

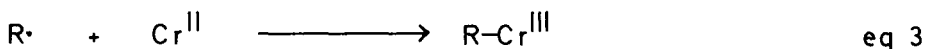
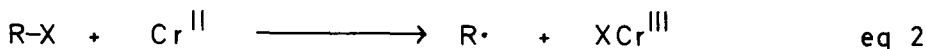
SELECTIVE COUPLING OF FREE RADICALS VIA ORGANOCHROMIUM COMPLEXES.

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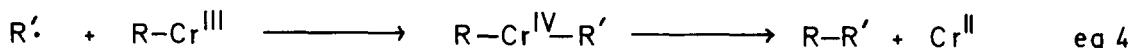
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Summary: Free radicals can be coupled in high yield to give either symmetric dimers or cross coupling products by reacting chromous chloride in THF with alkyl halides.

The reaction of free radicals with mono- σ -alkylchromium(III) complexes ¹⁾ leads to a concept by which selective coupling of radicals should be possible. Chromous(II) salts react with alkyl halides by halogen transfer according to eq. 1 ²⁾. It was shown by Kochi and coworkers ^{3,4)} that the reaction involves the intermediacy of radicals which are trapped by chromous(II) ion according to eq. 2 and 3.



This together with the result of the preceding communication suggests the following experimental procedure for selective radical coupling reactions: Form an alkylchromium(III) compound from an appropriate alkyl halide and two equivalents of Cr^{II} . React another equivalent of alkyl halide (eq. 2) in presence of R-Cr^{III} and one equivalent of Cr^{II} and trap the intermediate radical by R-Cr^{III} according to eq. 4.



Thermal decomposition of the chromium(IV) complex at room temperature yields the radical dimers. Depending on whether $R=R'$ or $R \neq R'$, symmetric dimers or cross coupling products should be formed. This scheme will be successful only if a radical formed in eq. 2 is trapped by CrCl_2 instead of being added to already formed $R\text{-Cr(III)}$. An excess of Cr^{II} might be valuable for this purpose. The reaction therefore should be carried out by having the total amount of Cr^{II} required present from the beginning. The reaction has to be effected in anhydrous medium in order to avoid reduction of $R\text{-Cr(III)}$ to alkanes⁵⁾. Tetrahydrofuran proved to be a suitable solvent for these reactions.

The feasibility of such a scheme is indicated by a recent publication⁶⁾ where symmetrical dimers are made by chromous(II) and alkylhalides in tetrahydrofuran. The following procedure was adopted for our reactions. A suspension of chromous chloride was prepared by reducing a suspension of CrCl_3 in THF with equimolar amounts of $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$ ⁷⁾ at 0°C . At the same temperature 1/3 equivalents of alkyl halide was added to generate the alkylchromium complex (eq. 2 and 3). The solution was stirred for 15-30 min at 0°C . Then 1/3 equivalents (relative to the original amount of CrCl_2) of alkyl halide, either the same as in the formation of $R\text{-Cr}^{\text{III}}$ or a different one, is added to form radicals $R\cdot$ according to eq. 2 which then should be trapped by $R\text{-Cr}^{\text{III}}$. The solutions were kept at room temperature for about 8 hours before they were hydrolysed and analysed either by isolation of the products or by GLC. In all cases the products were identified by comparison with authentic samples.

Table 1 lists some results for the formation of symmetric dimers, table 2 illustrates the possibility of formation of cross coupling products.

Table 1: Products of the reaction of organic halides $R\text{-X}$ with CrCl_2

R-X	product	yield %
$\text{Ph-CH}_2\text{-Br}$	$\text{Ph-CH}_2\text{-CH}_2\text{-Ph}$	87
$(\text{Ph})_2\text{-CHBr}$	$(\text{Ph})_2\text{CH-CH}(\text{Ph})_2$	99
$\text{CH}_2=\text{CH-CH}_2\text{-Br}$	$(\text{CH}_2=\text{CH-CH}_2)_2$	98
$(\text{CH}_3)_3\text{C-Br}$	$(\text{H}_3\text{C})_3\text{C-C}(\text{CH}_3)_3$	84
$(\text{CH}_3)_2\text{CH-Br}$	-	0

Table 2: Cross coupling products in the reaction of CrCl_2 with R-X and $\text{R}'\text{-X}$

R-X	R' -X	product	yield %
$\text{Ph-CH}_2\text{-J}$	$\text{CH}_2=\text{CH-CH}_2\text{-J}$	$\text{Ph-CH}_2\text{-CH}_2\text{-CH=CH}_2$	85
$\text{Ph-CH}_2\text{-Br}$	$(\text{H}_3\text{C})_3\text{CBr}$	$\text{Ph-CH}_2\text{-C}(\text{CH}_3)_3$	55
$\text{Ph-CH}_2\text{-J}$	$(\text{Ph})_3\text{CCl}$	$\text{Ph-CH}_2\text{-C}(\text{Ph})_3$	90
$(\text{Ph})_2\text{CHBr}$	$\text{CH}_2=\text{CH-CH}_2\text{Br}$	$(\text{Ph})_2\text{CH-CH}_2\text{-CH=CH}_2$	41
$(\text{Ph})_2\text{CHBr}$	$(\text{Ph})_3\text{CCl}$	$(\text{Ph})_2\text{CH-C}(\text{Ph})_3$	89

The high yield in dimer formation from t-butyl radical proves that the dimerization step does not occur via free radicals. In this case disproportionation should be the major process ⁸⁾. The exclusion of disproportionation makes this reaction an ideal way for synthesizing highly branched alkanes which otherwise are accessible only with difficulty ⁹⁾. Similarly the high yield in penta-phenylethane (last entry in table 2) shows the non radical nature of the dimerization step. Free radical dimerization of diphenyl methyl and triphenyl methyl radical should give predominantly or exclusively a Gomberg type dimer ¹⁰⁾. Lankamp, Nauta and MacLean ¹⁰⁾ in fact prepared symmetrical tetraarylethanes by a procedure which turns out to be similar to our reaction even though the function of Cr^{II} was not recognized at the time. They obtained symmetrical tetraarylethanes by reacting the diarylcarbinols with Cr^{2+} in acetone/HCl.

The last entry of table 1 indicates that so far only t-alkyl halides, benzylic halides or allylic halides do react. This is due to the difficulty to effect eq.2 with primary and secondary alkyl halides. However primary and secondary monoalkylchromium(III) complexes can be prepared by reacting for instance Grignard reagents with Cr^{III} ¹¹⁾. These complexes then can be subjected to the reaction with a radical. As is known from other studies ¹¹⁾ alkyl iodides react faster than alkyl bromides or alkyl chlorides. High reactivity in the initial formation of R-Cr^{III} is desirable in order to avoid the known unimolecular decomposition of R-Cr^{III} in $\text{R}\cdot + \text{Cr}^{2+}$ ¹²⁾. Therefore it is preferable to use alkyl iodides. In our examples the decomposition is a slow process at 0°C and therefore does not compete with the desired reaction.

Further work to explore the scope of this reaction and to expand its applicability is in progress.

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