(20) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Am. Chem. Soc.*, **95**, 1516 (1973).
(21) For other evidence favoring $a(H_\alpha) > 0$, see ref 8. Contrary conclusions are contained in ref 5, 6, and 19.
(22) Low and high temperature must be defined in terms of barrier height.[15]
(23) Using the theory and notation of ref 15 and truncating its eq 6 after the second term, yields for $a(H_\alpha) > 0$:

$$a(H_\alpha, \theta) = -|a_0| + a_2\alpha_m{}^2F_2(\theta, E_0) > 0$$

The temperature coefficient measured at two temperatures near θ where $a(H_\alpha)$ is still positive ($\theta_1 < \theta < \theta_2$), is given by

$$d|a(H_\alpha)|/d\theta = \frac{a_2\alpha_m{}^2}{\Delta T}[F_2(\theta_2, E_0) - F_2(\theta_1, E_0)]$$

Inspection of the curves[15] for F_2 reveals that with ≥3 vibrational levels $d|a(H_\alpha)|/dT < 0$ at low[24] and >0 at high temperatures,[22] while for 2 levels $d|a(H_\alpha)|/dT > 0$ at all temperatures.
(24) With these conditions the same conclusion can be deduced qualitatively for any double minimum potential function that has inner walls less steep than outer walls since the radical will become more bent as the temperature decreases and so H_α will acquire more positive spin.
(25) The opposite situation probably obtains with 7-norbornenyl for which it had been suggested[20] that $a(H_\alpha) > 0$ because the temperature coefficient and isotope effect[17] were positive. However, other studies[26] have indicated that $a(H_\alpha) < 0$ which is readily explicable[27] if the out-of-plane vibrations are governed by an asymmetric double-minimum potential function.
(26) T. Kawamura, Y. Sugiyama, M. Matsunaga, and T. Yonezawa, *J. Am. Chem. Soc.*, **97**, 1627 (1975).
(27) Footnote 11, ref 26.
(28) Photoelectron spectroscopy indicates that one lone pair is essentially a pure p-type orbital and the second lone pair is roughly an s-type orbital.[29] The p-type lone pair is of higher energy (lower I.P.) than the s type by ≥10 eV.
(29) See, e.g., D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 5599 (1972); D. A. Sweigart, *J. Chem. Educ.*, **50**, 322 (1973).
(30) The orbital energies of the unpaired electron and of the p-type lone pair are of similar magnitude.
(31) The role that such overlap plays in producing nonplanarity at C_α and influencing the magnitude of $a(H_\alpha)$ via this bending has been discussed in ref 6 and 32.
(32) See, e.g., R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **95**, 7182 (1973); P. J. Krusic and R. C. Bingham, *ibid.*, **98**, 230 (1976); F. Bernardi, N. D. Epiotis, W. Cherry, H. B. Schlegel, M. H. Whangbo, and S. Wolfe, *ibid.*, **98**, 469 (1976).
(33) The same conclusion will be reached if the common, but probably unrealistic,[29] assumption is made that the oxygens are sp^3 hybridized with two lone pairs of equal energy.
(34) For simplicity C_α is assumed to remain sp^3 hybridized in the radical. In the Newman projections, the dihedral angles between the O $2p_z$ direction and both the C_α–H_α bond and the C_α half-filled orbital are 30°.
(35) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley, New York, N.Y., 1965, p 251.
(36) A. Hudson and K. D. J. Root, *Tetrahedron*, **25**, 5311 (1969).
(37) N.R.C.C. Research Associate 1974–1976.

G. Brunton,[37] K. U. Ingold*
Division of Chemistry, National Research Council
Ottawa, Canada

B. P. Roberts
Department of Chemistry, University College
London, England

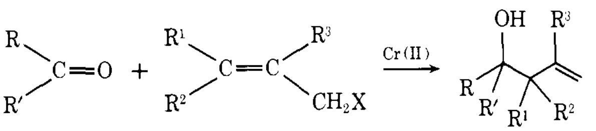
A. L. J. Beckwith
Department of Organic Chemistry, University of Adelaide
Adelaide, Australia

P. J. Krusic
Central Research and Development Department
E. I. du Pont de Nemours Co.
Wilmington, Delaware 19898

Received September 1, 1976

Grignard-Type Carbonyl Addition of Allyl Halides by Means of Chromous Salt. A Chemospecific Synthesis of Homoallyl Alcohols

Sir:



We wish to communicate that chromic chloride is easily reduced by a half molar equivalent of lithium aluminum hydride in tetrahydrofuran (THF) and the resulting salt, presumably Cr(II), can be utilized in the title reaction with high chemospecificity.

Lithium aluminum hydride (44 mg, 1.2 mmol) was added portionwise to anhydrous chromic chloride[1] (370 mg, 2.3 mmol) suspended in THF (5 mL) at 0 °C under an argon atmosphere. Spontaneous hydrogen evolution was observed, and a dark brown suspension was obtained.[2] To this suspension benzaldehyde (92 mg, 0.86 mmol) and subsequently prenyl bromide (173 mg, 1.2 mmol) dissolved in THF (5 mL) were added dropwise, and the mixture was stirred for 2 h at room temperature. Aqueous quenching, ether extraction, drying (Na_2SO_4), and distillation (Kugelrohr) gave an oil (124 mg, 82% yield based on benzaldehyde), bp (bath) 105–110 °C (0.12 mm): IR (neat) 3425, 3075, 3035, 1638, 1602, 1494, 1020, 1000, 910, 730, 702 cm^{-1}; NMR (CCl_4) δ 0.94 (s, 3 H), 0.99 (s, 3 H), 1.70 (br s, 1 H), 4.34 (s, 1 H), 4.8–6.2 (m, 3 H), 7.26 (s, 5 H); MS *m/e* 107 (base peak), no 176 (M^+).[3] The reagent prepared as above could be stored under an inert atmosphere in a refrigerator for more than a month without appreciable loss of its activity. The salt prepared from 2 M chromic chloride and 1 M lithium aluminum hydride was found most effective. When the ratio was larger than two, the yield of the adduct decreased, whereas a 1:1 mixture resulted in the reduction of the carbonyl group by the excess hydride. As the commercially available anhydrous chromous chloride (Research Organic/Inorganic Chemical Corp.) is also effective for the reaction (89% (GLC) yield of the product), the active species in the above reaction will be chromous ion. The results of the reaction between allylic halides (or tosylate) and carbonyl compounds are summarized in Table I, which shows that the reaction is general and applicable to a wide variety of both components.

As seen from the table the more substituted γ carbon of an allyl group was attached to the carbonyl carbon.[4] Two molar equivalents of chromous salt were required for the reduction of allyl halide. Although stoichiometric allyl halide was sufficient for the reaction (run 1 and 2), excess halide was much more effective (cf. run 3, 9, and 15). This is ascribed to the homocoupling of the halide,[5] the side products being easily removed by simple distillation or short-column chromatography.

The cyclohexanone/prenyl bromide reaction gave satisfactory yields only in dimethylformamide (DMF) (run 3), which dissolved the Cr(II) salt and probably enhanced the reducing ability of the salt.[6] The aprotic polar solvent was particularly indispensable for the reaction of allyl chloride and tosylate, which were not reduced effectively in THF (run 12 and 13).

A striking feature of the reaction is the high stereoselectivity and chemospecificity. In general, aldehydes were more reactive than ketones. Based on this reactivity difference we could attain selective attack on an aldehyde carbon of a polycarbonylated compound (run 16).[7] Furthermore, the Cr(II)-reduced allyl bromide could discriminate 2-heptanone from 4-heptanone. Noteworthy is the fact that only a single diastereomer

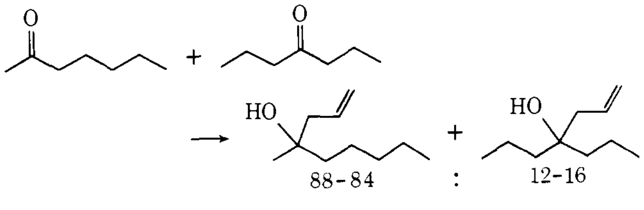
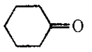
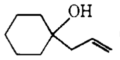
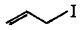
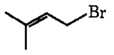
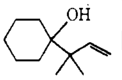
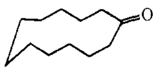
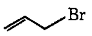
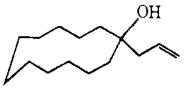
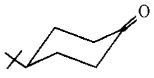
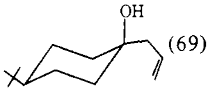
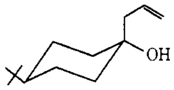
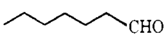
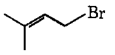
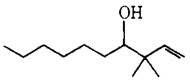
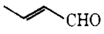
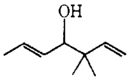
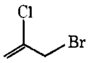
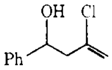
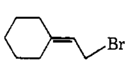
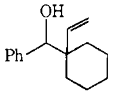
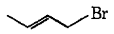
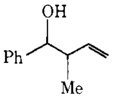
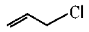
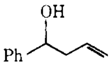
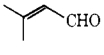
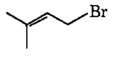
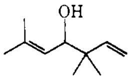
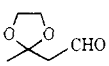
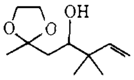
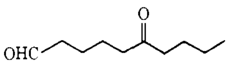
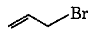
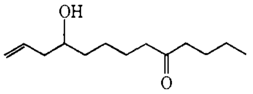
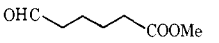
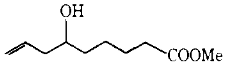
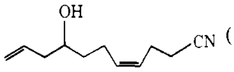


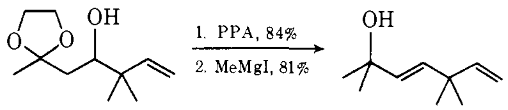
Table I. Reaction of Allyl Halides with Carbonyl Compounds

Run	RR'C=O	Allyl halide	Chromous salt[a]	Solvent	Halide/ RR'C=O	Product, %[b]
1			A	THF	1	 (78)
2			B	THF	1	" (74)
3			A	DMF	4	 [74][c]
4			A	THF	2	 (82) [99][d]
5			B	THF	2	 (69)  (19)
6			A	THF	2	(77) (10)
7			A	DMF	2	 (83)
8			A	THF	1.2	 (61) [82][c]
9	PhCHO		A	THF	3.5	 (94)[e]
10	PhCHO		A	THF	2	 (81)
11			A	THF	2	 (96)
12			B	DMF	2	 (54)
13			B	DMF	2	(55)
14			A	DMF	2	 [93][c]
15			A	DMF	4	 (91)[f]
16			B	THF	1.2	 (66)
17			B	THF	1.2	 (75)[g]
18			B	THF	3.7	 (66)[h]

[a] Salt A signifies the one prepared from chromic chloride and lithium aluminum hydride (2:1 molar ratio). Salt B means the commercially available anhydrous chromous chloride. The ratio, chromous salt/halide, was always 2. [b] Experiments were carried out in 1–2 mmol scale of the carbonyl components and isolated yields are given unless otherwise stated. [c] Estimated by GLC. [d] Based on the consumed ketone. [e] 0.6-mmol scale. [f] 10-mmol scale. [g] 0.8-mmol scale. [h] 0.5-mmol scale.

was obtained from benzaldehyde and crotyl bromide (run 11), which may exclude the possible participation of a free radical intermediate. The reaction of 4-*tert*-butylcyclohexanone with allyl bromide (run 5 and 6) gave predominant equatorial selectivity (81/19-88/12), which is comparable with allylzinc bromide (85/15) in contrast to allylmagnesium bromide (49/51) or allyllithium (35/65).[8] The allyl unit adds exclusively in 1,2-fashion with α,β-unsaturated aldehydes, as this is exemplified by the synthesis of artemisia alcohol (run 14).[9,10] On the other hand, conjugated enones were much less reactive to give practically none of the Grignard adduct.

Functional groups other than aldehydes and ketones are unreactive toward the allylation reagent. Nitriles and esters were recovered unchanged.[11] Thus, the allyl unit was selectively introduced at the aldehyde carbon of a compound which contains either an ester or a cyano group (run 17 or 18). Epoxides were converted to halohydrins thanks to the Lewis acidity of the chromous salt, but the ketal group remained intact (run 15). The adduct thus obtained was converted to yomogi alcohol[12] upon successive treatment with polyphosphoric acid and methylmagnesium iodide.



Another characteristic of the present reducing agent is that it does not reduce alkyl, aryl, or vinyl halides (see run 9) and, therefore, it will find further applications for selective carbon-carbon bond formation.

References and Notes

(1) A. R. Pray, *Inorg. Synth.*, **3**, 153 (1954).

(2) Although a large part of the chromic chloride apparently is undissolved, a small portion of the salt seemingly dissolved. To this the spontaneous hydrogen evolution can be ascribed.

(3) In another experiment [$LiAlH_4$ (1.2 mmol), $CrCl_3$ (2.4 mmol) in THF (2 mL), PhCHO (1 mmol), and prenyl bromide (1.2 mmol)] 90% yield was estimated by GLC assay.

(4) Similar allyl transposition is observed in the reaction of allyllithium and allylmagnesium halide: (a) T. E. Stanberry, M. J. Darmon, H. A. Fry, and R. S. Lenox, *J. Org. Chem.*, **41**, 2052 (1976); (b) F. Barbot and P. Miginiac, *Tetrahedron Lett.*, 3829 (1975), but allylzinc halide gives a mixture of regioisomers.

(5) Homocoupling of allylic and benzylic halides will be published elsewhere.

(6) (a) J. R. Hanson, *Synthesis*, 1 (1974); (b) J. K. Kochi and P. E. Mocadlo, *J. Am. Chem. Soc.*, **88**, 4094 (1966); (c) C. E. Castro and W. C. Kray, Jr., *ibid.*, **88**, 4447 (1966); (d) H. Nozaki, T. Aratani, and R. Noyori, *Tetrahedron*, **23**, 3645 (1967).

(7) The strict selectivity was not observed in the reaction of allylmangesium halides or allylzinc bromide: *Houben-Weyl Methoden Org. Chem.*, **13/2a**, 290 (1973).

(8) M. Gaudemar, *Tetrahedron*, **32**, 1689 (1976).

(9) T. Takemoto and T. Nakajima, *Yakugaku Zasshi*, **77**, 1310 (1957).

(10) A large-scale synthesis of artemisia alcohol: chromic chloride (4.28 g, 27 mmol) was reduced with lithium aluminum hydride (513 mg, 13.5 mmol) in THF (20 mL). After stirring at room temperature for 10 min, 3-methyl-2-butenal (0.56 g, 6.1 mmol) and subsequently prenyl bromide (2.01 g, 13.5 mmol) in THF (10 mL) were added dropwise during the period of 20 min. Stirring for 3 h, followed by workup and distillation (97–100 °C (4 mm), Kugelrohr), gave an oil (0.90 g, 88% yield) consistent with artemisia alcohol spectrometrically.

(11) This is in sharp contrast to allylzinc bromide, which attacks esters as well: J. F. Ruppert and J. D. White, *J. Org. Chem.*, **41**, 550 (1976).

(12) W. Sucrow and W. Richter, *Chem. Ber.*, **103**, 3771 (1970).

Yoshitaka Okude, Shigeo Hirano
Tamejiro Hiyama,* Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

Received December 20, 1976

Sepulchrate: A Macrobicyclic Nitrogen Cage for Metal Ions

Sir:

Ligands which effectively encapsulate metal ions inhibit ligand substitution but offer interesting prospects for the study of intramolecular rearrangements, electron transfer, and spectroscopic properties. The ligands classified as cryptates[1] are in this category and this note describes a structure and some chemistry of cobalt complexes of an octaazacryptate ligand synthesized on the metal by condensing the tris(ethylenediamine)cobalt(III) ion with formaldehyde and ammonia, (yield >95%).

The complex (*S*)-[(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane)cobalt(III)]$^{3+}$ has been given the trivial name [Co(sepulchrate)]$^{3+}$ in keeping with the cryptate nomenclature. The crystal structure (Figure 1) confirms that synthesis occurs with retention of the chirality of the $Co(en)_3{}^{3+}$ ion and shows the sexadentate nature of the capsule with the tris(methylene) amino cap added at both ends of the parent ion. The ethylenediamine rings have the *lel* conformation and the overall symmetry is very close to D_3. Quantitative conformational analysis calculations[2] were done for this unexpected conformation and two others indicated by Dreiding models: a C_3 *lel* and a D_3 *ob*. The C_3 conformer has catoptric caps and the D_3 conformers have caps of the same chirality. The strain energy differences of the conformers are 1.4, 1.4, and 0 kcal/mol, respectively. The calculations indicate that the conformer found in the crystal is not the most stable and most likely it is stabilized by hydrogen bonding to lattice Cl^- ions. The ^1H and ^{13}C NMR spectra indicate D_3 symmetry for the ion in solution or rapid interconversion of the conformers ({^{59}Co} ^1H signals at δ 4.0 ppm, 12 protons, AB doublet pair, $J \sim 12$ Hz; δ ~3.2 ppm, complex AA′BB′ pattern, 12 protons, relative to external tetramethylsilane for the N-deuterated complex; ^{13}C spectrum shows two signals of equal intensity at δ − 0.389 ppm and δ + 13.245 ppm relative to 1,4-dioxane). The low field proton signals are assigned to the methylene caps and the complex pattern to the ethylenediamine residues.

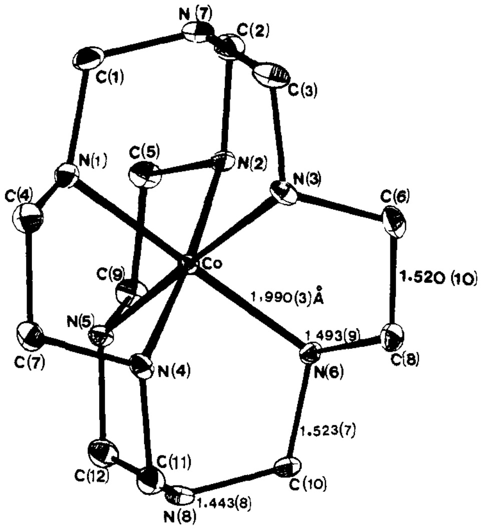


Figure 1. ORTEP diagram of Co(sepulchrate)$^{3+}$ with 20% thermal ellipsoids. Not shown are hydrogen atoms and hydrogen bonding of chlorides to cis pairs of NH groups. (The trichloride monohydrate salt crystallizes in space group $P2_12_12_1$ with a = 15.60 (1), b = 14.868 (7), and c = 8.757 (4) Å and Z = 4.) X-ray data (3166 reflections) were collected by diffractometer with monochromatic Mo Kα radiation. Anisotropic full-matrix least-squares refinement (hydrogen atoms isotropic at calculated positions) on F converged to a final R = 0.038.

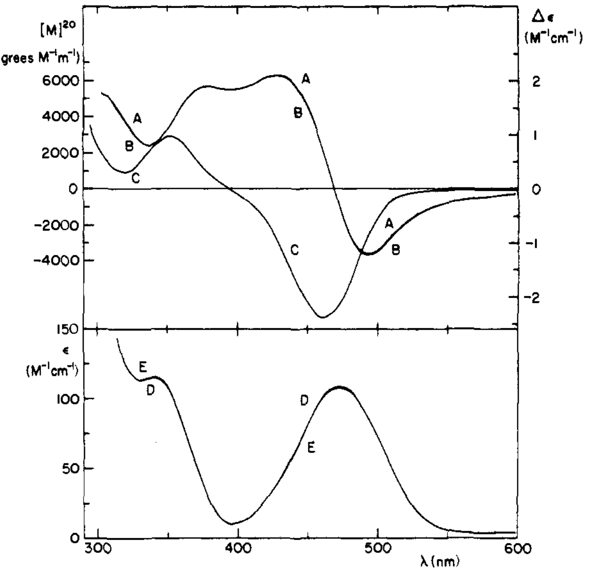


Figure 2. Rotatory dispersion (A, 0.1 M HCl), circular dichroism (C, H_2O), and visible absorption spectra (D, 0.1 M HCl) of (*S*)-[Co(sep)]$Cl_3 \cdot H_2O$. Curves B and E were obtained by oxidizing the Co(II) salt and measuring the solutions under the same conditions as A and D.

Cyclic voltammetry (100 mV/s in 0.1 M $NaClO_4$, 25 °C) showed an essentially reversible reduction wave at −0.54 V vs. the saturated calomel electrode (70 mV peak to peak, i_{pf}/i_{pb} 1.0, E^0 −0.30 V). The reduction potential is lower than that observed for $Co(en)_3{}^{2+/3+}$ (−0.45 V, irreversible) under the same conditions. E^0 for $Co(en)_3{}^{2+/3+}$ is −0.259 (1 M KCl).[3] Using Zn dust in excess the reduction to Co(II) occurs within seconds for $[H^+] = 10^{-2}$ to 10^{-7} M and the Co(II) salt was isolated as the $ZnCl_4{}^{2-}$ salt. The Co(II) ion reoxidizes with