A THESIS

entitled

Reactions With 1 (2H) - Naphthalenone - 3, 4- dihydro -2- Arylidenes and their analogues

Submitted by

AHMED HESHMAT MOUSTAFA

B. Sc., M.Sc.

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Faculty of Science

Ain Shams University

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Reactions with 1(2H)-naphthalenone-3,4-dihydro-2-arylidene

Thesis advisor Approved

Prof. W.I. Awad (D.Sc.) ....W. I. Awad........................

Prof. F.G. Baddar

F G Baddar

Head of Chemistry Department

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SUMMARY

Reactions with 2-Arylidene-3,4-dihydro 1(2H)-Naphthalenone

Various reactions were studied with 2-arylidene-3,4-dihydro 1(2H)-naphthalenone (LXVIII).

I) Grignard and Freidel-Crafts reactions.

The action of Grignard reagents on 2-arylidene-3,4-dihydro 1(2H)-naphthalenone (LXVIII) gave rise to three types of products namely, 2-diphenylmethyl-3,4-dihydro 1(2H)-naphthalenone (LXIX), 2-hydroxy-2-diarylcarbinol-3,4-dihydro 1(2H)-naphthalenone (LXX), and 2-diarylcarbinol-3,4-dihydro 1(2H)-naphthalenone (LXXI) respectively.

In case of the addition of phenylmagnesium bromide and o-tolylmagnesium bromide on 2-benzylidene-3,4-dihydro 1(2H)-naphthalenone (LXVIIIa) two products were obtained simultaneously (LXIXa, b) and (LXXa, b) (cf. page 73).

The other Grignard reagents RMgX where R=$C_6H_4OCH_3$-o; R = $C_6H_4CH_3$-p; R = CH_3 only one type of products were obtained (LXXc, d, e).

When phenylmagnesium bromide was allowed to react with 2-p-tolyidene and 2-p-chlorobenzylidene-3,4-dihydro 1(2H)-naphthalenone (LXVIIIb and d) also compounds of the type (LXXc, f) were the only products isolated.

However, in the case of o-tolylmagnesium bromide with

2-p-chlorobenzylidene and 2-anisylidene-3,4-dihydro 1(2H)-naphthalenone (LXVIIId and e) respectively, compounds of the type (LXXIa, b) were isolated. The study of the addition of Grignard reagents to 2-arylidene-3,4-dihydro 1(2H)-naphthalenone indicates that the addition took place through 1:4-addition followed by ketonisation forming compounds of the type (LXIX) and the other two types, (LXX) and (LXXI) were formed through 1:4-addition followed by a sort of oxidation on the Grignard complex and not on the final product (cf. page 73).

When 2-benzylidene and 2-p-tolylidene-3,4-dihydro-1(2H)-naphthalenone were treated with benzene in presence of anhydrous aluminium chloride. 2-Diphenylmethyl-3,4-dihydro 1(2H)-naphthalenone (LXIXa) was the only product isolated in an excellent yield. But when the above reaction was repeated with toluene two products were isolated, the main product was shown to be α-tetralone and the other solid product was shown to be a hydrocarbon for which structure (LXXIII) is suggested.

But in the case of m-xylene only α-tetralone was isolated. In case of 2-piperonylidene-3,4-dihydro 1(2H)-naphthalenone when treated with anhydrous aluminium chloride in benzene, toluene and s-tetrachloroethane one and the same product was obtained identified as 2-(3,4-dihydroxybenzylidene)-3,4-dihydro 1(2H)-naphthalenone (LXXIV).

In the case of 2-anisylidene and 2-*p*-chlorobenzylidene-3,4-dihydro 1(2H)-naphthalenone no reaction took place.

II) *Studies on* 2-*arylidene oxide* 3,4-*dihydro* 1(2H)-*naphthalenone* (LXXVI).

The action of acetic acid on 2-arylidene oxide 3,4-dihydro 1(2H)-naphthalenone was investigated. It has shown that 2-benzylidene oxide 3,4-dihydro 1(2H)-naphthalenone and 2-*p*-chlorobenzylidene oxide 3,4-dihydro 1(2H)-naphthalenone (LXXVI*a*, *d*) respectively were inert toward acetic acid, but, in case of 2-anisylidene oxide and 2-piperonylidene oxide (LXXVI*b*, *c*) two products were obtained, (LXXVII) and (LXXVIII) respectively.

When such epoxides were treated with trichloroacetic acid all the epoxides under consideration gave one type of products to which structures (LXXIX) were assigned.

2-Benzylidene oxide and 2-*p*-chlorobenzylidene oxide (LXXVI*a*,*d*)were treated with stannic chloride and structures (LXXXI) and (LXXXII) were assigned to the products.

When 2-benzylidene oxide (LXXVI*a*) was treated with a mixture of acetic acid and hydrochloric acid,the isomeric chlorohydrin (LXXX) was obtained.

The structure of such compounds were established in the light of their spectral data and analytical data.

III) Reactions of 2-arylidene-3,4-dihydro 1(2H)-naphthalenone (LXVIII) with :

a) hydrazine hydrate,

b) phenylhydrazine and

c) thiourea.

In case of hydrazine hydrate and phenylhydrazine the corresponding Δ^1-pyrazoline derivatives were isolated. Their structures (LXXXIII and LXXXVI) were verified in the light of their spectral data (cf. page 99, 103).

In the case of thiourea pyrimidine-2-thione derivatives were isolated, their structure, (LXXXVII) was verified in the light of their analytical data and spectral data (cf. page 103).

IV) Stobbe condensation.

When 2-benzylidene-3,4-dihydro 1(2H)-naphthalenone was allowed to react with dimethylsuccinate in presence of potassium tert. butoxide a solid product in poor yield was obtained identified as alkylidene half ester (LXXXVIII) besides a resinified oily material ill identified, very little could have been done with these products (cf. p.105).

GENERAL PART

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(1) Composition and Mechanism of Grignard reagents.

(2) Freidel-Crafts reaction with α,β-unsaturated ketones.

GRIGNARD REAGENTS

Composition and Mechanisms of Grignard Reagents

1) Introduction[x].

Without doubt one of the most fascinating and fundamental problems in organic chemistry today concerns the composition of Grignard reagents in ether as solvent. A different, but closely related, problem involves the mechanism or mechanisms by which these Grignard reagents react with organic functional compounds. Such as ketones, nitriles, etc. The solution to the second problem can only be forthcoming when the solution to the first problem is in hand. The importance and basic nature of these problems are well recognised, yet there has been no full scale assault for any length of time by anyone to bring about a complete solution. Many workers have become interested in the composition problem from time to time, but efforts have been somewhat sporadic and no real progress has appeared until recently.

2) Composition of Grignard compounds.

A- Early history.- In order to appreciate this problem

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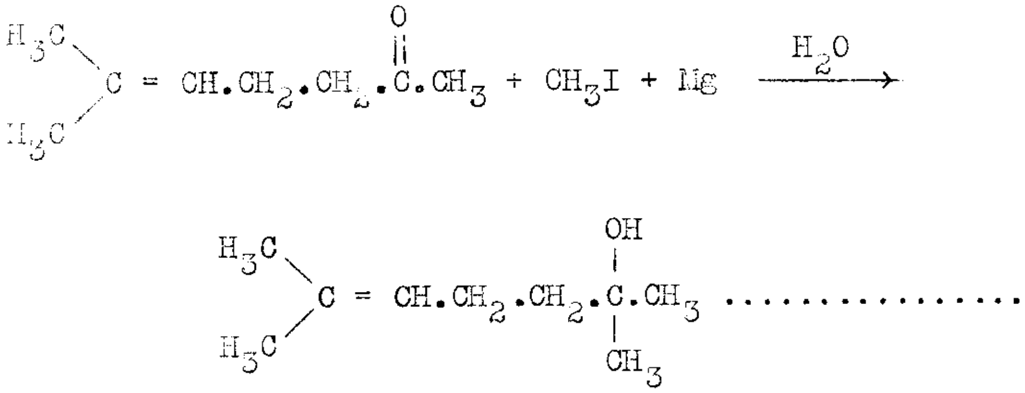
[x] E.C. Ashby Quarterly Reviews; No. 2; Vol. 21 (1967).

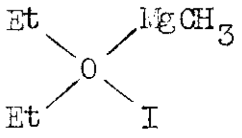
fully one should go back to the very beginning of this story when Grignard investigated Barbier reaction. The specific system involved is shown in (1).



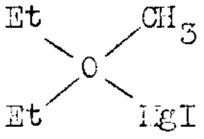
(1)

Grignard thought the intermediate in this reaction to be RMgX and thus concluded that yields might be improved by preparing this compound first and then adding it to the ketone. He found that alkyl halides do react readily with magnesium in ether as solvent and that the resulting reaction mixture reacts with aldehydes and ketones in higher yields than when the Barbier procedure is used to produce the corresponding addition product.[1] Grignard represented the composition of the reaction product of an alkyl halide and magnesium in ether as RMgX and represented the reaction of this reagent with ketones as a simple addition reaction.

The first serious suggestion, since Grignard's initial one, concerning the composition of Grignard compounds in ether solution was made by Baeyer and Villiger.[2] These workers suggested representing Grignard compounds in ether solution as an onium compound. The structure suggested for methylmagnesium iodide is shown in (I)



(I)



(II)

This suggestion was followed by a similar one from Grignard[3] depicting the onium compound differently as (II).

Although Standnikov[4] appeared to have evidence to support Grignard's suggestion, it was later proved by both Gorskij[5], and Chelintzev and Pavlov[6] that the evidence presented was not unequivocal. Shortly thereafter Thorpe and Kamm[7] demonstrated conclusively that Grignard compounds could not be represented by the onium structure. They did this by demonstrating that the products of reactions (2) and (3) are not identical. While the onium composition was being debated, Abegg[8] in 1905 suggested a polar composition for the Grignard

$$Et_2O + Ph.Br + Mg \xrightarrow{H_2O} C_6H_6 \ (60\%) \ \ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

$$Et.O.Ph + EtBr + Mg \xrightarrow{H_2O} C_2H_6\ (99.7\%)\ \ldots\ldots\ldots\ldots\ (3)$$

reagent ($R^- MgX^+$) and even suggested the possibility of an equilibrium (4) to describe the system.

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

Jolibois[9] in 1912 was the first to suggest what is referred to as the unsymmetrical dimeric structure ($R_2Mg.MgX_2$), to represent Grignard compounds in ether solution. This suggestion was based on the facts that:

1) Grignard compounds, in ether, were believed to be dimeric.
2) Et_2Mg and MgI_2 in ether had the same physical properties as a solution prepared from C_2H_5I and Mg.
3) Electrolysis of EtMgI under certain conditions deposited magnesium at the cathode without evolution of gas.

Grignard[10] suggested that the observations of Jolibois could be explained by a symmetrical dimeric $(RMgX)_2$ composition. Thus the contraversy began concerning the description of Grignard compounds by the symmetrical or unsymmetrical dimeric structure.[11]

Although Grignard[10] and Terentiev[12] reported dimeric association for methylmagnesium iodide, Meisenheimer and