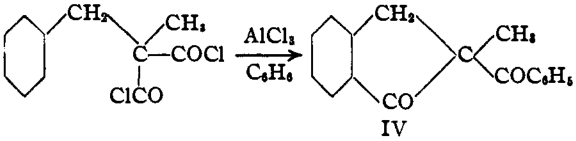


I II III

Implicit in the second explanation is the assumption that there is no bar to the initiation of cleavage, but only that it cannot proceed to such an extent as to allow a second mole of reagent to add to the resulting carbonyl group to yield an enolate-carbinolate. It is to be remarked that the conditions under which a β-diketone is allowed to react with a Grignard reagent will have an effect upon the nature of the reaction, and that a discussion of the presence or absence of cleavage in any case must take into account whether or not the reaction was carried out under conditions which would be expected to favor cleavage.

In the present paper are described the results of a study of the reaction between phenylmagnesium bromide and a β-diketone in which the carbonyl groups are disposed in such a way that chelation in the monoaddition product can occur, but in which the spatial arrangement of the groups is such that the sequence indicated by II→III could also occur.

2-Methyl-2-benzoylhydrindone (IV) was prepared by the treatment of methylbenzylmalonyl chloride with aluminum chloride in benzene solution. Simultaneous ring closure and condensation occurred smoothly to form IV in good yield.



IV

The structure of IV was proved by its cleavage with alkali to benzoic acid and 2-methylhydrindone, and by the nature of the products formed when it reacted with phenylmagnesium bromide.

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(1) Wedekind and Miller, *Ber.*, **44**, 3285 (1911).

(2) Geissman and Tulagin, THIS JOURNAL, **63**, 3352 (1941).

(3) Geissman and Morris, *ibid.*, **66**, 716 (1944).

(4) Kohler and Erickson, *ibid.*, **53**, 230 (1931).