[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Addition Reactions of Organometallic Compounds with Conjugated Systems[1]

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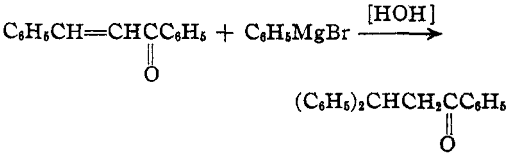
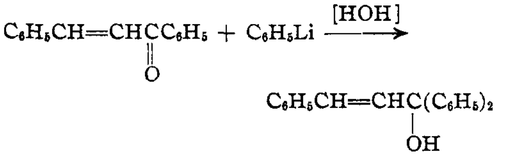
Extensive studies, particularly by Kohler and co-workers,[2] have indicated the effects of various factors on the course of addition of Grignard reagents to conjugated systems. No report has been made on the type of addition of a series of RM compounds (where M is varied) and a selected conjugated system like that contained in benzalacetophenone.

Phenylmagnesium bromide adds 1,4 to benzalacetophenone to give β,β-diphenylpropiophenone[3]



$$\mathrm{C_6H_5CH{=}CH\underset{\underset{O}{\|}}{C}C_6H_5 + C_6H_5MgBr \xrightarrow{[HOH]} (C_6H_5)_2CHCH_2\underset{\underset{O}{\|}}{C}C_6H_5} \quad [I]$$

and with phenyllithium, 1,2-addition has been reported to give diphenylstyrylcarbinol.[4]



$$\mathrm{C_6H_5CH{=}CH\underset{\underset{O}{\|}}{C}C_6H_5 + C_6H_5Li \xrightarrow{[HOH]} C_6H_5CH{=}CH\underset{\underset{OH}{|}}{C}(C_6H_5)_2} \quad [II]$$

Reaction [II] is inadequate, for we now find that phenyllithium also shows 1,4-addition to an extent of 13%.

On the basis of an examination of the reaction of benzalacetophenone with a series of phenylmetallic types it appears that the mode of addition is influenced markedly by the relative reactivities of the RM compounds. The lesser reactive phenylmetallic compounds of beryllium, magnesium, zinc, aluminum and manganese show predominantly, if not exclusively, 1,4-addition. The highly reactive compounds of potassium and calcium show 1,2-addition. The organometallic compounds of intermediate reactivity (those of lithium and sodium) show both 1,2-addition and 1,4-addition. Generalizations on the relative reactivities of RM compounds,[5] based on other reactions, are in satisfactory agreement with the correlations stated above with benzalacetophenone.

***p*-Dimethylaminobenzalacetophenone.**—Some of the phenylmetallic compounds used in the benzalacetophenone studies were also examined in reactions with *p*-dimethylaminobenzalacetophenone. Here, too, it was found that the compounds of beryllium and magnesium showed 1,4-addition; that phenylcalcium iodide showed 1,2-addition; and that phenyllithium showed both 1,2-addition (67%) and 1,4-addition (14%).

Benzophenone-anil.—Somewhat related to the 1,2-addition and 1,4-addition to benzalacetophenone is the addition of phenylmetallic compounds to benzophenone-anil. It has been shown that, under customary conditions, phenylmagnesium bromide reacts very slowly with benzophenone-anil. If, however, forced conditions are used an unusual type of lateral-nuclear 1,4-addition takes place resulting in the formation of *o*-phenylbenzohydrylaniline.[6] On the other hand, phenyllithium[7a] and phenylcalcium iodide[7b] react promptly with benzophenone-anil to give triphenylmethylaniline by a 1,2-addition.

$$\mathrm{(C_6H_5)_2C{=}NC_6H_5 + C_6H_5Li \xrightarrow{[HOH]} (C_6H_5)_3CNHC_6H_5} \quad [III]$$

We are now reporting that phenylsodium and phenylpotassium also show 1,2-addition [reaction (III)].

In general, one may conclude that the more reactive RM compounds tend to 1,2-addition; and the less reactive RM compounds tend to 1,4-addition.

Metal–Metal Interconversions.—The mode of addition to a compound like benzalacetophenone can be used to establish the following M–M interconversions.

$$\mathrm{BeCl_2 + 2C_6H_5Li \longrightarrow (C_6H_5)_2Be + 2LiCl}$$

$$\mathrm{MnI_2 + C_6H_5Li \longrightarrow C_6H_5MnI + LiI}$$

$$\mathrm{MgI_2 + }p\mathrm{\text{-}(CH_3)_2NC_6H_4Li \longrightarrow }p\mathrm{\text{-}(CH_3)_2NC_6H_4MgI + LiI} \quad [IV]$$

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[1] Paper XXXIX in the series: "Relative Reactivities of Organometallic Compounds." The preceding paper is: Gilman and Jones, THIS JOURNAL, **63**, 1443 (1941).

[2] A general discussion, together with appropriate references, is given by Allen and Blatt in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Chapter 6.

[3] Kohler, *Am. Chem. J.*, **31**, 642 (1904).

[4] Lüttringhaus, *Ber.*, **67B**, 1602 (1934).

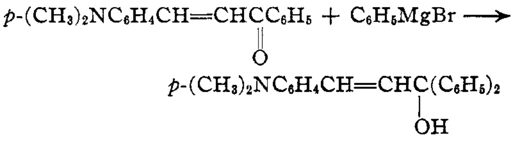
[5] See pp. 435–439 of Ref. 2.

[6] Gilman, J. E. Kirby, and Kinney, THIS JOURNAL, **51**, 2252 (1929). Other illustrations of a related 1,4-addition were described subsequently (see ref. 2).

[7] (a) Gilman and Kirby, *ibid.*, **55**, 1265 (1933); (b) Gilman, Kirby, Lichtenwalter and Young, *Rec. trav. chim.*, **55**, 79 (1936).

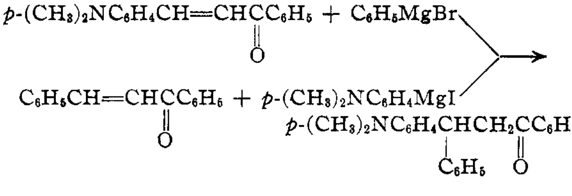
For example, the observation that a mixture of magnesium iodide and *p*-dimethylaminophenyllithium reacts with benzalacetophenone to give only 1,4-addition, shows that reaction [IV] occurred. Otherwise, one would have expected some 1,2-addition product from the known behavior of the RLi compound.[8]

***p*-Dimethylaminobenzalacetophenone and Phenylmagnesium Bromide.**—It was stated earlier[9] that there was a 1,2-addition of phenylmagnesium bromide to *p*-dimethylaminobenzalacetophenone to give *p*-dimethylaminostyryldiphenylcarbinol.



$$p\text{-}(CH_3)_2NC_6H_4CH{=}CH\underset{\underset{O}{\|}}{C}C_6H_5 + C_6H_5MgBr \longrightarrow p\text{-}(CH_3)_2NC_6H_4CH{=}CH\underset{OH}{\underset{|}{C}}(C_6H_5)_2 \quad [V]$$

A 1,2-addition seemed at variance with the general findings reported in this paper. Accordingly, the reaction with phenylmagnesium bromide was reinvestigated, and we found that the product was actually β-(*p*-dimethylaminophenyl)-β-phenylpropiophenone, formed by 1,4-addition. A synthesis of this ketone by an independent procedure left no doubt of the structure.



$$p\text{-}(CH_3)_2NC_6H_4CH{=}CH\underset{\underset{O}{\|}}{C}C_6H_5 + C_6H_5MgBr \longrightarrow$$
$$C_6H_5CH{=}CH\underset{\underset{O}{\|}}{C}C_6H_5 + p\text{-}(CH_3)_2NC_6H_4MgI \longrightarrow p\text{-}(CH_3)_2NC_6H_4\underset{C_6H_5}{\underset{|}{C}H}CH_2\underset{\underset{O}{\|}}{C}C_6H_5$$

Furthermore, the carbinol supposed to have been formed in accordance with reaction [V] was synthesized by a reaction between phenyllithium (known to give mainly 1,2-addition) and *p*-dimethylaminobenzalacetophenone. The chief product formed in this manner gave reactions characteristic of an unsaturated carbinol.

Experimental Part

Benzalacetophenone and RM Compounds.—The reactions were carried out in ether, unless otherwise stated, in a nitrogen atmosphere, and the benzalacetophenone was added to the RM compound to reduce secondary reactions. Hydrolysis was effected by cold ammonium chloride solution prior to the admission of air to the reaction flask. The results are given in Table I, and in the accompanying section on *p*-dimethylaminophenyl-magnesium iodide and -lithium.

TABLE I

BENZALACETOPHENONE AND C_6H_5M COMPOUNDS

RM	β,β-Diphenylpropiophenone (1,4-addition), %	Diphenylstyrylcarbinol (1,2-addition), %
$(C_6H_5)_2Be$[a]	90	
$(C_6H_5)_2Zn$[b]	91	
$(C_6H_5)_3Al$[c]	94	
C_6H_5MnI[d]	77	
C_6H_5CaI[e]		45
C_6H_5K[f]		52
C_6H_5Li[g]	13	69
C_6H_5Na[h]	3.5	39

[a] In this experiment, to a solution of 5.2 g. (0.025 mole) of benzalacetophenone was added diphenylberyllium prepared from 0.05 mole of anhydrous beryllium chloride and 0.1 mole of phenyllithium. See, Gilman and Schulze, THIS JOURNAL, **49**, 2904 (1927), for the preparation of phenylberyllium iodide. [b] The diphenylzinc was prepared in xylene from 0.022 mole of diphenylmercury and zinc [Kocheshkov and co-workers, *Ber.*, **67B**, 1138 (1934)]. If an appreciable amount of diphenylstyrylcarbinol had been present, the melting point of the solid obtained would have been distinctly lower than β,β-diphenylpropiophenone (m. p. 96°), for a synthetic mixture of one part of the carbinol (m. p. 111°) and twenty parts of the ketone melted from 86 to 89°. [c] The triphenylaluminum was prepared from aluminum and diphenylmercury [Gilman and Marple, *Rec. trav. chim.*, **55**, 133 (1936)]. [d] The phenylmanganese solution was prepared from 0.03 mole of anhydrous manganese iodide and 0.1 mole of phenylmagnesium iodide. The phenylmanganese product was free of magnesium, and analyzed for a mixture of C_6H_5MnI $(C_6H_5)_2Mn$. See, also, Gilman and Bailie, *J. Org. Chem.*, **2**, 84 (1937). The authors are grateful to E. Bindschadler for the manganous iodide. From a second experiment run for ten minutes instead of seventeen hours, the yield of β,β-diphenylpropiophenone was 51%. [e] The phenylcalcium iodide was prepared from calcium and iodobenzene (see, ref. 7b). An attempt to isolate the ketone by fractional distillation of the dark oil was unsuccessful; a small quantity of unidentified solid melting at 120° was isolated from the fraction distilling between 160–200° (7 mm.). Other studies with benzohydrylmetallic compounds indicate the possibility of thermally converting a 1,2-addition product to a 1,4-addition product. [f] The phenylpotassium was prepared from 0.015 mole of diethylmercury, potassium shavings and benzene [Schorigin, *Ber.*, **41**, 2723 (1908); **43**, 1938 (1910); Gilman and Kirby, THIS JOURNAL, **58**, 2074 (1936)]. [g] The oil, representing 18% of the reaction products, was resistant to crystallization. [h] The excess sodium used in the preparation of phenylsodium (by Schorigin's procedure) was removed by amalgamation with mercury.

From *p*-dimethylaminophenylmagnesium iodide (prepared from 0.024 mole of *p*-dimethylaminophenyllithium and magnesium iodide) and 0.02 mole of benzalacetophenone was obtained 71% of β-(*p*-dimethylaminophenyl)-β-phenylpropiophenone. There was qualitative evidence (red color with alcoholic hydrogen chloride) for *p*-dimethylaminophenylphenylstyrylcarbinol. Reaction with *p*-dimethylaminophenylmagnesium iodide (and bromide)

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(8) Additional support for Reaction [IV] was reported recently in a new color test for RM compounds: Gilman and Swiss, THIS JOURNAL, **62**, 1847 (1940).

(9) MacLean and Widdows, *J. Chem. Soc.*, **105**, 2169 (1914).

prepared directly from the RI (and RBr) compound with magnesium also gave the ketone, which was shown (mixed m. p.) to be identical with the product from *p*-dimethylaminobenzalacetophenone and phenylmagnesium bromide.

From 0.025 mole of *p*-dimethylaminophenyllithium and 0.02 mole of benzalacetophenone was obtained: 12% of β-(*p*-dimethylaminophenyl)-β-phenylpropiophenone, and 75% of *p*-dimethylaminophenylphenylstyrylcarbinol. The carbinol melts at 131°; is sensitive to the acidic atmosphere of the laboratory, and gives a ruby-red solution with alcoholic hydrogen chloride.

TABLE II

p-DIMETHYLAMINOBENZALACETOPHENONE AND C_6H_5M COMPOUNDS[a]

RM	β-Dimethylaminophenyl-β-phenylpropiophenone, %	*p*-Dimethylaminostyryldiphenylcarbinol, %
C_6H_5MgBr[b]	66	
$(C_6H_5)_2Be$[c]	71	
C_6H_5Li[d]	14	76
C_6H_5CaI[e]		64

[a] In each of these experiments, the *p*-dimethylaminobenzalacetophenone in benzene was added to the phenylmetallic compound in ether. [b] In this experiment 0.02 mole of the *p*-dimethylaminobenzalacetophenone and 0.08 mole of phenylmagnesium bromide gave the 66% yield of β-dimethylaminophenyl-β-phenylpropiophenone. This pure ketone melted at 101°, after crystallization from ethanol; gave a colorless solution in alcohol containing hydrogen chloride; liberated hydrobromic acid when added to a chloroform solution of bromine; and did not evolve methane when treated with methylmagnesium iodide. The products from two separate reactions gave, prior to distillation, red solutions with alcoholic hydrogen chloride, characteristic of small amounts of *p*-dimethylaminostyryldiphenylcarbinol. This evidence for traces of carbinol supports the general thesis that the several organometallic compounds undergo essentially the same reactions but at different rates. *p*-Dimethylaminobenzalacetophenone gave a light yellow solution with alcoholic hydrogen chloride. [c] A transitory red coloration was noted as each drop of *p*-dimethylaminobenzalacetophenone came into contact with the RM solution. [d] The *p*-dimethylaminostyryldiphenylcarbinol melted at 117° after crystallization from a mixture of benzene and petroleum ether, and traces of acids produced a red coloration with this carbinol. *Anal.* Calcd. for $C_{23}H_{23}ON$: C, 83.8; H, 7.04. Found: C, 83.5; H, 7.00. Zerewitinoff: Calcd.: 1.0. Found: 0.85. The filtrates from the crystallization of the carbinol yielded 14% of β-dimethylaminophenyl-β-phenylpropiophenone. A duplicate experiment gave approximately the same amounts of saturated ketone and of carbinol. [e] It is possible that some of the ketone (formed by 1,4-addition) may have been present in small amounts, and that the dark resinous materials, characteristic of the products of the reactions of phenylcalcium iodide, frustrated crystallization.

Anal. Calcd. for $C_{23}H_{23}ON$: C, 83.8; H, 7.04. Found: C, 83.6; H, 6.98. Zerewitinoff: Calcd. 1.0. Found: 0.80.

Table II contains the essential material on the reaction between *p*-dimethylaminobenzalacetophenone and phenylmetallic compounds.

Benzophenone-anil and RM Compounds.—The yield of triphenylmethylaniline (mixed m. p.) from a reaction between 0.01 mole of benzophenone-anil and phenylsodium (prepared from 0.01 mole of diphenylmercury and sodium) was 1.5%. The intractable oils made difficult the isolation of any possible 1,4-addition product.

From a related reaction between 0.04 mole of benzophenone-anil and phenylpotassium (prepared from benzene, 0.04 mole of di-*n*-butylmercury and potassium) was obtained 73% of triphenylmethylaniline.

Summary

The reactions of RM compounds with benzalacetophenone have been used to corroborate some metal–metal interconversions.

Moderately reactive phenyl-metallic compounds (those of beryllium, magnesium, zinc, aluminum and manganese) have been shown to give 1,4-addition with benzalacetophenone. The highly reactive RM compounds of calcium and potassium show 1,2-addition. RM compounds of intermediate reactivity (those of lithium and sodium) show both 1,2-addition and 1,4-addition.

Similar observations have been made with some phenylmetallic compounds in these three broad groups on the mode of addition to *p*-dimethylaminobenzalacetophenone. It has been shown that the reaction between *p*-dimethylaminobenzalacetophenone and phenylmagnesium bromide is a 1,4- and not a 1,2-addition as reported previously.

Phenylsodium and phenylpotassium show 1,2-addition to benzophenone-anil to give triphenylmethylaniline. It was shown earlier that phenylmagnesium bromide gives a 1,4-addition with benzophenone-anil.

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