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REDUCTION OF ALCOHOLS AND ORGANIC HALIDES BY METAL SALTS

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Abstract—It has been demonstrated that halide ions are not essential for the reduction of triphenylcarbinol and diphenylcarbinol to hexaphenylethane and *sym*-tetraphenylethane, respectively, by vanadous and chromous salts. Benzyl and allyl halides are reduced by chromous salts to either the coupled products, bibenzyl and biallyl, or to toluene and propylene, respectively. Anhydrous solvents and the slow addition of the chromous salt to the organic halide solution favor the formation of coupled products relative to the monomeric products of further reduction. The ratio of bibenzyl to toluene is much larger from benzyl iodide and benzyl bromide than from benzyl chloride. The intermediate benzylchromium complex, probably $C_6H_5CH_2Cr(H_2O)_5^{2+}$, reacts with allyl bromide to form 4-phenyl-1-butene. Saturated aliphatic halides, such as isopropyl iodide, are reduced only to monomeric hydrocarbons by chromous salts. A mechanism is proposed for these reactions.

INTRODUCTION

DURING a rather extensive study of metal ion reductions of organic molecules,[1] Conant *et al.* discovered that coupled products were formed by reaction of polyarylcarbinols with vanadous, chromous or titanous chloride in acidic, aqueous-acetone media. Metal ion reductions of carbonium ions to free radicals were postulated for these reactions. The reduction of intermediate organic halides has been proposed recently as an alternate reaction path.[2]

The reduction of organic halides, *per se*, by chromous salts has received considerable attention, especially for synthetic purposes in steroid and alkaloid systems.[3] Chromous chloride reduces benzyl chloride in hydrochloric acid[4] and benzal chloride in ethanol[5] to toluene and stilbene, respectively. In the latter case, 1,2-diethoxy-1,2-diphenylethane and hydrobenzoin monoethyl ether also were formed. Allyl chloride

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[1a] J. B. Conant and A. W. Sloan, *J. Amer. Chem. Soc.* **45**, 2466 (1923);
[b] J. B. Conant, L. F. Small and B. S. Taylor, *Ibid.* **47**, 1959 (1925);
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[d] J. B. Conant and N. W. Bigelow, *Ibid.* **53**, 676 (1931).

[2] C. E. Castro, *J. Amer. Chem. Soc.* **83**, 3262 (1961).

[3a] P. L. Julian, W. Cole, A. Magnani and E. W. Meyer, *J. Amer. Chem. Soc.* **67**, 1728 (1945);
[b] G. Rosenkranz, St. Kaufmann, J. Pataki and C. Djerassi, *Ibid.* **72**, 1046 (1950);
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[e] B. Ellis and V. Petrow, *Ibid.* 3869 (1953);
[f] J. J. Beereboom and C. Djerassi, *J. Org. Chem.* **19**, 1196 (1954);
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[i] R. H. F. Manske and L. Marion, *J. Amer. Chem. Soc.* **69**, 2126 (1947);
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[4] F. A. L. Anet and L. Leblanc, *J. Amer. Chem. Soc.* **79**, 2649 (1957).

[5] J. F. Neumer and S. Aktipis, *Absts.*, *140th ACS Meeting* p. 9Q. Chicago, September (1961).

is reduced to propylene and diphenyl methyl bromide to 1,1,2,2-tetraphenylethane by chromous sulfate.[2] Chloroform, carbon tetrachloride and phenacyl chloride react with chromous perchlorate but the products have not been identified.[6] Recently Kochi and Davis have made a kinetic study of the reaction of benzyl chloride with chromous salts to form an intermediate benzylchromous complex.[7]

We have made a non-kinetic study of the metal ion (especially chromous) reduction of several carbinols and organic halides. The results obtained have permitted significant conclusions regarding the mechanism of the reaction and the factors which control the type of product formed.

RESULTS AND DISCUSSION

Reduction of alcohols and the effect of chloride ions. The reduction of triphenylcarbinol to hexaphenylethane by VCl_2, $CrCl_2$ or $TiCl_3$ in acidic (HCl)-acetone solutions was quantitatively complete within 10 minutes at room temperature. Ferrous chloride under similar conditions reacted more slowly, producing a 5% yield of the coupled product in 1 hr whereas Cu_2Br_2 was ineffective. The yields of hexaphenylethane were estimated from the amount of triphenylmethyl peroxide obtained upon subsequent air oxidation of the product.

Reduction of diphenylcarbinol to tetraphenylethane by VCl_2 and $CrCl_2$ also occurs at room temperature but usually in lower yields (31–89%).

Conant *et al.*[1b] suggested that the coupled products obtained from polyarylcarbinols resulted from the metal ion reduction of the corresponding carbonium ions to free radicals (Eqs 1 and 2).

$$Ar_3COH + H_3O^+ \rightarrow Ar_3C^+ + 2H_2O \qquad (1)$$

$$Ar_3C^+ + M^{2+} \rightarrow Ar_3C\cdot + M^{3+} \qquad (2)$$

However, since they used VCl_2, $CrCl_2$ and $TiCl_3$, their data do not exclude the possibility of *in situ* polyarylmethyl chloride formation and subsequent reaction. In this regard, Castro[2] found that in a perchloric–hydrochloric acid mixture, but not in perchloric acid alone, 1,1-diphenylethylene and diphenylmethylcarbinol are converted by $CrSO_4$ to 2,2,3,3-tetraphenylbutane, the coupled product expected from the free radical, $(C_6H_5)_2\dot{C}CH_3$. Consequently, he generalized that polyarylmethyl cations are not reduced by Cr^{++} at an appreciable rate and that halide ions play an essential role in these transformations. Castro favored a reaction path proceeding *via* the direct reduction of the intermediate 1,1-diphenylethyl chloride to the radical which subsequently couples (Eq. 3).

$$R^+ + Cl^- \longrightarrow RCl \xrightarrow{Cr^{2+}} CrCl^{2+} + R\cdot \longrightarrow \tfrac{1}{2}R_2 \qquad (3)$$

We have found that halide ions are not essential in all cases since, in their absence, VSO_4 (dilute H_2SO_4–acetone medium) and $Cr(ClO_4)_2$ (dilute $HClO_4$–acetone medium) reduce triphenylcarbinol to hexaphenylethane in good yields (>75%). Furthermore, VSO_4, $CrSO_4$ and $Cr(ClO_4)_2$ readily convert diphenylcarbinol to *sym*-tetraphenyl ethane in 30–40% yields.

Nevertheless, as was clearly demonstrated by Castro, halide ions are beneficial.

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[6] F. A. L. Anet, *Canad. J. Chem.* 37, 58 (1959).

[7] J. K. Kochi and D. Davis, *Absts.*, 145*th ACS Meeting* p. 24Q. New York, September (1963).

For example, benzyl alcohol is not reduced to bibenzyl and toluene by $CrSO_4$ in H_2SO_4 media unless sodium chloride is added. In this last experiment, benzyl chloride was present in the product.

Reduction of benzyl halides. In aqueous or aqueous–dioxane solutions, benzyl chloride is reduced to toluene and bibenzyl by chromous and vanadous salts. Titanous chloride under the same experimental conditions was much less effective.

TABLE 1. CHROMOUS SALT REDUCTION OF BENZYL CHLORIDE (RX); 80–100°

Expt no.	RX, mmoles	Metal salt, mmoles	Solvent, ml	Procedure time, hrs	Product, % Yield[c]	
					Bibenzyl	Toluene
1	200	$CrSO_4$,[d] 44 (75 ml)	Dioxane, 100 Water, 50	C[a] 1·2	12·4	82
2	200	$CrSO_4$,[d] 44 (75 ml)	Dioxane, 100 Water, 50	C[a] 3·8	44·8	42·6
3	200	$Cr(ClO_4)_2$,[d] 38 (86 ml)	Dioxane, 100 Water, 50	C[a] 3·0	39·6	14·9
4	60 In 50 ml dioxane	$Cr(ClO_4)_2$,[d] 100 (227 ml)	Dioxane, 100	B[b] 2	1·8	77
5	100	$CrCl_2$,[e] 50	Dioxane, 200	A[f] 8	9·2	0
6	100	$CrCl_2$,[e] 50	Dioxane, 200 Water, 1·8	A[f] 8	56	45
7[g]	200	$CrCl_2$,[e] 100	THF,[g] 400	A[f] 63	70	0

[a] An acidic, aqueous solution of chromous salt was added slowly to the solution of benzyl chloride during the designated period (Procedure C: Experimental section). After addition of Cr^{++}, refluxing was continued 0·5 to 1·0 hr.

[b] Benzyl chloride was added slowly to the solution of the chromous salt during the designated period (Procedure B: Experimental section). After addition of benzyl chloride, refluxing was continued for 0·5 hr.

[c] Percent of chromous salt, assuming a stoichiometry of 2 mmoles of Cr^{++} for each mmole of bibenzyl or toluene.

[d] See Experimental section for preparation.

[e] Anhydrous, powdered solid.

[f] Solvent and all reagents were mixed and refluxed under nitrogen (Procedure A: Experimental section).

[g] Tetrahydrofuran. Reaction temperature was $\sim$65°.

The relative amounts of bibenzyl and toluene formed depend markedly upon the reaction conditions (*Table* 1). If benzyl chloride in dioxane is added slowly to a refluxing solution of $Cr(ClO_4)_2$ (Expt 4), the major product is toluene (bibenzyl/toluene = 0·02). On the other hand, the reverse procedure of adding $Cr(ClO_4)_2$ to a refluxing solution of benzyl chloride (Expt 3) produced considerably higher yields of bibenzyl (bibenzyl/toluene = 2·6). Furthermore, the bibenzyl/toluene molar ratio is inversely related to the rate of $CrSO_4$ addition to a benzyl chloride solution (Expts 1 and 2). The enhancement of the coupling reaction versus total reduction to toluene might be a consequence of lowering the chromous concentration relative to that of benzyl chloride. However, because of the qualitative nature of these experiments the solvent environments were not rigorously controlled and other factors besides chromous ion concentration could have been responsible for the observed effects.

In aprotic solvents, such as anhydrous tetrahydrofuran or dioxane, bibenzyl was the only product of reduction (Expts 5 and 7). The presence of even a small amount of water has a profound effect on the reaction (compare Expts 5 and 6). Since the solubility of chromous chloride in the aprotic solvents appeared to be low (solution only slightly colored by $CrCl_2$), these reactions may have been heterogeneous whereas those in the aqueous dioxane were homogeneous.

TABLE 2. EFFECT OF VARIOUS COMPOUNDS ON THE CHROMOUS PERCHLORATE REDUCTION OF BENZYL CHLORIDE[a]

Benzyl chloride:	75 mmoles
Tetrahydrofuran:	187 ml
Chromous perchlorate:	75 ml of 0·345 N; 25·9 mmoles
Compound added:	60 mmoles

Expt no.	Compound added	Bibenzyl/Toluene,[b] mole ratio
8	None	0·70
9	NaF	0·33
10	NaCl	0·28
11	NaBr	0·74
12	NaI	4·06
13	Pyridine	0·91
14	n-Bu_3P	0·30

[a] The benzyl chloride was injected into the refluxing THF solution of chromous perchlorate and added compound; reaction time, 3·0 hr; temperature, ~65°.

[b] The combined yields of bibenzyl and toluene were 80 to 90% of the chromous perchlorate, assuming a stoichiometry of 2 mmoles of Cr^{++} for each mmole of product.

The product composition also is dependent upon the particular benzyl halide used. Under identical conditions using $Cr(ClO_4)_2$ in aqueous–tetrahydrofuran, the ratio of bibenzyl/toluene increased from 0·70 to ~8·6 to ~9·4 for the series: benzyl chloride, bromide and iodide, respectively. The mechanistic significance of these results is discussed below.

The reduction of benzyl chloride by $Cr(ClO_4)_2$ is influenced by the presence of other species, such as halide ions. The relative extents of bibenzyl and toluene formation were determined with experimental conditions differing only in regard to the added substance (*Table* 2). The data show that the added components can either increase (Expt 12) or decrease (Expts 9, 10 and 14) the relative amount of the coupled product.

The promotion of the coupling reaction caused by the addition of sodium iodide possibly is due to the *in situ* conversion of benzyl chloride to benzyl iodide. Sodium bromide had little effect on the reaction (Expt 11). However, the *in situ* formation of benzyl bromide would be expected to be slower than that of benzyl iodide. The effects of the other compounds may result from complex formation with the chromium species.

The reductive coupling of diphenylmethyl chloride in acidic (HCl), aqueous-dioxane by chromous salts is more facile than that of benzyl chloride. Near quantitative yields of *sym*-tetraphenylethane were readily obtained. The formation of diphenylmethane occurred (13% yield) only when the halide was added very slowly to a refluxing solution of $CrSO_4$.

Reactions of aliphatic halides. Under the most favorable conditions found for the reductive coupling of benzyl halides, that is, the slow addition of chromous solutions to benzyl halide solution or the use of anhydrous, aprotic solvents, coupled products were not obtained from saturated aliphatic halides (*Table* 3). In aqueous-dioxane

TABLE 3. CHROMOUS SALT REDUCTION OF ALIPHATIC HALIDES (RX)[a]

Expt no.	RX, mmoles	Cr^{++} salt, mmoles	Solvent	Procedure time, hr	Product, yield
15	iso-PrI, 30	$CrCl_2$,[b] 50	D-H_2O[c]	B[d] 2·0	DMB,[e] 0% Propane, 49·4%[f]
16	iso-PrBr, 30	$CrCl_2$,[b] 50	D-H_2O[c]	B[d] 2·0	DMB,[e] 0% Propane, 17%[f]
17	iso-PrCl, 30	$CrCl_2$,[b] 50	D-H_2O[c]	B[d] 2·0	DMB,[e] 0% Propane, 0%
18	*t*-BuBr, 30	$CrCl_2$,[b] 50	D-H_2O[c]	B[d] 2·0	TMB,[e] 0% Isobutylene, 58%[f]
19	Iso-PrI, 200	$CrSO_4$,[g] 33 (65 ml)	D-H_2O[c]	C[h] 4·0	DMB,[e] 0% Propane, 93·4%[i]
20	*n*-BuI, 200	$CrSO_4$,[g] 33 (65 ml)	D-H_2O[c]	C[h] 4·5	*n*-Octane, 0% *n*-Butane, 6·1%[i]
21	Allyl bromide, 200	$CrSO_4$,[g] 33 (65 ml)	D-H_2O[c]	C[h] 7·0	Biallyl, 0% Propylene, 95·7%[i]
22	iso-PrI, 50	$CrCl_2$,[b] 25	THF[j]	A[k] 64	DMB,[e] 0% Propane, 6·4%[i]
23	Allyl bromide, 50	$CrCl_2$,[b] 25	THF[j]	A[k] 88	Biallyl, 83·3%[i] Propylene, 7·2%[i]
24	Allyl bromide, 50 Benzyl bromide, 50	$CrCl_2$,[b] 50	THF[j]	A[k] 47	Biallyl, 20%[i] Propylene, 8%[i] Bibenzyl, 15%[i] Toluene, 0% 4-Phenyl-1-butene, 16·8%[i]

[a] The temperatures were those of the refluxing solvents, i.e., 80–100° for the water–dioxane mixture and ~65° for tetrahydrofuran.

[b] Anhydrous, powdered $CrCl_2$.

[c] 100 ml of dioxane plus 50 ml of water.

[d] The aliphatic halide was added slowly to the solution of the Cr^{2+} salt during the period designated (Procedure B: See Experimental section).

[e] DMB is dimethylbutane and TMB is 2,2,3,3-tetramethylbutane.

[f] % of original aliphatic halide.

[g] See experimental section for preparation,

[h] An acidic aqueous solution of the Cr^{2+} salt was added to the dioxane–water solution of the aliphatic halide (Procedure C: See experimental section).

[i] % of Cr^{++} salt, assuming a stoichiometry of 2 Cr^{2+} for each propane or propylene formed.

[j] Tetrahydrofuran, 100 ml.

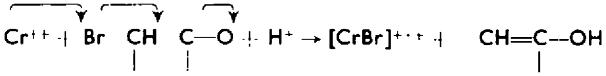
[k] Solvent and all reagents were mixed and refluxed under N_2 for the designated period (Procedure A: See experimental section).

media, isopropyl halides were converted exclusively to propane, and n-butyl iodide was reduced to n-butane. From the relative propane yields, the following ease of reduction is indicated: isopropyl iodide > isopropyl bromide > isopropyl chloride. t-Butyl bromide was converted exclusively to isobutylene. Independently, the chromic ion, a product of these reactions, was found to be a potent catalyst for the elimination of HBr from t-butyl bromide.

Castro[2] reported the reduction of allyl chloride to propylene by $CrSO_4$ in aqueous solution. We obtained the same results with allyl bromide in aqueous–dioxane media even though the chromous solution was added slowly to the allyl bromide (Expt 21). However, high yields of biallyl are obtained when an anhydrous solvent is employed (Expt 23).

A cross-coupled product, 4-phenyl-1-butene, was formed when a mixture of allyl bromide and benzyl bromide was treated with $CrCl_2$ in tetrahydrofuran (Expt 24). However, only biallyl (80%) was produced from a mixture of allyl bromide and benzyl chloride. Similarly, no cross-coupled product of isopropyl iodide and benzyl chloride was obtained.

Reduction of phenacyl bromide. In refluxing, anhydrous tetrahydrofuran, $CrCl_2$ converts phenacyl bromide to the following compounds (yields based on Cr^{2+}): 20% 1,4-diphenyl-1,4-butanedione, 49% acetophenone, 29% dypnone [$C_6H_5COCH{=}C(CH_3)C_6H_5$] and a trace of possibly 1,3,5-triphenylbenzene. The latter two compounds are likely condensation products of acetophenone. It was suggested[3d] that the debrominative reduction by $CrCl_2$ in acidic medium of 21-acetoxy-2,4-dibromo-17α-hydroxy-5α-pregnane-3,11,20-trione to the corresponding 4-bromo-ketone, proceeds thus:



$$Cr^{++} + Br\ \overset{|}{CH}\ \overset{|}{C}{-}O + H^{+} \rightarrow [CrBr]^{++} + CH{=}\overset{|}{C}{-}OH$$

Although 1,4-diphenyl-1,4-butanedione might result from reaction of an enol intermediate with phenacyl bromide, the mechanism below is favored for the formation of the coupled product.

Mechanism. The following mechanism proposals for the reaction of chromous salts with organic halides are directed specifically to homogeneous benzylic and allylic systems, although the concepts may be equally valid for other halides. In mixed solvents, such as aqueous–dioxane or aqueous–tetrahydrofuran, the reactions involving chromous sulfate and chromous perchlorate were homogeneous. However, the reactions with chromous chloride in anhydrous dioxane or tetrahydrofuran may have been heterogeneous since the chromous salt was only slightly soluble.

Anet and Leblanc[4] were the first to demonstrate that the initial reaction of chromous perchlorate with benzyl chloride produces a benzyl–chromium complex (I), $C_6H_5CH_2Cr(H_2O)_5{}^{2+}$. Kochi and Davis[7] recently have obtained kinetic data demonstrating that this transformation consists of two consecutive reactions involving the formation of an intermediate benzyl radical which then rapidly combines with a second chromous species (Eqs 4 and 5).

$$C_6H_5CH_2Cl + Cr^{+2} \xrightarrow{\text{slow}} C_6H_5CH_2\cdot + CrCl^{+2} \tag{4}$$

$$C_6H_5CH_2\cdot + Cr^{+2} \xrightarrow{\text{fast}} C_6H_5CH_2Cr^{+2} \tag{5}$$

Our data for diphenylmethyl chloride and chromous chloride in aqueous–dioxane indicate that the free diphenylmethyl radical, if formed, must have a short life since the addition of ethyl thioglycolate[8] to the reaction medium did not increase the yield of diphenylmethane. The diphenylmethyl radical is known to react with good hydrogen transfer agents such as thiophenol.[9] Although the chromous chloride was soluble in these media, the reaction mixtures were not homogeneous.

Regarding the formation of coupled products, Anet and Leblanc[4] found that the decomposition of I in the absence of oxygen by heating or by keeping for several days gave bibenzyl. We have obtained direct evidence that a reaction between I and reactive organic halides may also produce coupled products. The benzylchromium complex, $C_6H_5CH_2Cr(H_2O)_5{}^{2+}$ was prepared by reaction of phenyl-t-butyl hydroperoxide with $Cr(ClO_4)_2$.[10] Treatment of a perchloric acid-tetrahydrofuran solution of the complex with allyl bromide (0–5°) produced 4-phenyl-1-butene (Eq. 6). Bibenzyl and

$$C_6H_5CH_2Cr(H_2O)_5{}^{2+} + CH_2{=}CHCH_2Br \rightarrow C_6H_5CH_2CH_2CH{=}CH_2 + Cr(H_2O)_5Br^{2+}\,(?) \quad (6)$$

biallyl were not formed. Under these conditions, I reacted more rapidly with allyl bromide than it decomposed to bibenzyl. A solution of I and allyl bromide changed color from clear yellow to blue-green (chromic salt) within 2–3 hr at 0–5°. However, I alone was still yellow after 24 hr at room temperature.

The fact that higher bibenzyl/toluene ratios were obtained from the chromous perchlorate reductions of benzyl bromide and iodide than from the chloride (*vide supra*) suggests that reaction of the intermediate benzyl–chromium complex with the benzyl halide is the most important route to bibenzyl (Eq. 7). This coupling reaction would be expected to compete

$$C_6H_5CH_2Cr(H_2O)_5{}^{2+} + C_6H_5CH_2X \rightarrow C_6H_5CH_2CH_2C_6H_5 + Cr(H_2O)_5X^{2+}\,(?) \quad (7)$$

more effectively with the reactions producing toluene (*vide infra*) when X is iodine or bromine. On the other hand, the rate of thermal decomposition of I to bibenzyl should be independent of the benzyl halide used in its preparation.

For these same reasons, the mechanism proposed recently by Castro and Kray[11] (Eq. 8) to explain the formation of bibenzyl seems less important than Eq. 7.

$$\begin{tikzcd}
RCr^{++} \arrow[r, shift left] \arrow[d, "R\cdot"] & R\cdot + Cr^{++} \arrow[l, shift left] \arrow[d, "R\cdot"] \\
R{-}R + Cr^{++} & R{-}R
\end{tikzcd} \quad (8)$$

Anet and Leblanc[4] found the Cr(III) complex (I) to be rather substitution-inert since it did not solvolyze under their experimental conditions to toluene. However, toluene, rather than an organic–metallic compound, was obtained when benzyl chloride reacted with chromous chloride in hydrochloric acid. They reasoned that the complex initially formed under these conditions, presumably $C_6H_5CH_2CrCl(H_2O)_4{}^{+}$,

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[8] R. A. Gregg, D. M. Alderman and F. R. Mayo, *J. Amer. Chem. Soc.* **70**, 3740 (1948).

[9] C. Wang and S. G. Cohen, *J. Amer. Chem. Soc.* **79**, 1924 (1957).

[10] J. K. Kocki and F. F. Rust, *J. Amer. Chem. Soc.* **83**, 2017 (1961).

[11] C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.* **85**, 2768 (1963).

because of the chloride ion in the coordination sphere, would be reduced by bridging[12] with the reducing agent. The resultant Cr(II) complex should be more labile and dissociate to benzyl anions which react with the solvent to give toluene. From this reasoning, reduction to toluene, relative to coupling, should be favored by high chromous ion concentrations. Although we made no systematic study of the influence of chromous ion concentration, our observations on the effects of (1) the order of combination of $Cr(ClO_4)_2$ and benzyl chloride reagents and (2) the rate of $CrSO_4$ addition to a benzyl chloride solution are consistent with this view.

On the other hand, Castro and Kray[11] have proposed that total reduction can occur by a heterolytic scission of the RCr^{2+} complex *via* a proton transfer from a coordinated solvent molecule to the incipient carbanion. Since our experiments endeavoring to control the chromous ion concentration were only qualitative, we cannot eliminate this proposal as a route for toluene formation.

EXPERIMENTAL[13]

Reagents. The chromous chloride (anhydrous), titanium trichloride (20% aqueous solution), and cuprous bromide (reagent grade) were obtained from Fisher Scientific Company. The ferrous chloride ($FeCl_2 \cdot 4H_2O$) was obtained from Allied Chemical Company. Reagent grade triphenylcarbinol and diphenylcarbinol were Eastman Kodak products. The high purity benzyl alcohol was obtained from Aldrich Chemical Company.

Vanadous chloride. The reagent was prepared by the reduction of V_2O_5 with amalgamated zinc in 6N HCl according to the published procedures of Conant and Cutter.[1c] The amalgamated zinc was prepared by stirring zinc (~20 mesh) for 10 min in 1 l. 1N HCl (or 1N H_2SO_4) and 0·1M in mercuric chloride. The zinc was washed thoroughly with water, then 1N H_2SO_4 and finally with water.[14] The purple VCl_2 solution, containing zinc ions as well, was stored over the excess amalgamated zinc and, according to Conant and Cutter, should be ~1M.

Vanadous sulfate. Amalgamated Zn (90 g; 1·37 gram atoms) and 60 g (0·33 mole) V_2O_5 were placed in a 3-necked flask equipped with stirrer, reflux condenser and gas inlet tube. The flask was flushed with N_2 and 500 ml 20% H_2SO_4 added with stirring. After 30 min, the brown mixture first turned green and then gradually purple. The initial color change was accompanied by heat evolution requiring external cooling. The solution was assumed to be ~1M in VSO_4. The pH of the solution was 0·15. The chlorine content as determined by neutron activation was <50 ppm. The solution contained Zn ions.

Chromous sulfate. This reagent was prepared by reducing an aqueous solution of chromic sulfate with Zn powder according to published procedures.[3] The blue chromous sulfate solution was standardized by injecting a 10 ml aliquot into an aqueous solution of excess $FeCl_3$ under N_2. The ferrous solution thus produced was then titrated with 0·0972N ceric sulfate to the green ferric phenanthroline end-point (dilute solutions required for good end-point detection). The indicator, 0·025M solution of phenanthroline-ferrous sulfate, was prepared by dissolving a stoichiometric amount of phenanthroline monohydrate in a 0·025M solution of ferrous sulfate in water. The chromous sulfate solution was 0·58M and had a pH of 2·5. Chloride ion content was <50 ppm (neutron activation). The solution contained Zn ions.

Chromous perchlorate. The procedure of Lux and Illmann[15] was used for the preparation of this material. Seventy ml 70% $HClO_4$, 285 ml distilled water and 10 g (0·19 moles) electrolytic chromium platelets (A. D. Mackay, Inc.) ($\geq$99·9% purity) were placed in a suitable flask and stirred at room temp. under N_2 for several days. The resulting dark blue solution was titrated for Cr^{2+} content (0·44 normal) by the procedure described above for the $CrSO_4$ solution. Chloride ion content was <10 ppm (neutron activation analysis).

[12] H. Taube and E. L. King, *J. Amer. Chem. Soc.* 76, 4053 (1954); H. Taube and H. Myers, *ibid.* 76, 2103 (1954).

[13] M.ps and b.ps are uncorrected.

[14] *Inorganic Syntheses*, **III**, 148 (1950).

[15] H. Lux and G. Illmann, *Chem. Ber.* 91, 2143 (1958).

Reduction of triphenylcarbinol. In a 3-necked flask, equipped with stirrer, dropping funnel and gas inlet, 2 g (7·7 mmoles) triphenylcarbinol and 40 ml acetone were placed. After the flask was flushed with N_2, 14 ml (14 mmoles) VCl_2 solution was added followed by 12 ml conc. HCl. The purple color of the VCl_2 was lost immediately and a white precipitate formed. The solution, diluted with 50 ml water, was filtered under N_2 to recover the product. The solid, presumably hexaphenylethane, was dissolved in benzene and the solution dried ($CaCl_2$). After decanting, oxygen was bubbled through the benzene to oxidize the hexaphenylethane to triphenylmethyl peroxide which was collected by filtration and washed with ethanol. The peroxide melted at 187–188°; literature value, 185–186°,[16] yield = 2·07 g or ~100%. Similar treatment with oxygen of triphenylcarbinol or triphenylmethane did not produce triphenylmethyl peroxide. (Found: C, 87·95; H, 5·80. Calc. for $C_{38}H_{30}O_2$: C, 88·00; H, 5·83%.)

A similar procedure was employed for reductions with $CrCl_2$ (100% yield), $TiCl_3$ (100% yield), $FeCl_2$ (5% yield), Cu_2Br_2 (0% yield, $Cr(ClO_4)_2$ (73%) in 31% $HClO_4$-acetone solution and $CrSO_4$ (~90% yield). The reaction times varied between 10 and 60 min. Fifty per cent H_2SO_4 and ethanol rather than concentrated HCl and acetone was used for the last reduction.

Reduction of diphenylcarbinol. This alcohol (1·42 g; 7·7 mmoles) in 40 ml acetone or ethanol was treated for 0·3–3·0 hr at room temp. with $\leq$14 mmoles of either VCl_2 in 30 ml 18–80% H_2SO_4 (31–65% yield), $CrCl_2$ in 15 ml 80% H_2SO_4 (89% yield), VSO_4 in 30 ml 48% H_2SO_4 (39% yield), $CrSO_4$ in 30 ml 40% H_2SO_4 (27% yield), or $Cr(ClO_4)_2$ in 47 ml 31% $HClO_4$ (34% yield).

The *sym*-tetraphenylethane products, in the designated yields, were recovered by diluting the above solutions with water and filtering. The product, recrystallized from methanol, m.p. ~213°; literature value, 212·5.[17] A mixed m.p. with authentic material, synthesized by treating diphenylmethyl chloride with silver powder,[17] was not depressed. (Found: C, 92·95; H, 6·60; M.W., 346 (ebullioscopic, benzene). Calc. for $C_{26}H_{22}$: C, 93·37; H, 6·63%; M.W., 334.)

A second crop of crystals occasionally could be recovered from the above filtrate and were identified as unreacted diphenylcarbinol. In several experiments, the yields of products were determined by g.l.c. analysis on benzene extracts of the original product solutions.

Reduction of benzyl alcohol. Benzyl alcohol (0·83 g; 7·7 mmoles), ethanol (40 ml) and VCl_2 solution (14 ml; 14 mmoles) were placed in a 3-necked flask and swept with N_2. Fifteen ml 80% H_2SO_4 was added with external cooling while stirring and the solution then refluxed for 1·5 hr. The product was extracted with ether, and analyzed by g.l.c. techniques after concentration of the solution. The product consisted of benzyl ethyl ether, benzyl chloride, bibenzyl (0·014 g; 2% yield) and a trace of material which may have been toluene. The identities of the compounds emerging from the g.l.c. were confirmed by mass spectrometric analyses.

In one experiment, benzyl alcohol (0·15 moles) and chromous sulfate solution (300 ml; 0·174 moles) were stirred and refluxed under N_2 for 19 hr. The product recovered by benzene extraction consisted mainly of benzyl alcohol. Bibenzyl, toluene and dibenzyl ether were not present.

When this experiment was repeated with 0·1 mole NaCl added, toluene (20%), benzyl chloride (10·7%) and bibenzyl (5·3%) were formed. These yields are based on the original benzyl alcohol.

Reduction of organic halides. In general, one of three different procedures was employed for the reduction of all of the organic halides listed in *Tables* 1–3. All reactions were carried out under an atmosphere of oxygen-free nitrogen. The procedure of each experiment is indicated in the *Tables*.

Procedure A. Solvent(s) and all reagents were combined and stirred for the designated time at the stated temp. Where pertinent, the gaseous products were collected in a brine-displacement gas holder and analyzed by means of g.l.c. The non-gaseous products were usually recovered by benzene extraction and the extract analyzed by g.l.c. Occasionally, when the reaction product mixture was homogeneous, direct g.l.c. analysis was possible without extraction. The identities of *sym*-tetraphenylethane and bibenzyl, which were analyzed quantitatively by means of g.l.c., were confirmed by isolation, elemental analyses, and m.p. comparisons with authentic materials. Diphenylmethane and biallyl in the products were identified by coincidence of their g.l.c. emergence times and mass spectra with those of the authentic compounds.

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[16] M. Gomberg, *Ber. Dtsch. Chem. Ges.* **33**, 3150 (1900).

[17] L. Bert, *C.R. Acad. Sci. Paris* **177**, 324 (1923); J. Coops, W. Th. Nauta, M. J. E. Ernsting and A. C. Faber, *Rec. Trav. Chim.* **59**, 1109 (1940).

Procedure B. The solvent and metal salt were placed in a suitable flask and heated to the desired temp. The organic halide was slowly added with stirring over the period of time designated in the *Tables*. The products were isolated and analyzed as described above.

Procedure C. The solvent and organic halide were placed in the flask and the temp controlled at the desired level. The metal salt solution was added slowly with stirring over the period of time designated in the *Tables*. The products were isolated and analyzed as described above.

Reduction of benzyl chloride, bromide and iodide. Into three assembled flasks with accessories were placed 75 ml 0·345N $Cr(ClO_4)_2$ (25·9) mmoles and 187 ml tetrahydrofuran. The solutions were brought to reflux and 75 mmoles of benzyl chloride, benzyl bromide and benzyl iodide injected into the respective flasks. Refluxing (~65°) was continued for 3 hr. The products were analyzed by g.l.c. The molar ratio of bibenzyl/toluene increased from 0·7 to ~8·6 to ~9·4 for the series: benzyl chloride, bromide and iodide, respectively. The total yield of product was 75–85% of the $Cr(ClO_4)_2$, assuming two mmoles of Cr^{++} are required for each mmole of bibenzyl and toluene.

Reduction of benzyl chloride—effect of various compounds. Into seven assembled flasks with accessories, were placed 75 ml 0·345N $Cr(ClO_4)_2$ (25·9 mmoles) and 187 ml tetrahydrofuran. Sixty mmoles of NaF, NaCl, NaBr, NaI, pyridine and *n*-Bu_3P, respectively, were added to six of the flasks and the solutions then stirred at room temp for 45 min. The solutions were simultaneously brought to reflux and 75 mmoles of benzyl chloride injected into each flask. Refluxing (~65°) was continued for 3 hr. The products were analyzed by g.l.c. techniques to determine the relative amounts of bibenzyl and toluene (*Table* 2). With the assumed stoichiometry of two moles of $Cr(ClO_4)_2$ for each mole of product, 80–90% of the Cr^{2+} ion could be accounted for from the amounts of toluene and bibenzyl formed.

Reduction of diphenylmethyl chloride. A mixture of 50 mmoles chromous chloride, 50 ml water and 100 ml dioxane was stirred under N_2 and heated to the reflux temp (80–100°). Diphenylmethyl chloride (30 mmoles) was added slowly during 1 hr. Water was added and the product extracted with hot benzene. A g.l.c. analysis indicated that ~15 mmoles of *sym*-tetraphenylethane (~100%) had been formed. The *sym*-tetraphenylethane was identified further by its m.p. No diphenylmethane could be detected. The same results were obtained using 50 ml conc. HCl and 100 ml dioxane as the solvent.

Also, a mixture of 50 mmoles chromous chloride, 30 mmoles diphenylmethyl chloride, 50 ml water and 100 ml dioxane was stirred under N_2 for 19 hr at room temp; 8·6 mmoles (57·1%) of *sym*-tetraphenylethane were obtained. No diphenylmethane could be detected. When this experiment was repeated with 100 mmoles of either ethyl thioglycolate or thioglycolic acid incorporated, essentially identical results were obtained.

By adding 25 mmoles diphenylmethyl chloride in 50 ml dioxane slowly during 4 hr to 71 mmoles refluxing $CrSO_4$ solution (150 ml), 3·4 mmoles (13·4%) diphenylmethane and 1·5 mmoles (12%) tetraphenylethane were formed. The first product was identified mass spectrometrically as a $C_{13}H_{12}$ compound and had the same g.l.c. emergence time as authentic diphenylmethane.

Phenacyl bromide. One hundred mmoles $CrCl_2$, 75 mmoles phenacyl bromide and 40 ml anhydrous tetrahydrofuran were refluxed and stirred for 2 hr under N_2. As determined by quantitative g.l.c. analyses, the following compounds were formed: 20% 1,4-diphenyl-1,4-butanedione, 49·4% acetophenone, 28·8% dypnone and a trace of 1,3,5-triphenylbenzene. The yields are based upon the consumption of Cr^{2+}, assuming a stoichiometry of two moles of Cr^{2+} for each mole of 1,4-diphenyl-1,4-butanedione and acetophenone, and 4 moles of Cr^{2+} for each mole of dypnone. The above compounds were trapped at the exit of the g.l.c. column and analyzed mass spectrometrically. The mol. wts and cracking patterns were in agreement with the proposed structures.

The liquid product was filtered and extracted with n-pentane. Upon evaporation of the n-pentane, a semi-solid material remained which was dissolved in ethanol. The latter solution was heated with decolorizing charcoal, filtered and cooled. 1,4-Diphenyl-1,4-butanedione crystallized which, after recrystallization, melted at 144–145°. A dioxime derivative melted at 209°. Literature values are: 1,4-diphenyl-1,4-butanedione,[18] m.p. 144–145°; 1,4-diphenyl-1,4-butanedione dioxime,[18] m.p. 203–204°. (Found: C, 80·55%; H, 5·90%; carbonyl equivalents/100 g, 0·80. Calc. for diketone $C_{16}H_{14}O_2$: 80·65%; H, 5·92%; carbonyl equivalents/100 g, 0·84. Found: C, 71·75%; H, 6·15%. Calc. for dioxime $C_{16}H_{16}O_2N_2$: C, 71·62%; H, 6·01%).

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[18] S. Kapf and C. Paal, *Ber. Dtsch. Chem. Ges.* **21**, 3057 (1888).

Benzylchromium complex and reactions. A benzylchromium complex, $C_6H_5CH_2Cr(H_2O)_5^{2+}$, was prepared as described.[7,10] All operations were carried out in a N_2-filled box. α,α-Dimethylphenethyl hydroperoxide (4·0 g; 24 mmoles) dissolved in 20 ml of *t*-butyl alcohol was chilled to 0°. To this solution, 31 ml (32 mmoles) chromous perchlorate was added slowly. A rapid color change from blue to yellow-green occurred. After 10 min, the solution was chromatographed at ~5° through a column packed with cation exchange resin (20–50 mesh AG50W-X4; Bio-Rad) which had been washed with water. The column was eluted with 1M $HClO_4$. The solution emerging from the column was first blue then green and finally clear yellow. The last solution contained the benzylchromium complex. To confirm the presence of the complex, air was bubbled through a portion of the solution which rapidly turned green with the formation of benzaldehyde which was identified by the m.p. of its 2,4-dinitrophenylhydrazone derivative. This complex was previously shown to form benzaldehyde under these conditions.[4]

A 75 ml aliquot of the yellow solution at 0–5° was added to 50 ml tetrahydrofuran containing 40 mmoles allyl bromide. Within 3 hr, the solution had turned blue-green (0–5°). The untreated yellow solution of the complex was unchanged in color after 24 hr at room temp. The bluish-green solution was diluted with water and extracted with n-pentane. A g.l.c. analysis of the product indicated that no bibenzyl nor biallyl was formed; however, 4-phenyl-1-butene was present. To confirm its presence, a sample was trapped at the exit of the g.l.c. and analyzed mass spectrometrically. The cracking pattern of this material was identical to an authentic sample of 4-phenyl-1-butene. Because of the very low concentration of the benzylchromium complex, the amount of 4-phenyl-1-butene obtained was too small for identification by other methods.

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