The Mechanism of Toluene and Bibenzyl Formation from Benzylchromium Ion[1]

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The decomposition of benzylchromium(II) ion, $C_6H_5CH_2Cr(H_2O)_5^{+2}$, in aqueous ethanol solution to toluene has been studied. The protonolysis in the presence of acetate buffer in 35% ethanol–water solutions follows pseudo-first-order kinetics to greater than 95% reaction. From studies of the effect of pH, buffer, ionic strength, added ions, change in isotopic solvent, and substitution in the aromatic ring on the rate of protonolysis, it is concluded that the mechanism consists of a two-step process: a preequilibrium step in which benzylchromium ion associates with nucleophiles followed by a rate-determining protonolysis of the complex. The slow step involving proton transfer to the benzyl moiety is compared with mechanisms previously proposed for the acidolysis of organomercurials and areneboronic acids. The concept of nucleophilic assistance is extended. Bibenzyl is shown to arise during the course of the reaction between benzyl chloride and chromium(II) predominantly by oxidation of the intermediate benzylchromium ion by unreacted benzyl chloride. Ligand exchange between aralkylchromium ions and aralkyl halides occurs simultaneously with the coupling reaction. Mixed coupling between benzyl bromide (or chromium) and p-xylylchromium (or bromide) yields a mixture of toluene, p-xylene, bibenzyl, p-methylbibenzyl, and p,p'-dimethylbibenzyl. α,α-Dimethyl-β-phenethyl hydroperoxide is a source of the benzyl moiety and it reacts in place of benzyl bromide with aralkylchromium ion to afford bibenzyls in excellent yield. Common intermediates are suggested in the ligand exchange and coupling reactions involving aralkyl halides and dimethylphenethyl hydroperoxide, and a mechanism which includes aralkyl radicals and chromium(IV) ion as intermediates is favored.

Introduction

In the preceding paper[2] it was shown that benzylchromium ion (I, $C_6H_5CH_2Cr(H_2O)_5^{+2}$) which is formed in low yield during the reaction[3] between benzyl chloride and chromium(II) is the same as that synthesized quantitatively when benzyl bromide, benzyl iodide, α,α-dimethyl-β-phenethyl hydroperoxide, or bisphenylacetyl peroxide react with chromium(II). In the latter instances it was also shown that no significant amounts of toluene or bibenzyl accompanied the formation of benzylchromium ion. The formation of toluene and bibenzyl as ultimate products of the reaction between benzyl chloride and chromium(II) can be attributed to benzylchromium ion as an intermediate, and an allusion to this complex ion as a direct precursor to toluene and bibenzyl has been made.[3] The studies presented in the previous paper also support this hypothesis.

In this report we wish to establish that the formation of benzylchromium ion is, in fact, antecedent to both toluene and bibenzyl and to explore further the mechanism of the decomposition of benzylchromium ion and examine some of its chemical properties.

Experimental

Materials are the same as those used in the previous investigation.[2]

Chromous Perchlorate. Chromous perchlorate was prepared in solution by the method of Lux and Illman.[4] Electrolytic grade chromium metal chips (99.995% pure) were placed in a 500-ml., three-necked boiling flask equipped with a nitrogen bubbler and rubber serum caps containing 200 ml. of perchloric acid of the desired concentration which had been degassed for 1 hr. with a stream of nitrogen. No reaction occurred until a small piece of chromium metal, which had been freshly activated in concentrated hydrochloric acid and rinsed free of chloride ions with distilled water, had been added. Hydrogen evolution was vigorous and a considerable amount of heat was generated.

The concentration of chromous ion was determined by oxidation with ferric chloride solution and titration of the ferrous produced with cerium(IV) sulfate to the ferrous phenanthroline end point. For chromous solutions of concentrations between 1.5 and 2.0 *N* the following procedure was followed. Two milliliters of 2 *N* ferric chloride was placed in a 25-ml. erlenmeyer flask, capped with a serum cap, and degassed with pure nitrogen introduced with syringe needles. To this oxygen-free system, 1 ml. of chromous perchlorate was added with a hypodermic syringe. The resulting solution was diluted to 25 ml. in a volumetric flask and 5-ml. aliquots were taken for titration with standard cerium(IV) solution to the emerald green end point.

Preparation of Samples. All preparations of benzylchromium ion were carried out in a glove box in which an oxygen-free atmosphere could be maintained. Tank oxygen-free nitrogen was used initially to flush the box for about 10 hr. A solution of chromous chloride prepared from chromic chloride reduced with zinc dust in low open vessels to the sky blue color of chromous salt was placed in the drybox to act as an oxygen scavenger. The stability of these chromous solutions was taken as an indication of an anaerobic atmosphere. Under these conditions the chromous and benzylchromium solutions could be transferred *via* pipets without oxidation. No attempt was made to keep the atmosphere anhydrous.

Preparation of Benzylchromium Ion. A weighed amount of the organic starting material was placed in a

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[1] Part II. Reduction of Organic Halides with Chromium(II). Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[2] J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964).

[3] F. A. L. Anet and E. LeBlanc, *ibid.*, **79**, 2649 (1957).

[4] H. Lux and G. Illman, *Ber.*, **91**, 2143 (1958).

small erlenmeyer flask and put in the oxygen-free glove box. Oxygen-free aqueous ethanol solvent was added and the solution was treated with a quite stream of nitrogen. Chromous perchlorate was then added with a pipet, and the flasks were capped with rubber serum caps.

The ion-exchange column consisted of a 13 × 300 mm., water-jacketed column to which a dropping funnel was sealed. A 6-mm. side arm fitted with a rubber septum was located at the top of the column to enable the septum to be flushed with nitrogen and for sample introduction. An atmosphere of nitrogen was maintained over the eluent and in the receiver, and ice water circulated through the jacket. The column packed with Dowex-50 sulfonic acid resin (50–100 mesh) had a holdup volume of approximately 30 ml. Chilled (0°) deaerated solutions of perchloric acid (0.1, 1.0, and 5.0 *N*) were used for separations and regeneration of the resin. All spectral work was done on a Beckman DB (double beam) recording spectrophotometer equipped with a water-jacketed sample cell compartment connected to a large-capacity, constant-temperature bath. The sample cells used were 1 cm. square (3-ml. capacity) fused silica cells (range 210–800 mμ) with ground glass tops. The cells were capped with glass stoppers or in cases where oxygen-sensitive solutions were used a small rubber serum cap. Sample cells were degassed by bubbling nitrogen through the solvent for 5 min. using syringe needles. Samples were injected into the cell with a 50-μl. syringe.

All kinetic runs were conducted spectrophotometrically by following the absorption band of benzylchromium ion at 360 mμ.[2] Solutions of solvents were made up volumetrically. The pH of solutions of less than 35% ethanol–water (essentially aqueous) were made up with a standardized pH meter. In all cases, concentrations of acid, buffer, and salt far exceeded (by at least a factor of 100) the concentration of benzylchromium ($\sim 10^{-4}$ *M*). Under these conditions all reactions were essentially zero order in acidic and anionic reactants. The Powell plot[5] was employed to determine the kinetic order; the rate constants determined by plotting the logarithm of the absorbance at 360 mμ against time was linear to greater than 95% reaction.

Ethanol-*d* was prepared from sodium ethoxide and deuterium oxide (U. S. Nuclear Co., 99.5%). The former was prepared as a colorless crystalline solid from sodium and excess ethanol and dried at 100° for 24 hr. in a rotary evaporator. The ethanol-*d* of azeotropic composition was distilled from bulb to bulb *in vacuo* several times and distilled through a 20-plate Podbielniak column (b.p. 79.5°). The protium content was analyzed by examining its proton magnetic resonance spectrum after dilution in D_2O and employing the carbon–hydrogen absorption band of ethanol as an internal standard. Chromous perchlorate (0.8 *N*) in deuterium oxide was prepared from chromium metal in D_2O with perchloric acid.

Product Studies. Benzylchromium ion in solution is labile to molecular oxygen and in order to obtain reproducible results it was necessary to conduct all studies in a glove box from which oxygen had been rigorously purged as described previously. When oxygen contaminated the reaction, benzaldehyde was invariably in evidence. Reactions were run in erlenmeyer flasks filled in the drybox and fitted with rubber serum caps. All solvents were deoxygenated in the box. Products were isolated in large-scale runs and determined quantitatively by gas chromatography: (1-m. diethylene glycol succinate (DEGS) column at 150°) naphthalene (3 min.), benzyl alcohol (7 min.), bibenzyl (9.5 min.), γ-phenylbutyronitrile (13 min.), *p*-methylbibenzyl (13.6 min.), *m,m'*-dimethylbibenzyl (15.8 min.), and *p,p'*-dimethylbibenzyl (18.8 min.)[6]; (6-ft. silicon SF96 column at 115°) toluene (4.4 min.), *p*-xylene (5.7 min.), *t*-butylbenzene (11.8 min.), benzaldehyde (9.8 min.), and benzyl ethyl ether (15.1 min.).

Polarography. The polarograms were obtained with a Sargent Model XV recording polarograph using an H cell with a saturated calomel electrode at 25°. The drop time of the capillary was 3 sec. Solutions of 0.1 *N* lithium perchlorate used as supporting electrolyte were deoxygenated with a stream of pure nitrogen and the chromous or aralkylchromium solutions were introduced with an hypodermic syringe. The surface of the solution was swept gently with nitrogen during the measurements. The anodic wave of benzylchromium ion occurs very close to the anodic wave of chloride ion. Sufficient chloride ion is present in agar to obscure the benzylchromium wave. In this case the salt bridge was constructed with 0.5 *M* sodium sulfate and exposed repeatedly to fresh sodium sulfate solution in order to leach the chloride impurities. If the cell were rinsed and used quickly, the chloride problem was largely obviated. Both the cathodic and anodic waves appear reversible; however, to establish their reversibility chronopotentiometric studies are under investigation.

Results

Protonolysis of Benzylchromium Ion to Toluene. Benzylchromium ion I prepared in solution from the several benzyl halides, dimethylphenethyl hydroperoxide, or phenylacetyl peroxide and chromous ion is accompanied by a corresponding equivalent of chromic species: halopentaaquochromium(III), $CrX(H_2O)_5^{+2}$, from benzyl halide; hydroxopentaaquochromium(III), $Cr(OH)(H_2O)_5^{+2}$, from the hydroperoxide; and phenylacetatopentaaquochromium(III), $C_6H_5CH_2CO_2Cr(H_2O)_5^{+2}$, from the diacyl peroxide. Their presence is required by the mode of its formation given in reactions 1, 2, and 3 followed by 4.[2-7] These chromic species can be

$$C_6H_5CH_2X + Cr(II) \longrightarrow C_6H_5CH_2\cdot + CrX^{+2} \qquad (1)$$

$$C_6H_5CH_2C(CH_3)_2O_2H + Cr(II) \longrightarrow C_6H_5CH_2\cdot + (CH_3)_2CO + CrOH^{+2} \qquad (2)$$

$$(C_6H_5CH_2CO_2)_2 + Cr(II) \longrightarrow C_6H_5CH_2\cdot + CO_2 + CrO_2CCH_2C_6H_5^{+2} \qquad (3)$$

$$C_6H_5CH_2\cdot + Cr(II) \xrightarrow{\text{fast}} C_6H_5CH_2Cr^{+2}{}_{aq} \qquad (4)$$

separated from benzylchromium ion by ion-exchange chromatography. Attempts to isolate the ion as a salt were unsuccessful. However, the solution of benzylchromium ion obtained in this way reacted in an

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(5) R. E. Powell, cited in "Kinetics and Mechanism," A. A. Frost and R. Pearson, Ed., 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 14.

(6) C. Moritz and R. Wolfenstein, *Ber.*, **32**, 2531 (1899).

(7) In this and the following discussion solvent molecules in the first coordination sphere of chromium(II) and -(III) will not be shown; in these species chromium most likely shows a coordination number of six.

Table I. Products from the Decomposition of Benzylchromium Perchlorate[a]

Starting material	EtOH solvent, %	Temp., °C.	pH[b]	Toluene, %	Bibenzyl,[c] %	Material balance, %
Benzyl bromide	100	28	...[d]	94	3	97
Benzyl bromide	100	50	...[d]	91	2	93
Benzyl bromide	80	50	5.6	80	3	83
Benzyl bromide	80	28	0.9	85	4	89
Benzyl bromide[e]	70	28	0.9	91	2	93
Dimethylphenethyl hydroperoxide	100	50	...[d]	92	6	98
Dimethylphenethyl hydroperoxide	80	50	5.6	86	3	89
p-Methylbenzyl bromide	100	28	...[d]	88[f]	1[g]	89

[a] In approximately 0.1 *M* solution. [b] Apparent pH, measured with pH meter. [c] One mole equal to 2 equiv. [d] Natural pH was approximately 3. [e] Followed by an ion exchange. [f] *p*-Xylene. [g] *p,p'*-Dimethylbibenzyl.

indistinguishable manner from that obtained before separation of the chromic contaminants. This is especially true of the kinetics experiments since they were conducted in such dilute solutions $(<10^{-3}\ M)$ that any contribution from second-order reactions with the chromic species would be unimportant. Since 1 *M* perchloric acid is required for the ion exchange separation of benzylchromium ion, even after neutralization the ionic strength would be such to complicate quantitative interpretation of the kinetics. For these reasons kinetic experiments were carried out with solutions of benzylchromium ion derived directly for the reaction of chromous perchlorate with benzyl bromide or dimethylphenethyl hydroperoxide.

Benzylchromium ion I can be made quantitatively from benzyl bromide and iodide or α,α-dimethylphenethyl hydroperoxide. If these reactions were conducted at relatively low temperatures (0–25°) in neutral solutions, the competing decomposition of the complex ion can be completely eliminated and no toluene or bibenzyl complicated studies of its decomposition. Homogeneous solutions of benzylchromium perchlorate prepared in this manner were dark yellow-brown and stable in the absence of oxygen for periods of months at −10°. The high yields of benzylchromium ion obtained by this procedure is in sharp contrast to studies at higher temperatures[8] or with benzyl chloride. The maximum concentration of benzylchromium ion obtainable from the less reactive benzyl chloride did not exceed 35–40% due to its further reaction to form toluene and bibenzyl. Under these circumstances, benzylchromium ion is a reactive intermediate and its concentration reached a maximum during the course of the reaction.[1]

Attempts were also made to generate the benzylchromium species from benzylmagnesium chloride and chromic chloride in tetrahydrofuran (eq. 5). On addition of a stoichiometric equivalent of benzyl Grignard solution prepared in THF to the dark magenta

$$C_6H_5CH_2MgCl + CrCl_3 \longrightarrow C_6H_5CH_2CrCl_2 + MgCl_2 \qquad (5)$$

solution of chromic chloride in the same solvent[9] at 0°, the reaction turned dark yellow-brown and remained homogenous. This solution on standing at room temperature turned green much as the aqueous solution of benzylchromium ion prepared previously. It yielded mostly toluene and some bibenzyl. The yellow-brown color of the THF solution is characteristic of benzylchromium ion in aqueous solution. However, the visible absorption spectrum of this solution, highly diluted in water, was similar but not identical with benzylchromium ion. On the other hand the spectrum of benzylchromium ion prepared from benzyl bromide and chromous perchlorate, highly diluted in THF, was the same as that obtained by the Grignard reaction. The nature of the solvent coordination sphere surrounding the benzylchromium ion is seemingly responsible for this change. After these studies were initiated, a report by Glockling, Sneeden, and Zeiss[10] appeared, and we have postponed further work.

As shown in Table I, toluene is the principal product from the decomposition of benzylchromium ion in aqueous ethanol solutions.[11] The exiguous amounts of bibenzyl formed are due to extraneous reactions derived from the reactant since bibenzyl was also present as a minor product of decomposition of benzylchromium ion obtained from the ion-exchange column free of chromous and chromic salts and other possible organic adulterants.

The kinetics of decomposition of benzylchromium ion I was examined spectrophotometrically in aqueous ethanol solution at 28° by following the disappearance of the absorption band at 360 mμ.[2] The rate of disappearance of benzylchromium ion $(2 \times 10^{-4}\ M)$ in 80% ethanol–water at an apparent pH of less than 2.5 is half order to greater than 90% reaction, and it varied with acid strength (perchloric acid). For example, in 0.1 *M* perchloric acid, the time for half-disappearance was 38 min. and at 2 *M* perchloric acid it was 1.2 min. However, the apparent half-order kinetics was not followed at higher pH values in the presence of only perchloric acid and it also varied with the composition of the solvent, being faster in 90 vol. % ethanol–water than in 70 vol. % by several-fold. Though the decomposition of benzylchromium ion is accelerated by perchloric acid, the complex kinetics could not be unscrambled.

If the reaction in 35 vol. % ethanol–water is buffered, however, the disappearance of benzylchromium ion

(8) L. H. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964).

(9) W. Herwig and H. H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

(10) F. Glockling, R. Sneeden, and H. H. Zeiss, *J. Organometal. Chem.*, **2**, 109 (1964).

(11) Toluene is also the predominant product when benzylchromium ion was decomposed in water. However, due to the insolubility of toluene in this medium, the reaction became heterogeneous and yields were difficult to determine quantitatively. Under these conditions it is unlikely toluene is formed by a homolytic process.

followed clean first-order kinetics to greater than 95% reaction. The pseudo-first-order rate constant was invariant over a tenfold range of concentration. In an acetate–acetic acid buffer, maintained at constant ionic strength with lithium chloride, the pseudo-first-order rate constant varied linearly with pH as given in Table II. The slope of this line, −0.70, indicated that the pseudo-first-order rate constant contained an approximately first-order term in hydrogen ion. In these largely but not completely aqueous solutions of ethanol (to maintain homogeneity due to toluene formation) the apparent pH measured with a pH meter calibrated in water was taken to be an approximation to the value in water.[12]

Table II. Effect of pH on the Decomposition of Benzylchromium Ion in Acetate–Acetic Acid Buffers[a]

Acetic acid, *M*	pH[b]	k, sec.$^{-1c}$
1.27	2.64	$3.49 \pm 0.40 \times 10^{-2}$
0.55	3.00	$1.78 \pm 0.20 \times 10^{-2}$
0.18	3.50	$1.01 \pm 0.02 \times 10^{-2}$
0.06	4.00	$3.99 \pm 0.11 \times 10^{-3}$

[a] In 35 vol. % ethanol–water solutions containing 0.010 *M* lithium acetate, 0.090 *M* lithium chloride, and 2.4×10^{-4} *M* benzylchromium perchlorate at 28.3°. [b] Apparent pH measured with a pH meter. [c] Average of at least two runs, $k/2.3 = k_1$.

The pseudo-first-order rate constant was only slightly affected by changes in ionic strength. In Table III, decomposition in a solution of constant acetic acid–lithium acetate buffer (0.010 *M*) in the presence of varying amounts of lithium chloride shows decreasing rate constants with increasing salt concentrations.

At a constant pH 3.5 and ionic strength of 0.10 the pseudo-first-order rate constant was also proportional to the concentration of the buffer. The rate constant increased with increasing acetate ion concentration as given in Table III.

Table III. Effect of Ionic Strength and Buffer Concentration on the Decomposition of Benzylchromium Ion, at pH 3.5[a]

Lithium acetate, *M*	Lithium chloride, *M*	Ionic strength	First-order rate constant, sec.$^{-1}$
0.010	0.020	0.03	$1.34 \pm 0.03 \times 10^{-2}$
0.010	0.050	0.06	$1.15 \pm 0.02 \times 10^{-2}$
0.010	0.070	0.08	$1.10 \pm 0.02 \times 10^{-2}$
0.010	0.090	0.10	$1.01 \pm 0.02 \times 10^{-2}$
0.0080	0.092	0.10	$6.04 \pm 0.44 \times 10^{-3}$
0.0050	0.095	0.10	$4.03 \pm 0.30 \times 10^{-3}$
0.0050	0.14	0.14	$2.88 \pm 0.05 \times 10^{-3}$

[a] In 35 vol. % ethanol–water at 28.3° containing 2.4×10^{-4} *M* benzylchromium perchlorate and 0.18 *M* acetic acid, $k_1 = k/2.3$.

Under similar conditions, a chloroacetate–chloroacetic acid buffer was approximately 100-fold less effective than an acetate–acetic acid buffer. The reaction in the former buffer was also first order in benzylchromium to greater than 95% decomposition. The pseudo-first-order rate constant was much less dependent on the chloroacetate concentration when sodium iodide was used to maintain constant ionic strength (Table IV). Furthermore, bromide, chloride, and perchlorate at equivalent concentrations at pH 3.5 were as effective, within 10%, as iodide in the decomposition of benzylchromium ion. However, thiocyanate was approximately three to four times more effective than the halides in chloroacetate buffers, and the decomposition of benzylchromium ion in the presence of this anion also closely followed first-order kinetics to greater than 95% reaction. Unlike the other anions examined, the decomposition of benzylchromium ion in the presence of azide ion was exceedingly rapid, being half complete within 2 min. compared to approximately 60 min. for thiocyanate ion and to approximately 150 min. for the other salts. Moreover, the rate was second order in benzylchromium ion, and the pseudo-second-order rate constant (93.5 l./mole sec. at 28.3°) was invariant over a threefold variation in the concentration of benzylchromium ion. The usual second-order plot was linear to approximately 70% reaction. The increase in rate beyond this region indicated that a reaction of lower order was becoming significant.

Table IV. Decomposition of Benzylchromium Perchlorate in Chloroacetate–Chloroacetic Acid Buffer[a]

Sodium chloroacetate, *M*	Added salt, *M*	First-order rate constant, 10^5 sec.$^{-1}$
0.0100	NaI, 0.090	6.36 ± 0.3
0.0100	NaI, 0.090	2.20 ± 0.3[b]
0.0082	NaI, 0.092	5.81 ± 0.2
0.0060	NaI, 0.094	5.52 ± 0.5
0.010	LiBr, 0.090	6.85 ± 0.15
0.010	LiCl, 0.090	7.05 ± 0.55
0.010	$LiClO_4$, 0.090	6.55 ± 0.5
0.010	NaSCN, 0.090	19.7 ± 2.0
0.010	NaN_3, 0.090	9.35×10 l./mole sec.[c]

[a] In 35 vol. % ethanol–water at 28.3° containing 2.4×10^{-4} *M* benzylchromium perchlorate and 0.10 *M* chloroacetic acid, at pH 3.5 and $\mu = 0.10$. [b] At 33°. [c] Second-order rate constant, $k_1 = k/2.3$.

In separate and equivalent experiments the absorption spectrum of benzylchromium ion in buffered solutions containing various added salts was scanned in the region 400–220 mμ. No gross alteration in the spectrum was apparent except for a time-dependent change in the absorbance at 360, 299, and 274 mμ (benzylchromium absorption). We were, therefore, assured that the spectral method of analysis was associated with the benzylchromium ion. Salts examined were lithium chloride, bromide, and perchlorate; potassium iodide and thiocyanate; and sodium sulfate, thiosulfate, bisulfite, azide, and cyanide. Cyanide, thiosulfate, bisulfite, and sulfite wrought more than the usual changes in the spectra, and were exceedingly rapid in their reaction with benzylchromium ion.

The effect of substitution on the aromatic ring of the benzylchromium ions was also examined. Several aralkylchromium ions listed in Table V were prepared from the aralkyl bromides and chromium(II) and decomposed in 40 vol. % ethanol–water solutions of acetate buffer at pH 3.5. All of these complex ions de-

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(12) B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559, 565 (1953).

Table V. Decomposition of Substituted Benzylchromium Ions[a]

Substituent	First-order rate constant, sec.$^{-1}$
None[b]	1.01×10^{-2}
m-Methyl	5.40×10^{-3}
p-Bromo	4.59×10^{-3}
p-Methyl	4.18×10^{-3}
m-Bromo	3.45×10^{-3}
m-Chloro	2.68×10^{-3}
o-Methyl	2.45×10^{-3}

[a] In 40 vol. % ethanol-water containing approximately 10^{-4} *M* aralkylchromium perchlorate, 0.18 *M* acetic acid, 0.010 *M* lithium acetate, and 0.12 *M* lithium chloride, at 28°. [b] In 35 vol. % ethanol–water, containing 0.09 *M* lithium chloride, otherwise the same as others, $k_1 = k/2.3$.

Table VI. Temperature and Solvent Isotope Effect on the Decomposition of Benzylchromium Perchlorate[a]

Temp., °K.	Ionic strength	Lithium acetate, *M*	First-order rate constant, sec.$^{-1}$
300.2	0.10	0.010	$1.01 \pm 0.02 \times 10^{-2}$
306.2	0.10	0.010	$1.85 \pm 0.07 \times 10^{-2}$
310.8	0.10	0.010	$2.76 \pm 0.13 \times 10^{-2}$
318.1	0.10	0.010	$4.51 \pm 0.10 + 10^{-2}$
299.8	0.11	0.0081	5.25×10^{-3}
299.7[b]	0.11	0.0081	$1.18 \pm 0.02 \times 10^{-3}$
310.0	0.11	0.0081	1.27×10^{-2}
309.1[b]	0.11	0.0081	$3.04 \pm 0.01 \times 10^{-3}$

[a] In 35 vol. % ethanol–water containing 2.4×10^{-4} *M* benzylchromium perchlorate and 0.18 *M* acetic acid. [b] In ethanol-water 80% deuterated, $d_8 = k/2.3$.

Table VII. Decomposition of Mixed Aralkyl Systems[a]

Reactants			Products,[b] %					
						Composition[c]		
$PhCH_2Br$, mg.	*p*-CH_3-$C_6H_4CH_2Br$, meguiv.	$Cr(ClO_4)_2$, meguiv.	$PhCH_3$	$(CH_3)_2C_6H_4$	Total bibenzyls	$(PhCH_2)_2$	$PhCH_2CH_2$-$C_6H_4CH_3$	$(CH_3C_6H_4CH_2)_2$
0.975	1.31	4.60	82	88	5	1	8	91
0.925	0.845	3.54	80	89	4	9	27	64
$PhCH_2Cr^{+2}$	*p*-$CH_3C_6H_4$-CH_2Cr^{+2}							
1.12	1.05		83	89	3	9	32	59
1.30	1.12		81	90	5	10	37	53

[a] In 95% ethanol containing *ca.* 0.1 *M* reactants at 27°. [b] Yields based on aralkyl moiety. [c] Molar composition of bibenzyl fraction.

composed cleanly with pseudo-first-order kinetics to greater than 95% reaction.

It is apparent from these results that substituents do not affect the decomposition of benzylchromium ion in a manner characteristic of a Hammett correlation. Thus, it cannot be determined by studying substitution in the aromatic ring alone, whether the aralkyl moiety during hydrolysis is exhibiting anionic, cationic, or free-radical behavior.

The rate of decomposition of benzylchromium ion I in buffered acetate (0.010 *M* solution at pH 3.5 and ionic strength of 0.10) was determined over an 18° temperature range. The results[13] shown in Table VI yielded, by the standard technique, a value for the apparent enthalpy of activation ΔH^* of 16.2 kcal./mole and an apparent entropy of activation ΔS^* of -13.9 cal./deg. mole.

The decomposition of benzylchromium I was also examined in acetate (0.0081 *M*) buffer at pH 3.5 and ionic strength of 0.11 at 26.8 and 36.0°. The same reaction in an equivalent solution of ethanol-*d* and deuterium oxide which was 80% deuterated was approximately four times slower as shown in Table VI.

The Formation of Bibenzyl. In homogeneous solutions, the reaction of benzyl chloride and chromous ion carried to completion yielded a mixture of toluene and bibenzyl, although benzyl bromide and iodide yielded mainly toluene if the reactions were conducted in the presence of a slight excess of chromous ion. However, in the latter cases if the reaction was made slightly heterogeneous by operating in aqueous solutions containing less ethanol (<60 vol. %) so that the benzyl halide was not completely soluble (though undetectable visually), bibenzyl was a significant product. These were essentially the conditions in which benzylchromium ion is in the presence of excess benzyl halide. Slaugh and Raley[8] observed equivalent results in other media and under different experimental conditions and their studies can be interpreted on this basis.

If 1 equiv. of benzyl bromide was added to a solution of benzylchromium ion in 80–95 vol. % ethanol-water at room temperature the yellow-brown solution was converted to the green chromic solution at a rate estimated visually to be several times faster than the ordinary hydrolysis of benzylchromium ion (*vide supra*). The products of the reactions were toluene (30–40%) and bibenzyl (60–70%).[14] The reaction of benzylchromium ion with benzyl chloride was several times slower than benzyl bromide and qualitatively proceeded as rapidly as the decomposition of benzylchromium ion alone. Less bibenzyl (20–30%) and more toluene (70–80%) were found under these circumstances.

Due to the simultaneous formation of toluene and bibenzyl, kinetic studies were not conducted on the reaction of benzylchromium ion and benzyl halide. Qualitatively, however, it was apparent that the decomposition of benzylchromium ion was accelerated by benzyl bromide and iodide, and much less so by benzyl chloride (eq. 6). Moreover, the formation of bibenzyl is mainly associated with the reaction of benzylchromium with benzyl halide.

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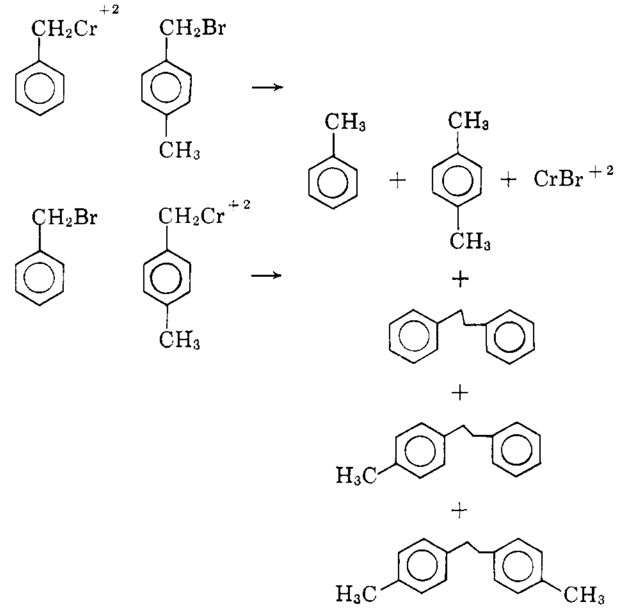
[13] In these experiments it was assumed that the extinction coefficient of I was temperature invariant. The limitation of this assumption has been pointed out: H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5015 (1957).

[14] In the symmetrical reactions, yields are based on the concentration of benzylchromium plus benzyl bromide.

$$C_6H_5CH_2Cr^{+2} + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2CH_2C_6H_5 + CrBr^{+2} \quad (6)$$

p-Xylyl bromide was treated with chromous perchlorate in 95% ethanol to afford *p*-xylene in 90% yield and 1% *p,p'*-dimethylbibenzyl. An equimolar mixture of benzyl bromide and *p*-xylyl bromide under similar conditions yielded 80–82% toluene, 89% *p*-xylene, and small amounts (~5%) of various bibenzyls. The same results were obtained if the aralkylchromium ions prepared separately were decomposed together. The composition of the mixture of minor amounts of bibenzyls formed in these reactions are listed in Table VII.

The bibenzyl fraction was substantially increased if 1 equiv. of *p*-xylyl bromide was added to a solution of benzylchromium ion. In addition to toluene and bibenzyl, large amounts of *p*-xylene, *p*-methylbibenzyl, and *p,p'*-dimethylbibenzyl were also formed. Similar, though not identical, results were obtained if benzyl bromide and *p*-xylylchromium ion were mixed. The results from a number of duplicate runs are summarized in Table VIII. The yields of products were highly reproducible if reactants were present in stoichiometrically equal amounts in the concentration range 0.08 to 0.15 *M*.



In these reactions the aralkylchromium reactant can be generally accounted for quantitatively as toluenes and bibenzyls. The material balance obtainable for the aralkyl bromide was not as good since some of it underwent competitive sovolysis in the aqueous ethanol solution. The composition of the bibenzyl fraction in these mixed coupling reactions was highly reproducible and represented a sensitive measure of the stoichiometric amounts of benzylchromium salt and *p*-xylyl bromide employed. At equimolar concentrations of each reactant, the composition of the bibenzyl mixture was bibenzyl (32%), *p*-methylbibenzyl (45%), and *p,p'*-dimethylbibenzyl (23%). The same reaction in the presence of a slight excess (8%) of *p*-xylyl bromide yielded a mixture of composition: bibenzyl (21%), *p*-methylbibenzyl (49%), and *p,p'*-dimethylbibenzyl (30%).

These experiments indicate that there is extensive though incomplete exchange between benzyl halide and benzylchromium ion, since the reaction of benzyl bromide and *p*-xylylchromium ion gave similar but not identical results as the reaction of *p*-xylyl bromide and benzylchromium ion (eq. 7).

$$C_6H_5CH_2Cr^{+2} + p\text{-}CH_3C_6H_4CH_2Br \rightleftarrows C_6H_5CH_2Br + p\text{-}CH_3C_6H_4CH_2Cr^{+2} \quad (7)$$

Benzylchromium ion reacted with α,α-dimethyl-β-phenethyl hydroperoxide readily at 0° in 95% ethanol (eq. 8). This reaction was at least an order of magnitude faster than the reaction with benzyl bromide and was estimated visually to be complete (color change from yellow-brown to green) in 1 hr. at this temperature. The products were acetone, toluene (7%), and bibenzyl (85%). This reaction, thus, is similar to the coupling reaction with benzyl bromide. Similar intermediates are apparently involved in both reactions since extensive exchange of ligands occurred between the aralkyl moiety of the organochromium ion and the hydroperoxide. Thus, 1 equiv. of *p*-xylylchromium ion reacted rapidly with dimethylphenethyl hydroperoxide at 0° to yield toluene (8%), *p*-xylene (7%), bibenzyl (43%), *p*-methylbibenzyl (39%), and *p,p'*-dimethylbibenzyl (39%). The molar composition of the bibenzyl fraction, bibenzyl (27%), *p*-methylbibenzyl (49%), and *p,p'*-dimethylbibenzyl (24%), is close to a statistical value and was unchanged if the reaction was conducted at 25°.

$$C_6H_5CH_2Cr^{+2} + C_6H_5CH_2C(CH_3)_2O_2H \longrightarrow (C_6H_5CH_2)_2 + (CH_3)_2CO + Cr(OH)^{+2} \quad (8)$$

Polarography of Benzylchromium Ion. Cathodic and anodic polarography of benzylchromium was investigated in aqueous solution. Lithium perchlorate was used as supporting electrolyte and gelatin as the maximum suppressor. The half-wave potentials are given in Table IX. The value for the simple aquochromium ions agrees with values obtained in the presence of lithium chloride as electrolyte.[15]

Oxidation of Benzylchromium Ion. Benzylchromium is a moderately strong reducing agent as evidenced by its polarographic oxidation potential and facile reaction with dimethylphenethyl hydroperoxide. In addition it reacted with a variety of mild metal salt oxidants as shown in Table X.

The ceric titer of the solution of benzylchromium remained unchanged after reaction with ferric and cupric salts, which indicated that ferrous and cuprous species were being formed quantitatively. A reaction scheme (*vide infra*) compatible with these results can be written[16]

$$C_6H_5CH_2Cr^{+2} + FeCl_3 \longrightarrow C_6H_5CH_2\cdot + CrCl^{+2} + FeCl_2$$
$$C_6H_5CH_2\cdot + FeCl_3 \longrightarrow C_6H_5CH_2Cl + FeCl_2$$

and

$$C_6H_5CH_2Cr^{+2} + Fe(III) \longrightarrow C_6H_5CH_2\cdot + Cr(III) + Fe(II)$$
$$C_6H_5CH_2\cdot + Fe(III) \xrightarrow[CH_3OH]{} C_6H_5CH_2OCH_3 + Fe(II)$$

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(15) J. J. Lingane and R. L. Pecsok, *J. Am. Chem. Soc.*, **71**, 425 (1949); **72**, 189 (1950).

(16) (a) These reactions can also be written as proceeding *via* a metastable Cr(IV) species, such as $C_6H_5CH_2Cr^{+3}$ and $C_6H_5CH_2CrCl^{+2}$, which are expected to be substitution labile. (b) *Cf.* A. E. Ogard and H. Taube, *J. Phys. Chem.*, **62**, 357 (1958). *Vide infra.*

Table VIII. Mixed Reactions of Aralkylchromium Ion with Aralkyl Bromide[a]

Reactants (material balance, %)[b] $C_6H_5CH_2Cr^{+2}$	$YC_6H_4CH_2Br$	Products, %[c] $C_6H_5CH_3$	$YC_6H_4CH_3$	$(C_6H_5CH_2)_2$	$C_6H_5CH_2$-$CH_2C_6H_4Y$	$(YC_6H_4CH_2)_2$
98	*p*-CH_3 73	20	9	46 (32)	32 (45)	32 (23)
99	*o*-CH_3 76	21	5	43 (29)	35 (48)	34 (23)
98	*p*-Br 50	19	7	61 (50)	17 (28)	26 (22)
99	*m*-Cl 64	19	10	67 (50)	16 (23)	38 (27)
94[d]	H 76	18	15[e]	38 (28)	20 (29)	59 (43)[f]

[a] In 95 vol. % ethanol containing 0.1 *M* of each reactant at 25°; average of several experiments. [b] Letter indicates substituent; number following is material balance of the reactant accounted for. [c] Number in parenthesis is molar composition in bibenzyl fraction. Yields based on 1:1 stoichiometry except for symmetrical bibenzyls (2:1). [d] *p*-Xylylchromium ion. [e] *p*-Xylene. [f] *p,p'*-Dimethylbibenzyl.

Table IX. Polarography of Chromium Salts[a]

	$E_{1/2}$[b]
Cathodic wave	
$Cr(III)_{aq} + e \rightarrow Cr(II)_{aq}$	−0.84
$Cr(III)_{aq} + 3e \rightarrow Cr(O)$	−1.54
$Cr(II)_{aq} + 2e \rightarrow Cr(O)$	−1.46
$C_6H_5CH_2Cr_{aq}^{+2} + ne \rightarrow Cr(O)$	−1.53[c,d]
Anodic wave	
$Cr(II)_{aq} \rightarrow Cr(III)_{aq} + e$	−0.24
$C_6H_5CH_2Cr_{aq}^{+2} \rightarrow Cr(III)_{aq}$	+0.18[d]

[a] In aqueous solution at 25°, lithium perchlorate, 0.1 *N*. [b] *vs.* saturated calomel electrode. [c] One-electron wave not detected. [d] Half-cell equation uncertain.

Table X. Oxidation of Benzylchromium Ion[a]

Oxidant	Solvent[b]	Product, %[c] $C_6H_5CH_2X$	Bibenzyl	Benzaldehyde
$FeCl_3$	CH_3OH-H_2O	Cl (87)	0	0
$CuCl_2$	CH_3OH-H_2O	Cl (91)	0	0
LiCl (HCl)	CH_3OH-H_2O	Cl (10) H (85)	..	..
$Fe(ClO_4)_3$	$C_2H_5OH-H_2O$	EtO (67) HO (5)	0	0
$CuSO_4$	CH_3OH-H_2O	MeO (75) HO (9)	0	0
$CuSO_4$	$C_2H_5OH-H_2O$	EtO (60) HO (7)	3	0
$Cu(NO_3)_2$	$C_2H_5OH-H_2O$	EtO (55) HO (11)	0	10
AgO_2CCF_3	$C_2H_5OH-H_2O$	EtO (39) HO (8)	3	0
$Hg(ClO_4)_2$	$C_2H_5OH-H_2O$	EtO (39) HO (7)	0	0
$KFe(CN)_6$	$C_2H_5OH-H_2O$	HO (5)	0	0
$Fe(NO_3)_3$	$C_2H_5OH-H_2O$	HO (11) EtO (3)	0	0
$Co(NO_3)_2$	$C_2H_5OH-H_2O$	HO (5) EtO (4)	29	0
$KMnO_4$	$C_2H_5OH-H_2O$	HO (8) EtO (6)	0	38

[a] At ambient temperature. [b] CH_3OH-H_2O ~50 vol. %, $C_2H_5OH-H_2O$ ~80 vol. %. [c] Only products sought, inorganic salts not examined.

Discussion

Results show that benzylchromium ion I, $C_6H_5CH_2Cr(H_2O)_5{}^{+2}$, originally detected[3] in the reaction of benzyl chloride and chromium(II) is the direct precursor to toluene and bibenzyl. Though benzylchromium can be obtained in only low yields from this reaction, it can be prepared[2] from chromium(II) quantitatively by reaction with the more reactive benzyl bromide and iodide or from α,α-dimethylphenethyl hydroperoxide.

Isolation of benzylchromium ion in solution in this manner and examination of its mode of decomposition have shown that it yields toluene (Table I) and bibenzyl largely by two independent routes. The decomposition of benzylchromium ion in protic media to toluene is largely uncomplicated by the simultaneous formation of bibenzyl. In the subsequent discussion the sequence of reactions involved in the formation of toluene and bibenzyl will be treated separately.

Protonolysis of Benzylchromium Ion. Qualitatively, perchloric acid catalyzes the protonolysis of benzylchromium ion I to toluene in aqueous ethanol solutions. In the region 0.1 *M* to 1 *M* perchloric acid, the kinetics of benzylchromium (10^{-4} *M*) decomposition are complex and as yet unresolved. However, in the presence of 0.01 *M* acetate or chloroacetate buffer the disappearance of the complex ion follows strict first-order kinetics to greater than 95% decomposition. The logarithm of the pseudo-first-order rate constant decreases linearly with pH in the range 2.4 to 4, and contains an approximately first-order hydrogen ion term (Table II). The rate exhibits a slightly negative general salt effect, but increases linearly with acetate ion concentration (Table III).

Acetate ion is approximately 100 times more effective than chloroacetate, chloride, bromide, or iodide at the same pH. These salts have only a slightly greater catalytic constant than perchlorate, while thiocyanate ion is approximately three times more effective (Table IV). The protonolysis of benzylchromium ion shows characteristics of a reaction which is general base and general acid catalyzed and dependent on specific anion effects. Of the several mechanisms which are consistent with these facts, we propose[17] that the solvolysis of benzylchromium ion occurs in two steps: a preequilibrium reaction (eq. 9) involving benzylchromium ion with nucleophilic species (X), followed by a rate-determining protonolysis (eq. 10) of the coordinated

$$C_6H_5CH_2Cr^{+2} + X^- \rightleftharpoons C_6H_5CH_2CrX^+ \qquad (9)$$

II

$$C_6H_5CH_2CrX^+ + H^+ \longrightarrow C_6H_5CH_3 + CrX^{-2} \qquad (10)$$

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[17] Acid catalysis was also observed by Anet and LeBlanc who found that only toluene was formed (but, see Table X) when benzyl chloride was reduced by Cr(II) in hydrochloric acid. However, they attributed the effect to chloride ion which facilitated the formation of the more readily reducible benzylchlorochromium ion. Since neither

$$C_6H_5CH_2CrCl^+_{aq} + Cr(II)_{aq} \longrightarrow C_6H_5CH_2Cr^+_{aq} + CrCl^{+2}_{aq}$$

$$C_6H_5CH_2Cr^+_{aq} \longrightarrow C_6H_5CH_2^- + Cr(II)_{aq} \longrightarrow C_6H_5CH_3$$

chloride nor chromous ion are necessary for toluene formation from I, we prefer the alternative scheme.

intermediate II. The equilibrium constant does not appear to be related to the usual nucleophilic reactivity of anions toward carbon substrates measured by Swain's constant.[18] A better correlation is found with the spectrochemical series,[19] which is a qualitative measure of the effect ligands have on the ligand field splitting of d-orbitals of the metal ion.

The rate of protonolysis of benzylchromium ion is subject to a sizable deuterium isotope effect of solvent (Table VI). The lack of a significant perturbation on the rate by substituents in the aromatic nucleus (Table V) indicates that anionic character is poorly if at all developed on the benzylic moiety in the transition state of the solvolysis. It is suggested that the formation of the new carbon–hydrogen bond slightly precedes the breaking of the old carbon–chromium bond so that at no time is there a substantial buildup of negative charge on the carbon center. The transition state of the rate-determining protonolysis of benzylchromium ion is probably closely akin to that of the acid cleavage of alkylmercuric iodides.[20] A transition state in which the carbon, chromium, and hydrogen atoms define a triangle is probably characteristic of electrophilic substitutions. They have been discussed by Kreevoy[21] and Lewis.[22]

The over-all activation parameters for the solvolysis of benzylchromium ion is similar to those obtained by Kreevoy and co-workers for the acid cleavage of mercurials, and is characterized by a reasonably large negative entropy of activation. Thus, for benzylchromium ion $\Delta H^* = 16.2$ kcal./mole and $\Delta S^* = -13.9$ cal./deg. mole (*vide infra*). These compare with values obtained for methylmercuric iodide[20] $\Delta H^* = 22.2$ kcal./mole, and $\Delta S^* = -23$ cal./deg. mole; isopropylmercuric iodide[23] $\Delta H^* = 25.0$ kcal./mole and $\Delta S^* = -21 \pm 6$ cal./deg. mole; and vinylmercuric iodide[21] $\Delta H^* = 22.2$ kcal./mole and $\Delta S^* = -29$ cal./deg. mole. In the latter cases a solvent isotope effect was also observed.

The acidolysis of areneboronic acids examined by Kuivila and Nahabedian[24] is a further example of an electrophilic substitution involving a rate-determining proton transfer. Protonation in these cases is on a trigonal carbon atom associated with a conjugated system and there is a wide variation in rate of cleavage as a result of substitution in the aromatic ring. The rate is also correlated by the Hammett equation. The activation parameters show characteristic negative values for the entropy of activation (in the range -18 to -23 e.u.) and activation enthalpies in the region 18–23 kcal./moles, the magnitudes of which depend on the acid strength and arene.

The activation parameters obtained for the protonolysis of benzylchromium ion are composite values since they include the enthalpy and entropy change in the preequilibrium step (eq. 9). Though these values are not known, they can be crudely estimated from related studies of simple chromic equilibria in aqueous solution. King and co-workers[25] have obtained values for the enthalpy and entropy change of reactions 11 and 12 as 6.6 and 5 kcal./mole and +17 and +7.5

$$\mathrm{Cr(H_2O)_6^{+3} + Cl^- \rightleftharpoons CrCl(H_2O)_5^{+2} + H_2O} \qquad (11)$$

$$\mathrm{CrCl(H_2O)_5^{+2} + Cl^- \rightleftharpoons CrCl_2(H_2O)_4^{+} + H_2O} \qquad (12)$$

e.u., respectively. If the enthalpy and entropy changes in the preequilibrium reaction are taken into account, the enthalpy and entropy of activation for the rate-determining proton transfer step 10 should be corrected to a value of approximately 21 kcal./mole and -20 e.u./mole, respectively.

The inclusion of a preequilibrium step which precedes the rate-determining proton transfer is attractive for several reasons. It accounts for the general base (nucleophilic) catalysis especially by acetate and thiocyanate[26] ion, the relative unselectivity among iodide, bromide, chloride, and perchlorate, and the negative general salt effect. The solvent, water or alcohol, may itself serve as a nucleophile ($X = H_2O$, C_2H_5OH, etc.) in the equilibrium step. With such weakly activating salts as the halides and perchlorate such may be the case. In the absence of buffer, perchloric acid may also be behaving in this manner since the solvolysis is much faster in 95% ethanol solution than it is at lower alcohol concentrations. Baltisberger and King[27] in an elegant study of the formation of aquochlorochromic ion from aquochromic ion in aqueous methanol came to the conclusion that methanol is more readily removed from the inner solvation sphere of chromium(III) than water and such reactions are faster than the analogous reactions of fully hydrated species.

The coordinated benzylchromium intermediate II, $C_6H_5CH_2CrX^+$, is undoubtedly more readily protonated than the doubly charged benzylchromium ion due to decreased electrostatic repulsion between the cationic chromium species and the proton in the transition state. In addition, the separation of the benzyl moiety from chromium should be facilitated by the nucleophile X, which would help to diminish the electron deficiency of the metal atom by coordination. This effect has been termed nucleophilic assistance by Dessy and Paulik[28] and used to postulate a five-coordinate intermediate in the acetolysis of tributyltin hydride. Catalysis by nucleophiles has also been observed in the cleavage of organomercurials.[28a] Their studies were directed specifically toward aprotic media in which anions are poorly solvated. However, nucleophilic assistance can be important even in aqueous solution if sufficient driving force is provided by a high local charge density on the metal ion, as it is in benzylchromium ion. Solvation of anions is presumably a less significant factor with benzylchromium due to its increased susceptibility to nucleophilic assistance than the less highly charged organomercurials and tin compounds.

The pseudo-second-order dependence of the rate on the benzylchromium concentration in the presence of

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(18) C. G. Swain, *et al.*, *J. Am. Chem. Soc.*, **75**, 141, 4627 (1953); **77**, 3727, 3731, 3737 (1955).

(19) M. C. Day and J. Selbin, "Theoretical Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1962, p. 323.

(20) M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 5927 (1957).

(21) M. M. Kreevoy and R. A. Kretchmer, *ibid.*, **86**, 2435 (1964).

(22) E. S. Lewis and R. H. Grinstein, *ibid.*, **84**, 1158 (1962).

(23) M. M. Kreevoy and R. L. Hansen, *ibid.*, **83**, 626 (1961).

(24) H. G. Kuivila and K. V. Nahabedian, *ibid.*, **83**, 2159, 2164, 2167 (1961).

(25) K. Schug and E. L. King, *ibid.*, **80**, 1089 (1958); H. S. Gates and E. L. King, *ibid.*, **80**, 5011 (1958).

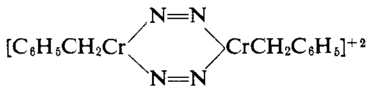
(26) J. T. Houghen, K. Schug, and E. L. King, *ibid.*, **79**, 519 (1957); E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952).

(27) R. J. Baltisberger and E. L. King, *ibid.*, **86**, 795 (1964).

(28) (a) R. E. Dessy and F. E. Paulik, *ibid.*, **85**, 1812 (1963); (b) R. E. Dessey, T. Hieber, and F. Paulik, *ibid.*, **86**, 28 (1964).

excess azide ion is unusual among the ions examined. It is possible that the species undergoing protonolysis is a dimeric azidochromium complex such as III. A doubly bridged chromium dimer as a structure has

$$2C_6H_5CH_2Cr^{+2} + 2N_3^- \rightleftarrows$$


(13)

III

been postulated[29] for the transition state in the exchange between chromium(II) and *cis*-diazidotetraaquochromium(III) ion. The observed rapid rate of the reactions necessitates the postulation of sizable concentrations of a dimeric species if such were responsible for the pseudo-second-order kinetics.[29b]

Formation of Bibenzyl from Benzylchromium Ion. It has been shown that bibenzyl arises from benzylchromium ion I by a route quite independent of the toluene formation. Though small amounts of bibenzyl accompany toluene when benzylchromium is decomposed protolytically, the amount is not significant relative to the total bibenzyl formed during the reaction of benzyl chloride with chromium(II). The absence of bibenzyl when either benzyl bromide or iodide is reduced with at least a stoichiometric amount of chromium(II) and the formation in large yields of bibenzyl from benzylchromium ion and benzyl bromide is taken as evidence that bibenzyl arises by reaction 14.

$$ArCH_2Cr^{+2} + Ar'CH_2Br \longrightarrow ArCH_2CH_2Ar' + CrBr^{+2} \quad (14)$$

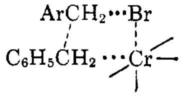
A mixture of benzyl bromide and *p*-xylyl bromide reacts with chromium(II) in a manner largely indistinguishable from a mixture of benzylchromium and *p*-xylylchromium ion (Table VII). In both cases each component behaves quite independently of the other, including the formation in low yields of a mixture of the three possible bibenzyls bibenzyl, *p*-methylbibenzyl, and *p,p'*-dimethylbibenzyl. These are formed in much higher yields from the direct reaction of aralkylchromium ion with aralkyl bromide (Table VIII). The unsymmetrical coupling of benzylchromium ion with *p*-xylyl bromide is similar but not equivalent to a coupling of *p*-xylylchromium with benzyl bromide. In both cases the substantial amounts of toluene, xylene and bibenzyl, *p*-methylbibenzyl, and *p,p'*-dimethylbibenzyl which are formed account satisfactorily for the material balance. Extensive scrambling of the aralkyl moieties from the organochromium compound and bromide is abundantly evident in the bibenzyl portion. The formation of *p*-xylene from benzylchromium and *p*-xylyl bromide and toluene from *p*-xylylchromium and benzyl bromide in almost equivalent amounts is further evidence that a ligand exchange (reaction 15) between aralkylchromium and bromide has occurred during the reaction. Similar results are obtained with other aralkyl moieties. Though extensively reversible,[30] reaction 15 does not appear to attain equilibrium during

$$ArCH_2Cr^{+2} + Ar'CH_2Br \rightleftarrows ArCH_2Br + Ar'CH_2Cr^{+2} \quad (15)$$

the reaction under our experimental conditions. The large extent of the two kinds of reactions leads us to postulate that the exchange reactions occur simultaneously with the coupling reaction and that similar intermediates are involved in both reactions.

An analogous mixed coupling product, 4-phenylbutene-1, was observed by Slaugh and Raley[8] when allyl bromide and benzyl bromide were simultaneously reduced or when benzylchromium reacted with allyl bromide. In the latter case, no bibenzyl or biallyl was detected, and an exchange such as 15 does not seem likely with this dissimilar pair of halides.

Any mechanism for the coupling reaction must be consistent with an important observation made by Neumer and Khan,[31] who found that optically active α-phenethyl chloride gave a *threo*-2,3-diphenylethane fraction which was optically active. It is possible that the coupling reaction 14 proceeds in one step *via* a four-centered transition such as IV. A related transition state will accommodate the exchange reaction 15.



IV

Alternatively, it is possible that benzyl radicals are formed by an oxidation–reduction reaction (eq. 16) involving halogen atom transfer from benzyl halide to benzylchromium ion. Such a reaction is similar to the slow step (eq. 1) in the formation of I.

$$\underset{\text{I}}{C_6H_5CH_2Cr^{+2}} + ArCH_2Br \longrightarrow \underset{\text{IV}}{C_6H_5CH_2CrBr^{+2}} + ArCH_2\cdot \quad (16)$$

$$ArCH_2\cdot + C_6H_5CH_2CrBr^{+2}(C_6H_5CH_2Cr^{+2}) \rightleftarrows ArCH_2CrBr^{+2}(ArCH_2Cr^{+2}) + C_6H_5CH_2\cdot \quad (17)$$

$$ArCH_2\cdot + C_6H_5CH_2CrBr^{+2}(C_6H_5CH_2Cr^{+2}) \longrightarrow ArCH_2CH_2C_6H_5 + CrBr^{+2}(Cr^{+2}) \quad (18)$$

A reaction sequence such as 16–18[32] would account for the simultaneous exchange of aralkyl moieties (eq. 15)[30] and coupling reactions (eq. 14) which lead to scrambling in the bibenzyl fractions. The relatively large amounts of toluenes which accompany the bibenzyls during the facile reaction of aralkylchromium ions with aralkyl halides in neutral ethanol solution is slightly greater than that expected for merely by protonolysis of the aralkylchromium ions. Some of the toluene fractions may arise from the homolytic reaction of the aralkyl radical with solvent, and some of it may be derived from the metastable intermediate

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(29) (a) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962). (b) In aqueous solution at pH 4, Cr(III) exists mainly as hydroxo and oxo complexes in the presence of azide ions: M. Ardon, *J. Inorg. Nucl. Chem.*, **20**, 173 (1961). However, the acid dissociation constant of hydrazoic acid in ethanol–water is unknown. Whether an analogous situation exists with I under our conditions, and the dimer is an oxygen-bridged species formed as an artifact of pH, is under investigation.

(30) It is possible that aralkylchromium ion I alone is not responsible for the exchange as given in eq. 15, but it may also involve the intermediate IV as suggested by eq. 17. Such an intermediate with chromium in a formal oxidation state of four would have a labile aralkyl moiety and be susceptible to ligand exchange[16b] as well as dissociation. If such were the case, the exchange reaction $C_6H_5CH_2CrBr^{+2} \rightleftarrows C_6H_5CH_2\cdot + CrBr^{+2}$ would be induced or accelerated by benzyl halide or equivalent species which are required to generate a species such as IV (eq. 16 and 23).

(31) J. F. Neumer and S. Khan, private communication.

(32) This mechanism cannot, of course, provide for stereospecific reaction, since some (greater than 50%) of the coupled product must arise from racemized α-phenethyl radicals. Neumer's results that α-phenethyl chloride ($[\alpha]^{25}D$ $-48.5°$) is converted to *threo*-2,3-diphenylbutane ($[\alpha]D$ $+1.4°$) can only be accounted for by this mechanism, if the observed rotation in the product represents an extensively racemized material. Both mechanisms predict that the coupled product has one completely racemic center.

IV.[16b] Such intermediates as IV in which the chromium has a formal oxidation state of four have been discussed by Kopple.[33] Reactions 16–18 alone cannot account for the retention of optical activity found by Neumer and Khan. In addition a reaction such as 19 involving a direct homolytic displacement by aralkyl radical on the aralkyl halide may be involved.[34]

$$\mathrm{ArCH_2\cdot + ArCH_2Br \longrightarrow ArCH_2CH_2Ar + Br\cdot} \qquad (19)$$

$$\mathrm{Br\cdot + C_6H_5CH_2Cr \longrightarrow \underset{IV}{C_6H_5CH_2CrBr^{+2}}\ etc.} \qquad (20)$$

An important feature of the coupling reaction 14 is the functioning of the aralkylchromium ion as a reducing agent. Polarographic studies indeed show that it is a reducing agent, albeit significantly weaker than chromous ion. However, its ready reaction with hydroperoxides, such as α,α-dimethyl-β-phenethyl hydroperoxide at 0°, is characteristic of reducing metal ions which react by a process involving one-electron change to generate benzyl radicals (eq. 21).[35] Excellent

$$\mathrm{C_6H_5CH_2C(CH_3)_2O_2H + M^{+n} \longrightarrow C_6H_5CH_2\cdot + (CH_3)_2CO + MOH^{+n}} \qquad (21)$$

yields of bibenzyl are obtainable from benzylchromium and dimethylphenethyl hydroperoxide. A product composition is derived from *p*-xylylchromium ion and dimethylphenethyl hydroperoxide which is quite analogous to that obtained from *p*-xylylchromium ion and benzyl bromide. In the former case, the molar distribution of the bibenzyls indicates that the coupling of aralkyl groups is occurring in a more or less random manner. The striking similarity between the reactions of halides and hydroperoxides suggests that similar intermediates are also involved in both reactions, and a reaction sequence consistent with that of the halides can be postulated for the hydroperoxide.

$$\mathrm{ArCH_2Cr^{+2} + C_6H_5CH_2C(CH_3)_2O_2H \longrightarrow ArCH_2CrOH^{+2} + (CH_3)_2CO + C_6H_5CH_2\cdot} \qquad (22)$$

$$\mathrm{C_6H_5CH_2\cdot + ArCH_2CrOH^{+2} \rightleftharpoons C_6H_5CH_2CrOH^{+2} + ArCH_2\cdot} \qquad (23)$$

$$\mathrm{C_6H_5CH_2\cdot + ArCH_2CrOH^{+2} \longrightarrow C_6H_5CH_2CH_2Ar + CrOH^{+2}} \qquad (24)$$

An alternative reaction sequence (22–24) is one involving a one-step reaction between aralkyl-chromium and the hydroperoxide and involving a transition state analogous to IV but involving six centers. However, we disfavor such a reaction, and would expect that if optically active hydroperoxides are employed there would be no retention of activity in the coupled product.

The exchange of the aralkyl ligand from chromium is also demonstrated by the rapid exchange of benzylchromium with pentacyanocobalt(II) ion to form pentacyanobenzylcobalt, etc. (eq. 25). The latter complex cobalt ion has been prepared by Halpern and Maher[36] by ligand exchange with benzyl bromide.

$$\mathrm{C_6H_5CH_2Cr^{+2} + Co(CN)_5^{-3} \longrightarrow C_6H_5CH_2Co(CN)_5^{-3} + Cr(II)\ ?} \qquad (25)$$

$$\mathrm{2Co(CN)_5^{-3} + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2Co(CN)_5^{-3} + BrCo(CN)_5^{-3}} \qquad (26)$$

Anet and LeBlanc[3] have reported a facile ligand exchange accompanied (or followed) by oxidation.

$$\mathrm{C_6H_5CH_2Cr^{+2} + Hg^{II}Cl_2 \longrightarrow C_6H_5CH_2HgCl + Cr(III) + Cl^-} \qquad (27)$$

The small but significant amounts of bibenzyl which are formed from the decomposition of benzylchromium ion in the absence of any halide may arise from the slower reversible dissociation (eq. 28)[37] of benzylchromium ion. We do not feel that such a dissociation plays a significant role in the coupling process, although an earlier report[3] can be interpreted as indicating that bibenzyl is an important product of decomposition of benzylchromium perchlorate in protic media. Halpern

$$\mathrm{C_6H_5CH_2Cr^{+2} \rightleftharpoons C_6H_5CH_2\cdot + Cr(II)} \qquad (28)$$

$$\mathrm{C_6H_5CH_2\cdot + C_6H_5CH_2Cr^{+2} \longrightarrow C_6H_5CH_2CH_2C_6H_5 + Cr(II)} \qquad (29)$$

and Maher have obtained bibenzyl in indeterminate yield from the thermal decomposition of pentacyanobenzylcobaltate salt in the solid state.

The coupling of aralkyl halides by chromium(II) to yield bibenzyls is similar to the reaction induced by biscyclopentadienylvanadium(II), CP$_2$V. Meijer and co-workers[38] have postulated biscyclopentadienylbenzylvanadium as an intermediate in this reaction.

$$\mathrm{(C_6H_5)_2V + C_6H_5CH_2Cl \longrightarrow (C_5H_5)_2VCl + {}^1/_2C_6H_5CH_2CH_2C_6H_5} \qquad (30)$$

It reacts with benzyl chloride to form bibenzyl in a manner similar to benzylchromium ion.

$$\mathrm{C_6H_5CH_2V(C_5H_5)_2 + C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2CH_2C_6H_5 + (C_5H_5)_2VCl} \qquad (31)$$

The formation of bibenzyl from benzylchromium ion and benzyl halide is highly reminiscent of reactions between Grignard reagents and transition salts examined by Kharasch and co-workers.[39] Recently Parker and Noller[40] have postulated the simultaneous participation of homolytic and heterolytic processes in the analogous copper-catalyzed exchange of Grignard reagents and alkyl halides. All of these reactions may indeed proceed through related intermediates and such studies are under investigation.

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(33) K. D. Kopple, *J. Am. Chem. Soc.*, **84**, 1586 (1962); *cf.* also T. B. Joyner and W. K. Wilmarth, *ibid.*, **83**, 516 (1961); M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959). See also F. Westheimer, *Chem., Rev.*, **45**, 419 (1949); *J. Am. Chem. Soc.*, **74**, 4383 (1952), and related papers.

(34) We are presently investigating such homolytic displacement reactions (SH$_2$); *cf.* W. A. Pryor and H. Guard, *ibid.*, **86**, 1150 (1964); D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

(35) J. K. Kochi, *ibid.*, **84**, 1193 (1962).

(36) J. Halpern and J. P. Maher, *ibid.*, **86**, 2311 (1964).

(37) There is other evidence that reaction 4 is reversible as written in eq. 29. It is part of a more general phenomena (J. K. Kochi and F. F. Rust, *ibid.*, **83**, 2017 (1961)) and the addition of I to acrylonitrile can be interpreted in this manner.[1]

(38) H. J. de Liefde Meijer, M. J. Janssen, and G. J. M. van der Kerk, *Rec. trav. chim.*, **80**, 831 (1961).

(39) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954.

(40) V. D. Parker and C. R. Noller, *J, Am. Chem. Soc.*, **86**, 1112 (1964).