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REDUCTION OF ORGANIC HALIDES BY MEANS OF $CrCl_3$-$LiAlH_4$ REAGENT IN ANHYDROUS MEDIA

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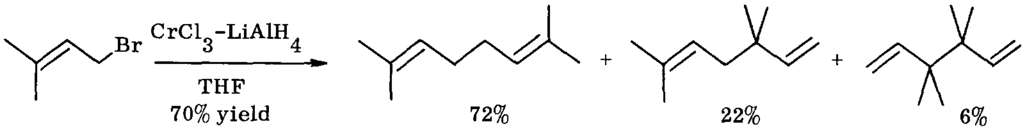
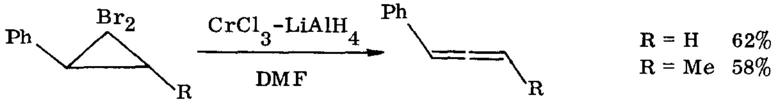
Chromium(II) salts are extensively utilized in organic syntheses especially for reduction of organic halides,[1] and the intermediacy of organochromium has been proposed on the basis of kinetic study.[2] The organometallic species are, however, rarely employed for carbon-carbon bond forming reaction, as most of the reactions are performed in the presence of water.[3,4] This limitation is principally ascribed to the preparation of the chromous salts,[1,5] whereas the recently developed reduced chromium reagent[6] is prepared from chromium(III) chloride and lithium aluminum hydride (1/2 M) in tetrahydrofuran (THF) and the reduction can be carried out in anhydrous organic media. Herewith are communicated some results of the title reaction.

We first studied the dehalogenative dimerization of an allylic bromide. Reduction of 1-bromo-3-methyl-2-butene with $CrCl_3$-$LiAlH_4$ at room temperature in THF resulted mainly in head-to-head coupling.[7] The intermediary chromium species is evidenced in the reaction with carbonyl compounds.[6]



The salient feature of the title reagent is recognized in the reduction of gem-dibromocyclopropanes. 9,9-Dibromobicyclo[6.1.0]nonane was quantitatively (GLC) converted to 1,2-cyclononadiene in anhydrous dimethylformamide (DMF), in sharp contrast to the reduction of the same substrate in DMF where only 30% yield of the allene is formed along with remarkable amount of by-products derived from the coexistent water.[4] Similarly, 1,1-dibromo-2-phenylcyclopropane and trans-1,1-dibromo-2-methyl-3-phenylcyclopropane were reduced to the corresponding allenes. The results strongly advocate the intermediacy of chromium carbenoids as expected previously[3,4] which instantly decompose to allenes.[8,9]



Benzylic halides also are reduced to give dimeric products: benzyl bromide → 1,2-diphenylethane, 49%; dichloromethylbenzene → stilbene (cis/trans 1/2), 48%; trichloromethylbenzene → diphenylacetylene, 43%.

Reduction of *dl*-1,2-dibromocyclododecane proceeded in non-stereospecific manner, giving *cis*- and *trans*-cyclododecene (29 and 41% yield respectively).

Finally, α-bromocyclododecanone was reduced with $CrCl_3$-$LiAlH_4$ to give 96% yield of cyclododecanone after work-up. Anticipating the intermediacy of the chromium enolate of cyclododecanone, we attempted to couple the enolate with methyl iodide or trimethylsilyl chloride. The sole product isolated was cyclododecanone in every case.

Although we could not fully characterize the organochromium intermediates, the present reagent may find wide applicability in selective carbon-carbon bond formation. Study is in progress in our laboratory on the synthetic application.[10]

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7. When the halide was reduced by means of anhydrous chromium(II) chloride purchased from Research Organic/Inorganic Chemical Corp), coupling occurred in a quantitative yield with the ratio of 62%, 27%, and 11%.
8. All attempts to trap the carbenoid failed in the reaction with benzaldehyde or cyclohexene.
9. Typical experimental procedure is as follows. Anhydrous chromium(III) chloride (824 mg, 5.2 mmol) in THF (5 ml) was reduced by portionwise addition of lithium aluminum hydride (98.8 mg, 2.6 mmol) at 0°C. After stirring at room temperature for 10 min the solvent was evaporated *in vacuo* and the residue was redissolved in DMF (5 ml). Addition of 1,1-dibromo-2-phenylcyclopropane (289 mg, 1.0 mmol), stirring for 4 hr at room temperature, and the subsequent work-up gave phenylallene (75 mg, 62% yield) upon distillation at 80-95°C/20 Torr (Kugel Rohr) consistent with the authentic spectra. The commercially available anhydrous chromium(II) chloride (see note 7) still involves protic source which hence complicated the reaction path and appreciable amount of phenylcyclopropane was produced.
10. Financial support by the Ministry of Education, Japanese Government, (Grant-in-Aid #247077) is acknowledged.