complex in 16% yield,[11] was acidified with acetic acid and treated with 0.1*M* sodium tetraphenylboron. The resulting yellow precipitate was recrystallized from acetone, and 0.1 g. of yellow crystals was obtained, m.p. *ca.* 298° dec. The sample gave a negative Beilstein test and was recrystallized for analysis.

Anal. Calcd. for $C_{36}H_{32}CrB$: C, 81.97; H, 6.12. Found: C, 81.63; H, 6.29.

The infrared spectrum was identical with that of bisbenzenechromium(I) tetraphenylboron, m.p. *ca.* 290° dec., prepared from benzene by the method of Fischer.[3a]

Bis(p-chlorobiphenyl)chromium complex from p-chlorobiphenyl. In a 125-ml. Erlenmeyer flask were mixed 5.0 g. (0.0315 mole) of anhydrous chromic chloride,[12] 1.7 g. (0.063 mole) of aluminum powder, 8.4 g. (0.063 mole) of anhydrous aluminum chloride, and 17.5 g. (0.093 mole) of *p*-chlorobiphenyl (Monsanto Chemical Co., recrystallized from ethanol). The mixture was kept under a nitrogen atmosphere and was stirred occasionally while heating for 5 hr. at 145–160°. The mixture was hydrolyzed with 50 ml. of methanol and 200 ml. of ice water, then treated with excess 5*N* sodium hydroxide and *ca.* 50 g. of sodium hydrosulfite. The mixture was extracted with benzene, and the red-black benzene, solution was added to distilled water and placed under an air stream to re-oxidize the chromium complex. When the benzene had evaporated, the aqueous mixture was heated to 70° and filtered, and the residue was re-extracted with hot water. The aqueous filtrates were combined to give an orange solution C that contained chromium(I) complex in yields of 31–36%.[11]

Bis(p-chlorobiphenyl)chromium(I) tetraphenylboron. Upon cooling, solution C afforded a voluminous yellow precipitate. The precipitate was dissolved in water and the solution was washed with benzene, acidified with acetic acid, and treated with 0.1*M* sodium tetraphenylboron. When the resulting yellow precipitate was recrystallized from acetone, 1.32 g. (6%) of orange plates was obtained. After a second recrystallization the sample melted at 200.5–202° dec.

Anal. Calcd. for $C_{48}H_{38}Cl_2CrB$: C, 77.01; H, 5.12; Cl, 9.48. Found: C, 76.93; H, 5.06; Cl, 9.43.

In experiments in which the reaction mixture was heated for 16 hr. instead of 5 hr., and the tetraphenylboron salts were precipitated directly from solution C, the salts contained less than the calculated amount of chlorine.

Bis(p-chlorobiphenyl)chromium(O). All operations were conducted under a blanket of nitrogen. Solution C, after cooling and refiltering, was treated with a basic solution of sodium hydrosulfite. The mixture was extracted with benzene, and the black benzene extract was dried over anhydrous magnesium sulfate and filtered. The benzene was removed by vacuum freeze drying, which left 4.4 g. (33%) of voluminous orange powder. It was washed with anhydrous ether, dried *in vacuo*, and stored in an evacuated tube. The purified product melted at 105–108° dec.

Anal. Calcd. for $C_{24}H_{18}Cl_2Cr$: C, 67.14; H, 4.23; Cl, 16.52; Cr, 12.12. Found: C, 68.33; H, 5.00; Cl, 13.65; Cr, 12.8.

In preliminary experiments, attempted sublimation of the crude product was accompanied by extensive decomposition. Sublimates were obtained in maximum yields of 6% and contained only 8–9% chlorine.

Bis(p-chlorobiphenyl)chromium tetraphenylboron from p,p'-dichlorobiphenyl. In a 12 × 100 mm. Pyrex tube were placed 0.50 g. (3.15 mmoles) of anhydrous chromic chloride (Fisher Scientific Co.), 0.17 g. (6.30 mmoles) of aluminum powder, 0.84 g. (6.30 mmoles) of anhydrous aluminum chloride, and 2.79 g. (12.5 mmoles) of *p,p'*-dichlorobiphenyl (Federal Phosphorus Co., recrystallized from ethanol, m.p. 146–148.5°). The tube was evacuated, sealed, and shaken vigorously to mix the reagents. The tube was heated with rotation for 5 hr. at 155–160° in a small electric furnace. The mixture was hydrolyzed and extracted as in the procedure for bis(*p*-chlorobiphenyl)chromium complex from *p*-chlorobiphenyl. The aqueous filtrate contained chromium(I) complex in 16% yield.[11] Acidification of the filtrate with acetic acid and treatment with 0.1*M* sodium tetraphenylboron afforded a precipitate which was recrystallized from acetone to give 0.2 g. of orange crystals, m.p. 196–198° dec. After a second recrystallization, the compound melted at 197.5–198.5° dec.

Anal. Calcd. for $C_{48}H_{38}Cl_2CrB$: C, 77.01; H, 5.12; Cl, 9.48. Found: C, 77.43; H, 5.32; Cl, 9.72.

The infrared spectrum was identical with that of bis(*p*-chlorobiphenyl)chromium(I) tetraphenylboron prepared from *p*-chlorobiphenyl.

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Action of Grignard Reagents on Heterocyclic Compounds. III.[1] Action of Arylmagnesium Halides on 2-Phenyl-4-benzylidene-2-imidazoline-5-one

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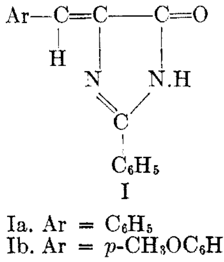
Received November 12, 1959

Mustafa and Harhash[2] claimed that methyl-, and phenylmagnesium halides react with 2-phenyl-4-benzylidene-2-imidazoline-5-one (Ia) to give colorless products believed to have structures IIa and IIb respectively. No proof was given for such structures.



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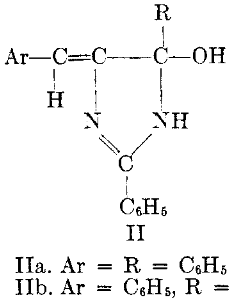

II

Ia. Ar = C_6H_5
Ib. Ar = p-$CH_3OC_6H_4$

IIa. Ar = R = C_6H_5
IIb. Ar = C_6H_5, R = CH_3

We have now reinvestigated the action of phenyl-, and naphthylmagnesium halides on Ia and Ib and we believe that the products have structure III: *i.e.*, 1,4-addition followed by ketonization according to the following scheme:

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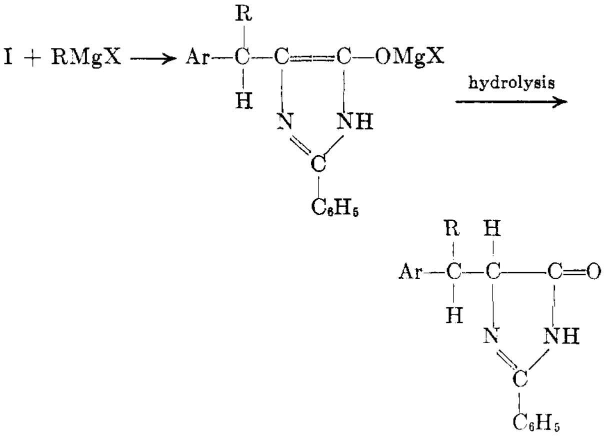
(11) The amount of chromium(I) ion in solution was determined from an aliquot containing 0.05 to 0.2 mmole of chromium. The complex was decomposed by boiling with concd. sulfuric acid. The chromium was oxidized by sodium peroxide to chromium(VI) and was titrated as dichromate.

(12) The authors wish to thank Dr. John H. Wotiz of the Research Center of the Diamond Alkali Co., Painesville, Ohio, for the gift of anhydrous chromic chloride.

(1) W. I. Awad and M. S. Hafez, *J. Org. Chem.*, in press.

(2) A. Mustafa and A. H. E. Harhash, *J. Org. Chem.*, **21**, 575 (1956).



III

IIIa. Ar = R = C_6H_5
IIIb. Ar = C_6H_5, R = α-$C_{10}H_7$
IIIc. Ar = p-$CH_3OC_6H_4$, R = C_6H_5
IIId. Ar = p-$CH_3OC_6H_4$, R = α-$C_{10}H_7$

Actually there are three possibilities for such a reaction: 1) ring opening which would necessitate the addition of two molecules of the Grignard reagent and which disagreed with the analytical data—in reality the analysis shows that I adds one mole of the Grignard reagent; 2) 1,2-addition as suggested by Mustafa,[2] in which case the carbonyl group would disappear; and 3) 1,4-addition which leads to III as suggested here, in which case the carbonyl group is still present.

Infrared spectra of the Grignard products show clearly that the carbonyl stretching frequency of amide I and amide II is present (*cf.* Table I), both in the starting materials and in the Grignard products. This favors structure III. A similar 1,4-addition was observed by Panizzi[3] when phenylmagnesium bromide reacted with 3-methyl-4-benzyliden-isooxazolone.

TABLE I[a]

INFRARED SPECTRA OF STARTING MATERIAL AND PRODUCTS

Compound	Stretching Frequency, Cm.$^{-1}$[b] Amide I	Amide II
Ia	1709	1605
IIIa	1723	1587
IIIb	1723	1587
Ib	1681	1587
IIIc	1681	1612
IIId	1723	1587

[a] The infrared measurements were carried out on Perkin-Elmer infrared Model 137, in nujol medium. [b] For the comparison of the stretching frequencies of amide I and amide II see Bellamy[4] and Awad.[5]

EXPERIMENTAL

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

Action of phenylmagnesium bromide on 2-phenyl-4-benzylidene-2-imidazolin-5-one.[6] (Ia). A solution of Ia (2 g.) in dry benzene (50 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 3.8 g., and magnesium, 0.72 g.) and the reaction was carried out as described by Mustafa.[2] Recrystallization of the product from benzene gave 0.5 g. of IIIa as colorless needles, m.p. 220–221°.

Anal. Calcd. for $C_{22}H_{12}$ O N_2: C, 81.0; H, 5.52; N, 8.58. Found: C, 81.52; H, 5.55; N, 8.48. The product gave an orange color with concd. sulfuric acid.

Action of naphthylmagnesium bromide on Ia. A solution of Ia (2 g.) in dry benzene (50 ml.) was added to an ethereal solution of naphthylmagnesium bromide [from α-bromonaphthalene (5 g.) and magnesium (0.72 g.)] and the reaction mixture was completed as usual. Recrystallization of the product (IIIb) from benzene gave 0.5 g. as colorless needles, m.p. 218–219°.

Anal. Calcd. for $C_{26}H_{20}$ ON_2: C, 82.9; H, 5.32; N, 7.47. Found: C, 82.39; H, 5.37; N, 6.88. The product gave a pink color with concd. sulfuric acid.

Preparation of 2-phenyl-4-(p-methoxybenzylidene)-2-imidazolin-5-one (IB). Hippuric acid (9 g.) and fused sodium acetate (4.9 g.) were mixed with acetic anhydride (5.3 g.) and anisaldehyde (13.7 g.). The reaction mixture was heated on a water bath for 30 min. It was then filtered, washed with hot water, and finally with a little alcohol.

The above product (40 g.) was mixed with water (100 ml.), alcohol (200 ml.), and concd. ammonia (20 g.). The mixture was refluxed until all the solid was completely soluble. Concentrated ammonia (20 ml.) and potassium carbonate (20 g.) were then added and heating was continued for 1 hr. more, during which time some more ammonia was added. A yellow crystalline product (Ib) was obtained, filtered, and washed with hot water, alcohol, and finally with hot benzene. It was then recrystallized from acetic acid as yellow needles m.p. 285–286°, yield 30 g. Erlenmeyer and Wittenberg[7] reported a melting point of 283°.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 72.82; H, 5.14; N, 10.02.

Action of phenylmagnesium bromide on 2-phenyl(p-methoxybenzylidene)-2-imidazolin-5-one. (IB). A solution of Ib (2 g.) in dry benzene (50 ml.) was added to an ethereal solution of phenylmagnesium bromide [from bromobenzene (3.4 g.) and magnesium (0.72 g.)] and the reaction was completed as usual. Recrystallization from benzene gave 0.5 g. of IIIc as colorless needles; m.p. 203–204°.

Anal. Calcd. for $C_{23}H_{20}O_2N_2$: N, 7.86; Found: N, 7.40. The product gave a yellow color with concd. sulfuric acid.

Action of naphthylmagnesium bromide on Ib. A solution of Ib (2 g.) in dry benzene (50 ml.) was added to an ethereal solution of naphthylmagnesium bromide [from α-bromonaphthalene (5 g.) and magnesium (0.72 g.)] and the reaction was completed as usual. Recrystallization of the product from benzene gave 0.5 g. of IIId as colorless needles, m.p. 239–240°.

Anal. Calcd. for $C_{27}H_{22}O_2N_2$: N, 6.36. Found: N, 6.44. The product gave a permanganate color with concd. sulfuric acid.

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