

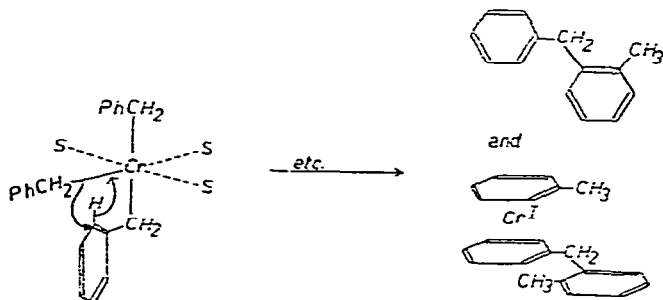
π -COMPLEXES OF THE TRANSITION METALSXVIII*. REACTION OF *p*-TOLYLMAGNESIUM BROMIDE WITH CHROMIUM(III) CHLORIDE TETRAHYDROFURANATE

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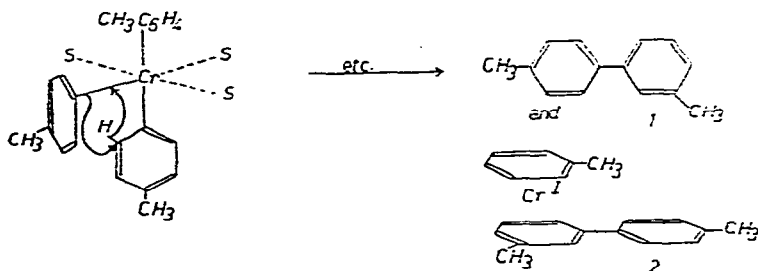
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It has recently been observed¹ that benzylmagnesium chloride undergoes reaction in diethyl ether with $\text{CrCl}_3(\text{THF})_3$ in the molecular ratio of three to one, to give, among other products, 2-benzyltoluene and π -(2-benzyltoluene)- π -toluene-chromium(I). The 2-benzyltoluene, both free and in the bis-arene π -complex, can only arise by the coupling of one "benzyl species" with the *ortho* position of a second accompanied by hydrogen transfer.



It is known² that phenylmagnesium bromide with $\text{CrCl}_3(\text{THF})_3$ in the molecular ratio of three to one in diethyl ether solution gives biphenyl and a mixture of π -bis-benzene- and π -benzene- π -biphenyl-chromium(I). However, in this case it is not possible to say whether the biphenyl, both free and in the bis-arene π -complex, arises



* For Part XVII, see ref. 1.

by "ortho-coupling" as above, or by "para-coupling" of two phenyl radicals within the confines of the organochromium compound.

To settle this point, the reaction of *p*-tolylmagnesium bromide and $\text{CrCl}_3(\text{THF})_3$, ratio 3:1, in diethyl ether, has been reinvestigated*. Thus, if the reaction proceeds by "ortho-coupling" the expected "dimeric product" is the unsymmetrical 3',4-dimethylbiphenyl, both free and in the bis-arene π -complex (1 and 2 respectively). Whereas, if the reaction involves "para-coupling" of two *p*-tolyl radicals within the confines of the organochromium compound, the anticipated "dimeric product" is the symmetrical *p,p'*-bitolyl, both free and in the bis-arene π -complex (3 and 4, respectively).



The products isolated from the reaction, *p*-tolylmagnesium bromide and $\text{CrCl}_2(\text{THF})_3$, ratio 3:1 in diethyl ether, after final hydrolysis were toluene and *p,p'*-bitolyl, identified by direct comparisons with authentic specimens and a mixture of bis-arene π -complexes, isolated as their tetraphenylboron salts. From the latter mixture it was possible to isolate π -bis-toluene-chromium(I) tetraphenylboron as orange crystals, m.p. 232° (dec.)**, identified by a direct comparison of its infra-red spectrum and X-ray powder photograph with those of an authentic specimen.

In a second experiment, the crude mixture of bis-arene π -complexes (isolated as their tetraphenylboron salts) was pyrolyzed, and the products were shown to consist of benzene and biphenyl (from the decomposition of tetraphenylboron ion), toluene and *p,p'*-bitolyl. The latter was identified by a direct comparison with an authentic specimen.

In order to ensure that the formation of the bis-arene π -complexes resulted from the "rearrangement" of tri-*p*-tolylchromium, the latter was prepared in tetrahydrofuran suspension, filtered, and "rearranged" in pure diethyl ether. This latter reaction was not rapid. After hydrolysis, the crude mixture of bis-arene π -complexes (isolated as their tetraphenylboron salts) was pyrolyzed, and the products were found to consist of benzene and biphenyl (from tetraphenylboron ion), toluene and *p,p'*-bitolyl.

It follows, therefore, that in the reaction of *p*-tolylmagnesium bromide and $\text{CrCl}_3(\text{THF})_3$, ratio 3:1 in diethyl ether, the formation of the "dimeric products", both free and in the bis-arene π -complex, is one of "para-coupling" of *p*-tolyl radicals within the confines of the organochromium compound. The same concept accounts for the formation of the bis-arene π -complexes in the "rearrangement" of tri-*p*-tolylchromium in diethyl ether.

Furthermore it is evident that the reactions of benzylchromium compounds differ markedly from those of arylchromium compounds, since in the former case the products (both organic and π -complexed) originate by "ortho-coupling" and hydrogen transfer. In the latter they originate by radical coupling, both reactions taking place within the confines of the organochromium complex.

* Hein³ has reported the action of *p*-tolylmagnesium bromide on CrCl_3 in diethyl ether without comment on the structure of the bis-arene π -complex.

** Seus⁴ described the preparation of this compound, but did not quote a melting point.

EXPERIMENTAL

All experiments were carried out under pure, dry nitrogen. The diethyl ether and tetrahydrofuran used were freshly distilled from lithium aluminum hydride. The concentrations of the organomagnesium halide solution were determined by acid-base titrations using a pH meter. The toluene was estimated by gas chromatography with *p*-xylene as internal standard, in an F & M Model 720 gas chromatography apparatus fitted with a silicone rubber column.

Chromium trichloride tris-tetrahydrofuranate

A filtered solution of commercial chromium trichloride hexahydrate (66 g, 0.25 moles) in commercial tetrahydrofuran (200 ml) was treated, over a period of 40 minutes with thionyl chloride (120 ml). During the addition the temperature of the reaction mixture rose rapidly, and the reaction was completed by heating under reflux for 1.5 h. The deep purple $\text{CrCl}_3(\text{THF})_3$, which crystallized overnight from the cool reaction mixture, was filtered under dry nitrogen and purified by boiling with pure, dry tetrahydrofuran (200 ml), cooling, and filtering under pure, dry nitrogen. The moist crystals were finally dried at 40° in high vacuum. The purple $\text{CrCl}_3(\text{THF})_3$ (70 g) obtained in this way, was shown to be identical with the compound prepared more indirectly⁵ by a comparison of the X-ray powder photographs.

p-Tolylmagnesium bromide and $\text{CrCl}_3(\text{THF})_3$, ratio 3:1 in diethyl ether

(a) *Analysis of Grignard solution.* An aliquot of the solution of *p*-tolylmagnesium bromide in diethyl ether (50 ml, 35 mmoles) was hydrolyzed at 0°, and the organic material which remained, after removal of the ether, was chromatographed to give *p,p'*-bitolyl (0.257 g, 1.4 mmoles), m.p. and mixed m.p. 121–122°, and unidentified oil (0.281 g).

(b) *Preliminary run* —78 to 20°. An ethereal solution of *p*-tolylmagnesium bromide (58 ml, 40.6 mmoles) was added to a briskly stirred suspension of $\text{CrCl}_3(\text{THF})_3$ (5 g, 13.3 mmoles) in ether (70 ml) at —78°. The color of the insoluble material changed rapidly from deep purple to light pink. After 1.5 h at —78°, (Gilman color test I, faintly positive) the reaction mixture was allowed to warm to 20°. The resulting dark solution and black solid were treated with water (80 ml) and the resulting mixture filtered, in the presence of air, the residue being washed with water and hot acetone until the filtrate was colorless.

Chromatography of the residue, obtained by evaporating the ether layer, gave *p,p'*-bitolyl (1.598 g, 8.8 mmoles) (blank content 0.307 g, 1.68 mmoles), m.p. and mixed m.p. 121–122°, and an unidentified oil (0.309 g). The acetone extract was concentrated by distillation under reduced pressure, and the residue combined with the aqueous phase. This clear solution was treated with excess sodium tetraphenylboron (5.5 g in 50 ml water) and the crude π -complex (0.8 g) crystallized from acetone to give yellow crystals, m.p. 222° (decomp.), recrystallized from acetone to give π -bis-toluene-chromium(I) tetraphenylboron, m.p. 232° (decomp.). The infra-red spectrum and X-ray powder photograph were superposable on those of an authentic specimen. It was obvious that there was another π -complex present in the mother liquors, but this was difficult to isolate since it decomposed on standing in acetone solution.

(c) *Analytical*, —78° to 20°. In a similar experiment with a total of (40.6 mmoles)

of *p*-tolyl Grignard, the ether layer, remaining after the extraction of the water soluble compounds, was shown to contain: toluene (17.78 mmoles), *p,p'*-bitolyl (1.52 g, 8.35 mmoles), m.p. and mixed m.p. 121–122°, and an unidentified oil (0.389 g); total toluene equivalent (34.48 mmoles). The aqueous together with the acetone solution yielded, after the usual treatment, a crude π -complex (A) (as its tetraphenylboron salt) (1.180 g), m.p. 220° (decomp.).

Pyrolysis of the π -complex (A)

The crude π -complex (A), isolated as its tetraphenylboron salt, from two of the above reactions in ether, was pyrolyzed in vacuum at 190°. All the volatile material was collected in a trap cooled in liquid nitrogen. When the pyrolysis was complete, all the material was assembled in the trap by distilling chloroform slowly through the apparatus. The total pyrolysate was shown by gas chromatography to consist of benzene, toluene, *p,p'*-bitolyl, and traces of biphenyl. Evaporation of the bulk solution and crystallization from ethanol gave *p,p'*-bitolyl, as white crystals, m.p. and mixed m.p. 121–122°.

p-Tolylmagnesium bromide and CrCl₃(THF)₃, ratio 3:1 in THF, at -78° to 20°

A solution of *p*-tolylmagnesium bromide (125 ml, 79.8 mmoles) in tetrahydrofuran was added to a briskly stirred suspension of CrCl₃(THF)₃ (10 g, 26.6 mmoles) in tetrahydrofuran at -78°. After 1 h at -78°, the Gilman color test I was negative, and the contents of the flask had set to a thick paste. The mixture was diluted with oxygen-free tetrahydrofuran (100 ml), warmed to room temperature and filtered under nitrogen. The deep red tri-*p*-tolylchromium so obtained was used directly in the next experiment.

Decomposition of tri-p-tolylchromium tetrahydrofuranate with diethyl ether

The tri-*p*-tolylchromium tetrahydrofuranate obtained above was covered with pure, dry, oxygen-free ether, and the whole stirred for six hours. During this time the color of the solid changed gradually to black. Finally the black precipitate and solution were hydrolyzed, and the yellow aqueous solution treated with aqueous sodium tetraphenylboron. The crude π -complexes (B) obtained in this way, (0.72 g), m.p. 220° (decomp.) had an infrared spectrum identical with that of (A) prepared above.

Pyrolysis of the π -complex (B)

The crude π -complex (B) was pyrolysed, and the products isolated as described under (A). The products, identified by gas chromatography, were: benzene, toluene, *p,p'*-bitolyl and traces of biphenyl. The *p,p'*-bitolyl was obtained by crystallizing from ethanol the residue from the total pyrolysate as white crystals, m.p. and mixed m.p. 122–123°.

1-p-Tolyl-4-methylcyclohexanol (cis and trans)

A solution of 4-methylcyclohexanone (5.6 g, 50 mmoles) in ether (20 ml) was added dropwise to a briskly stirred ethereal solution of *p*-tolylmagnesium bromide (100 ml, 70 mmoles). The reaction mixture was stirred and heated for an additional hour, prior to being hydrolyzed at 0° with a solution of ammonium chloride (100 ml

of 10 %). The organic material, isolated from the ether layer, was chromatographed to give: (i) *p,p'*-bitolyl (0.57 g), m.p. and mixed m.p. 121–122°, (ii) a 1-*p*-tolyl-4-methylcyclohexanol (4.8 g), m.p. 64–66°, (iii) a 1-*p*-tolyl-4-methylcyclohexanol (3.8 g), m.p. 66–67°, mixed m.p. with fraction (ii), m.p. 39–42°, (iv) an unidentified yellow oil (0.593 g).

p,p'-Bitolyl

One of the isomeric 1-*p*-tolyl-4-methylcyclohexanol, m.p. 64–66°, (0.5 g) in acetic anhydride (10 ml) was heated under reflux, for eight hours, with palladized charcoal (0.5 g, of 10 %). The cooled, filtered solution was poured into a large excess of water. The crude reaction product, isolated by filtration, crystallization and drying gave *p,p'*-bitolyl as white plates m.p. 122–123°.

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SUMMARY

The products formed by the action of *p*-tolylmagnesium bromide on $\text{CrCl}_3 \cdot (\text{THF})_3$, ratio 3:1 in diethyl ether, and in the rearrangement of tri-*p*-tolylchromium in diethyl ether suspension have been isolated and characterized. The significance of these results with respect to the mechanism of the rearrangement of σ -bonded organochromium compounds is discussed.

REFERENCES

- 1 F. GLOCKLING, R. P. A. SNEEDEN AND H. H. ZEISS, *J. Organometal. Chem.*, 2 (1964) 109.
- 2 H. H. ZEISS, *Organometallic Chemistry*, Am. Chem. Soc. Monograph No. 147, Reinhold Publ. Corp., New York, 1960, p. 380 *et seq.*
- 3 F. HEIN AND R. SPAETE, *Ber.*, 57 (1924) 899.
- 4 D. SEUS, Thesis, Technische Hochschule Munich, June (1956).
- 5 W. HERWIG AND H. H. ZEISS, *J. Org. Chem.*, 23 (1958) 1404.