As mentioned earlier, IV is enolic in nature and we were interested to see if it could be converted into its keto form, an observation made earlier by Bhave in the case of similar compounds.[13] When IV was therefore subjected to the action of concentrated sulfuric acid, an isomeric high melting substance (VIII) was obtained. Unlike IV, VIII did not give any coloration with ferric chloride, but, like IV, it gave the keto acid VII by treatment with alkali and the lactone V by treatment with hydrochloric acid. From these observations and by analogy with previous work,[3,13] the high melting compound VIII can be considered as the keto form of the enolic compound IV. The reverse change, namely, the conversion of the keto VIII to the enol IV has not been observed.

## EXPERIMENTAL[14]

*3-(2-Methoxy-4-methylphenyl)glutaconylacetic acid* (IV). This acid was prepared following the general procedure of Bhave.[3] To an intimate mixture of 11.5 g. (0.05 mole) of β-(2-methoxy-4-methylphenyl)glutaconic anhydride (III) and an equal quantity of powdered fused sodium acetate, 15 ml. of acetic anhydride was added. The mixture was heated on a steam bath for about 10 min. The resulting hot red solution was poured with stirring into 200 ml. water, filtered, and to the clear filtrate, 20 ml. of concd. hydrochloric acid was added. The precipitated solid was collected, washed with several portions of water and the dry solid was crystallized from acetic acid to give 9.5 g. (67% yield) of IV as gray crystals, m.p. 138–139°. A pure sample was obtained by two recrystallizations from alcohol, m.p. 142–142.5°.

*Anal.* Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.11; neut. equiv., 274.0. Found: C, 65.37; H, 4.82; neut. equiv., 271.7.

*3-(2-Methoxy-4-methylphenyl)-5-keto-3-hexenoic acid* (VII). A solution of 13.7 g. (0.05 mole) of IV in 250 ml. of 1*N* sodium hydroxide was kept at room temperature for 12 hr. and then heated on a steam bath for 0.5 hr. to effect complete hydrolysis. After the alkaline solution had been washed with several portions of ether, it was carefully neutralized with dilute hydrochloric acid at ice-bath temperature. The precipitated gummy substance was taken up in ether and the ethereal extracts, after having been washed with several portions of water, were concentrated. The residual gum solidified upon trituration with acetic acid. Recrystallization of the solid from acetic acid gave 5.7 g. (46% yield) of VII as colorless crystals, m.p. 102–104° dec.

*Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45; neut. equiv., 248.0. Found: C, 67.90; H, 6.71; neut. equiv., 250.1.

A *semicarbazone* of VII was prepared in usual manner, m.p. 164–165.5°.

*Anal.* Calcd. for $C_{15}H_{19}N_3O_4$: neut. equiv., 305.0. Found: neut. equiv., 304.2.

A *phenylhydrazone* of VII was prepared by heating a solution of VII in glacial acetic acid with an equimolar quantity of phenylhydrazine on a steam bath for 15 min. The hydrazone was recrystallized from alcohol to give colorless plates, m.p. 182–183°.

*Anal.* Calcd. for $C_{20}H_{22}N_2O_3$: neut. equiv., 338.0. Found: neut. equiv., 340.0.

*3-(2-Methoxy-4-methylphenyl)-5-keto-3-hexenoic acid lactone* (V). *Method A.* A hard glass test tube containing 5 g. of IV was heated in an oil bath at 155–160° for 0.5 hr. After the evolution of carbon dioxide had subsided, the contents of the tube was thoroughly washed with 5% sodium bicarbonate solution. The solid residue was collected, washed with several portions of water, and after drying was recrystallized from alcohol to give 2.8 g. (68% yield) of V, m.p. 74–75°.

*Method B.* A mixture of 5 g. of IV and 10 ml. of concd. hydrochloric acid was heated at reflux temperature on a sand bath for 2 hr. The contents of the flask were poured into water and the solid was collected on a filter. It was washed with several portions of water, dilute sodium hydroxide solution and again with water. After drying, it was recrystallized from alcohol (60%) to give V in 53% yield, m.p. 74–75.5°. A mixed melting point of this sample with the one obtained by method A showed no depression.

*Method C.* A mixture of 5 g. of VII in 7.5 ml. of acetic anhydride was heated on a steam bath for 2 hr. The contents of the flask was poured into water with stirring and the resulting solid mass was processed as in method B, to give V in 58% yield, m.p. 73.5–74.5°.

*Anal.* Calcd. for $C_{14}H_{14}O_3$: C, 73.05; H, 6.09. Found: C, 73.21; H, 6.37.

*3-(2-Methoxy-4-methylphenyl)glutaconylacetic acid (keto form)* (VIII). A mixture of 10 g. of finely powdered enolic glutaconylacetic acid (IV) and 10 ml. of concd. sulfuric acid was heated cautiously at 80° for 2 min. The resulting red solution was filtered through a sintered glass funnel and the clear filtrate was slowly poured into 150 ml. of water. The gummy mass that separated was washed with several portions of water and then after drying, was triturated with acetic acid, affording a solid. It was recrystallized from acetic acid to give 6.2 g. (62% yield) of VIII, m.p. 218–220°.

*Anal.* Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.11; neut. equiv., 274.0. Found: C, 65.82; H, 5.18; neut. equiv., 275.2.

Laboratory of Chemistry
Ramnarain Ruia College
University of Bombay
Bombay, India

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[13] V. M. Bhave, M.S. thesis, University of Bombay, 1932.

[14] All melting points are uncorrected.

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# Bisarene-Chromium Compounds from Aryl Chlorides[1]

Richard W. Bush[2] and H. R. Snyder

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Bisarene-chromium compounds of benzene, toluene, *p*-xylene, mesitylene, hexamethylbenzene, tetralin, and biphenyl have been prepared by the action of anhydrous chromic chloride upon the appropriate aromatic hydrocarbon in the presence of anhydrous aluminum chloride and powdered aluminum, the so-called reducing Friedel-Crafts conditions.[3] Only by the alternative synthesis, from arylmagnesium bromides, have bisarene-chromium compounds been prepared that contain substituents other than alkyl and aryl on the aromatic rings. By carbonating the mixture from the reac-

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[1] Grateful acknowledgment is made of the partial support of this research by a grant from the National Science Foundation (G6223).

[2] National Science Foundation Fellow, 1956–1957. Phillips Petroleum Co. Fellow, 1957–1958.

[3] (a) E. O. Fischer and W. Hafner, *Z. anorg. u. allgem. Chem.*, **286**, 146 (1956); (b) E. O. Fischer and D. Seus, *Chem. Ber.*, **89**, 1809 (1956).

tion of phenylmagnesium bromide and anhydrous chromic chloride, Zeiss[4] isolated a biscarboxybenzene-chromium complex as the double salt $Ba^{++}(C_6H_5COO^-)_2Cr^+B(C_6H_5)_4^-$. Earlier, Hein[5] had studied the action of anhydrous chromic chloride upon *p*-bromophenylmagnesium bromide and upon *m*-chlorophenylmagnesium bromide. Although the chromium complexes obtained were difficult to isolate and purify, one substance[5a] that Hein isolated in relatively pure state conforms in its analysis to bis(*p,p'*-dibromobiphenyl)chromium(I) bromide. This formulation was not suggested by Hein, as the now accepted structure of the aromatic chromium compounds was not known at that time.

In the present study the applicability of the reducing Friedel-Crafts method to the preparation of bisarene-chromium complexes of aromatic chlorides was investigated. In general, the procedure of Fischer[3] was followed, but in agreement with recent reports,[6,7] relatively larger proportions of aluminum chloride improved the yields.

A bisarene-chromium complex was formed in 16% yield by the action of chromic chloride upon chlorobenzene, but the tetraphenylboron salt isolated contained no chlorine and was shown to be a bisbenzene-chromium complex. Dehalogenation of aromatic compounds occurs in the presence of anhydrous aluminum chloride.[8]

A bisarene-chromium complex was formed in 31-36% yield by the action of chromic chloride upon *p*-chlorobiphenyl. From treatment of the product with sodium tetraphenylboron, a salt A was isolated that had the correct composition for bis(*p*-chlorobiphenyl)chromium(I) tetraphenylboron. However, that some dechlorination occurred during the reaction was indicated by the isolation of several samples of tetraphenylboron salt containing less than the expected amount of chlorine. These samples as well as a sample of bisbiphenylchromium(I) tetraphenylboron exhibited infrared peaks at 760 cm.$^{-1}$, attributable to a monosubstituted benzene ring. The infrared spectrum of A possessed no peak at 760 cm.$^{-1}$, a fact which suggests that the molecules of A possess free chlorophenyl rings. The evidence presented requires only that A contain monochlorophenyl rings. The suggestion that A is a bis(*p*-chlorobiphenyl)chromium complex is based upon the assumption that there was a minimum of migration of the chlorine atoms. The bis(*p*-chlorobiphenyl)chromium(I) cation could be reduced to a chromium(O) compound, but this compound could not be isolated in pure state.

That the reducing Friedel-Crafts conditions are not applicable to the preparation of complexes in which the chromium atom is bonded to chlorine-containing rings is suggested by comparison of the results obtained with chlorobenzene and with *p*-chlorobiphenyl. To test this possibility further, *p,p'*-dichlorobiphenyl was treated with chromic chloride under the usual conditions. A chromium complex was produced in about half the yield obtained when *p*-chlorobiphenyl was used. The tetraphenylboron salt B was identical in its infrared spectrum with A. The analysis of B was consistent with its formulation as bis(*p*-chlorobiphenyl)chromium(I) tetraphenylboron. Extensive dechlorination would be necessary to allow the formation of a compound with this composition from *p,p'*-dichlorobiphenyl. The significance of the experiment is that none of the chromium complex contained more chlorine than the maximum allowed if the chromium is to be bonded only to nonchlorinated rings. This consideration suggests that the chromium atom in the bis(*p*-chlorobiphenyl)-chromium complex is bonded to the phenyl rather than to the chlorophenyl rings.

It is not known whether the dehalogenation occurs before or after the formation of the bisarene-chromium complexes. However, the process that appears best to correlate the results consists of the initial formation of a chromium complex with either chlorinated or nonchlorinated rings. If the chromium bonding weakens the aryl-chlorine bonds, then chlorine should be selectively lost from those rings bonded to the chromium atoms. Such a process would account for the observed formation of bisbenzenechromium from chlorobenzene, of bis(*p*-chlorobiphenyl)chromium from *p,p'*-dichlorobiphenyl, and of bis(*p*-chlorobiphenyl)chromium, along with dehalogenated derivatives, from *p*-chlorobiphenyl.

## EXPERIMENTAL[9,10]

*Bisbenzenechromium tetraphenylboron from chlorobenzene.* 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 2.3 ml. (23 mmoles) of chlorobenzene (Eastman white label, redistilled). The tube was evacuated, sealed, and shaken vigorously to mix the reagents. The tube was heated with rotation for 16 hr. at 150° in a small electric furnace. The mixture was hydrolyzed with 5 ml. of methanol and 20 ml. of ice water. Ammonium hydroxide was added, the mixture was heated to 70°, and the chromium and aluminum hydroxides were removed by filtration. The filtrate was treated with 5*N* sodium hydroxide and boiled until free of ammonia. The yellow solution, containing chromium(I)

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[4] H. H. Zeiss and W. Herwig, *J. Am. Chem. Soc.* **78,** 5959 (1956).

[5] (a) F. Hein and R. Späte, *Ber.,* **59,** 751 (1926); (b) F. Hein and W. Retter, *Ber.,* **71,** 1966 (1938).

[6] F. Hein and K. Eisfeld, *Z. anorg. u. allgem. Chem.,* **292,** 162 (1957).

[7] E. O. Fischer and H. P. Fritz, *Advances in Inorganic Chemistry and Radiochemistry,* **1,** 99 (1959).

[8] C. A. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry,* Reinhold Publishing Corp., New York, N. Y., 1941, pp. 610, 692-696.

[9] All melting points are corrected.

[10] Microanalyses by Mr. Josef Nemeth and his associates. Infrared spectra by Mr. Paul McMahon and Mrs. Mary Verkade.

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.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

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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.

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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

WILLIAM IBRAHIM AWAD AND ABD ELAZIZ ALI GAD ALLAH

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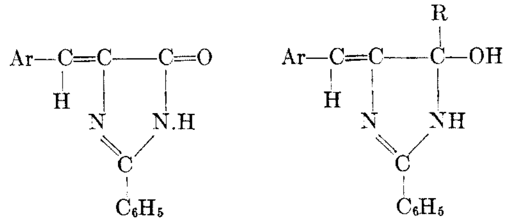
Mustafa and Harhash[2] claimed that methyl-, and phenylmagnesium halides react with 2-phenyl-4-benzylidene-2-imidazoline-5-one (Ia) to give colorless products believed to have structures IIa and IIb respectively. No proof was given for such structures.



I II

Ia. Ar = $C_6H_5$
Ib. Ar = $p\text{-}CH_3OC_6H_4$

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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[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).