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Reactions Involving Electron Transfer. IV. Reduction of Enones with Chromium(II) Compounds[1a]

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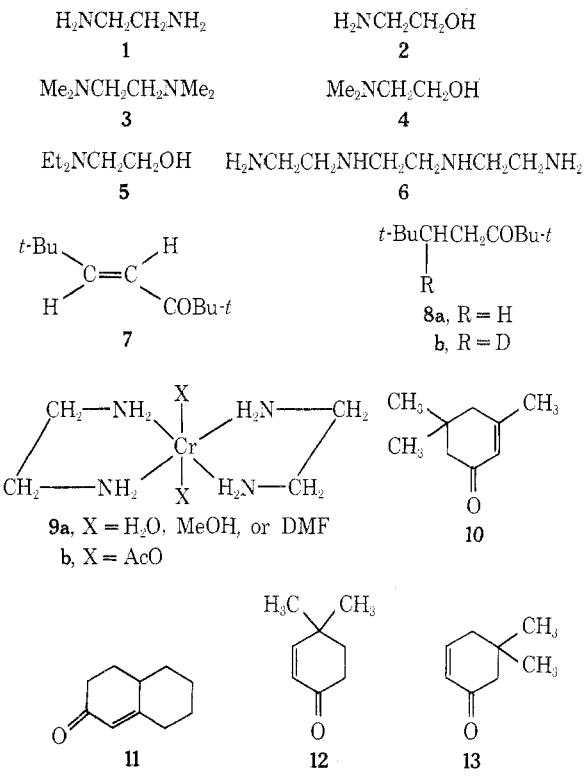
Solutions of the Cr(II) complex, $Cr(en)_2(OAc)_2$, in MeOH are capable of reducing simple α,β-unsaturated ketones to the corresponding saturated ketones. With 2-cyclohexenone derivatives **10** and **11** that contain a 3-alkyl substituent, preparatively useful yields of the reduced products may be obtained provided a proton donor (HOAc) and a good hydrogen atom donor (*n*-PrSH or *n*-BuSH) are also present in the reaction mixture. With enones **7**, **12**, and **13** that have only one β-alkyl substituent, the presence of the above additives still does not afford high yields of saturated ketones because of a competing addition of the mercaptan to the enone system. Various types of evidence are offered to support the proposal that these reductions proceed by successive reactions of the enone with 2 equiv of the Cr(II) complex to form the intermediates illustrated in Scheme III.

Solutions containing salts of the chromium(II) ion, either aquated or coordinated with various nitrogen ligands such as ammonia or ethylenediamine, have been used for the reduction of various organic compounds[2] including alkyl and aryl halides,[3b,4] certain α,β-unsaturated carbonyl compounds[3a,5] certain acetylenes,[6] and various unsaturated nitrogen compounds such as oxime acetates,[7a] azides,[7b] and nitro compounds.[7c] In connection with our earlier studies of reductions of α,β-unsaturated carbonyl compounds by processes involving successive electron transfers,[8] we wished to examine various Cr(II) derivatives as potential agents for effecting reductions of this type. Previous studies[5a,c,e,6a,b] had indicated that doubly activated multiple C–C bonds such as that present in compounds of the type RCOCH=CHCOR or RCOC≡CCOR could be reduced with solutions of $CrCl_2$ or $CrSO_4$ in water or aqueous dimethylformamide (DMF). With this reducing agent, $Cr(H_2O)_6^{2+}$, less easily reduced conjugated carbonyl compounds (*e.g.*, RCH=CHCOR) were either recovered unchanged or converted to dihydro dimers $RCOCH_2CH(R)CH(R)CH_2COR$.[5a] Studies with solutions $CrSO_4$ in aqueous NH_3, where the ion $Cr(NH_3)_4(H_2O)_2^{2+}$ was the probable reducing agent, indicated that a more powerful reducing agent was obtained when part of the H_2O ligands surrounding Cr(II) were replaced with NH_3 groups.[5b] This observation, coupled with later studies[3b,4c] demonstrating that the reducing power of Cr(II) toward alkyl and aryl halides was enhanced substantially by the presence of bidentate ligands such as the diamine **1** (en) or the amino alcohol **2**, suggested that complexes of Cr(II) with bidentate or polydentate ligands (*e.g.*, **1**–**6**, Scheme I) may be substantially more effective reducing agents for α,β-unsaturated carbonyl compounds. The present paper reports our investigation of this possibility.

Our initial studies used $Cr(ClO_4)_2$, a reagent that could conveniently be prepared in aqueous solution by reaction of aqueous $HClO_4$ with excess chromium.[3b,4d] Solutions of this reagent in aqueous DMF were ineffective in reducing unsaturated ketones such as **7** and various cyclohexenone derivatives and unchanged enones were recovered.[9] The ability of these solutions to reduce the enone **7** to the ketone **8a** was substantially enhanced by the addition of 2–3 molar equiv of one of the bidentate ligands, **1**, **3**, and **5**; the diamine **1** was especially convenient for this purpose. Previous studies of complexes of Cr(II) salts with the diamine **1** have established that these complexes have the compositions (and probably the stereochemistry) indicated in structure **9**;[4c,10] the tris complex $Cr(en)_3^{2+}$ is normally unstable in solution and decomposes to the bis complex **9** even when excess diamine **1** is present.[10] Thus, the reducing agent employed in our studies can be represented as the bis en complex **9** in which the apical ligands X are relatively labile[11] oxygen ligands such as water, MeOH, DMF, or acetate. Although solutions of the complex **9**, prepared from $Cr(ClO_4)_2$, in aqueous DMF were employed successfully for the reduction of several enones **7**, **10**, and **11** (see Experimental Section), the experimental procedure was complicated by the fact that substantial amounts of the cosolvent, DMF, were often required with the aqueous Cr(II) solution in order to dissolve the enone and separation of the reaction products from large volumes of aqueous DMF was tedious. Consequently, we were prompted to examine use of the dimeric salt, $[Cr(OAc)_2 \cdot H_2O]_2$, which is relatively insoluble in water and can be isolated as a crystalline solid.[12] Although the acetate salt was insoluble in most of the common organic solvents (see Experimental Section), after treatment with 2–3 molar equiv of one of the bidentate ligands **1** or **2** (ligands **3** and **4** were not effective) or 1 molar equiv of the tetradentate ligand **6**, a solution of the corresponding complex was obtained in several solvents, including MeOH, EtOH, *i*-PrOH, *t*-BuOH, and DMF. Among these

Scheme I



solvent and ligand combinations, we found the most convenient reagent to be a MeOH solution of the bis diamine complex designated **9b** in this paper; solutions that contained concentrations of the complex **9b** greater than 1 *M* were readily obtained.

Solutions of the Cr(II) complex **9b** in MeOH exhibited a characteristic[4c] absorption maximum at 552 mμ (ε 32) which changed to give maxima at 384 (ε 51) and 520 mμ (ε 69) after air oxidation to form the Cr(III) species. Similar values [Cr(II), λ_{max} 520 mμ (ε 45), and Cr(III), λ_{max} 380 (ε 50) and 520 mμ (ε 54)] were observed for solutions of the complex **9b** in DMF. Addition of the unhindered enone **13** to these solutions of the Cr(II) complex **9b** resulted in the appearance of a new, more intense maximum at 378 mμ (ε ~400) characteristic[4c,5b,11] of a σ alkyl-Cr(III) complex. Similar, although less intense, maxima were observed when solutions of the complex **9b** were treated with the α,β-unsaturated ketones **7**, **10**, and **12**, which possess more steric hindrance to bond formation at the β carbon. This absorption, attributable to an intermediate σ alkyl-Cr(III) complex, persisted for several hours in MeOH solution, but was rapidly discharged when HOAc was added.

The enones **7** and **11** were treated with a solution of the complex $Cr(en)_2(ClO_4)_2$ in a mixture of DMF and D_2O, and the saturated ketone products **8**, **14**, and **15** (Scheme II) were subjected to base-catalyzed exchange to remove any deuterium present at the α carbon. In each case, the saturated ketones contained *ca.* 40% of the products **8b**, **14b**, and **14b** with a single deuterium atom at the β carbon. Since each of these reaction mixtures contained both D^+ and H^+ donors[13] and the kinetic isotope effect favoring the formation of a β-C–H rather than a β-C–D bond is estimated to be *ca.* 4,[2b] these results indicated that at least half (but perhaps not all) of the saturated ketones **8**, **14**, and **15** were formed under these conditions by reaction of an intermediate with a proton donor rather than a hydrogen atom donor.

Solutions of the Cr(II) complex **9b** were examined by polarography and cyclic voltammetry to determine the redox potential for the process $Cr(en)_2(ligand)_2^{2+} \rightleftharpoons Cr(en)_2(ligand)_2^{3+} + e$.[14] The solutions of the Cr(II) complex **9b** [and the corresponding Cr(III) complexes obtained by air oxidation] in either MeOH or DMF exhibited behavior characteristic of reversible electron transfer. In DMF solution the half-wave potential was −1.77 V (*vs.* sce) and in MeOH solution the value was −1.09 V (*vs.* sce).[15] Table I lists the polarographic reduction potentials for the various ketones included in this study. In each case the reduction potential is *ca.* 0.5 V less negative in the protic solvent, MeOH, than in DMF. However, in both solvents the ketones reduced have reduction potentials (−1.5 to −1.7 V in MeOH, −2.1 to −2.2 V in DMF) 0.3 to 0.6 V more negative than the redox potential of the $Cr(en)_2^{2+}$–$Cr(en)_2^{3+}$ system (−1.1 V in MeOH, −1.8 V in DMF) and only the very difficultly reduced ketone **20** (−2.4 V in DMF, −1.9 V in MeOH) was recovered unchanged. We believe that this difference between the re-

Scheme II

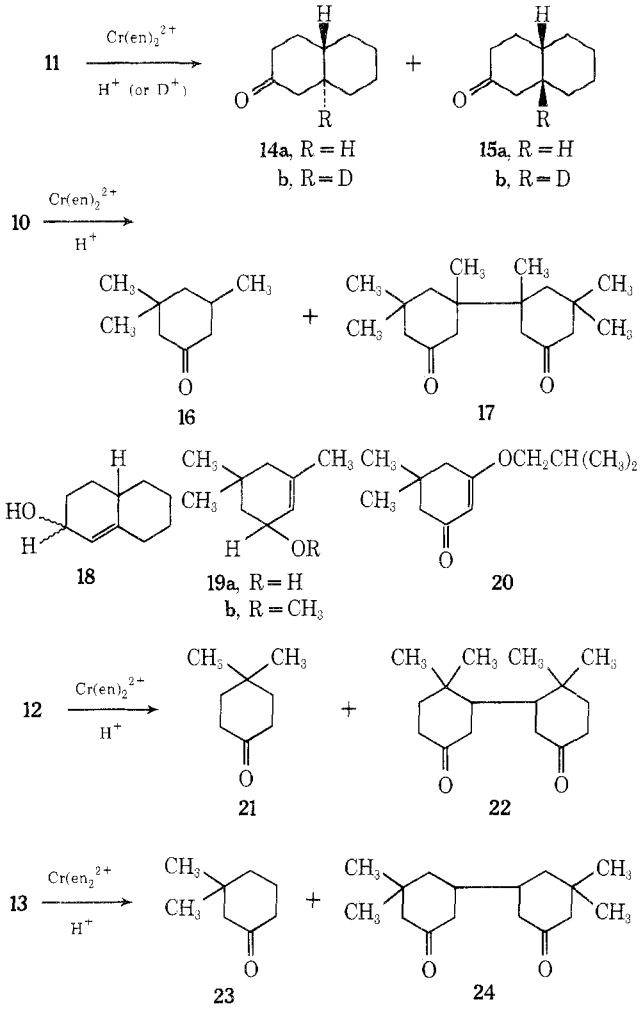
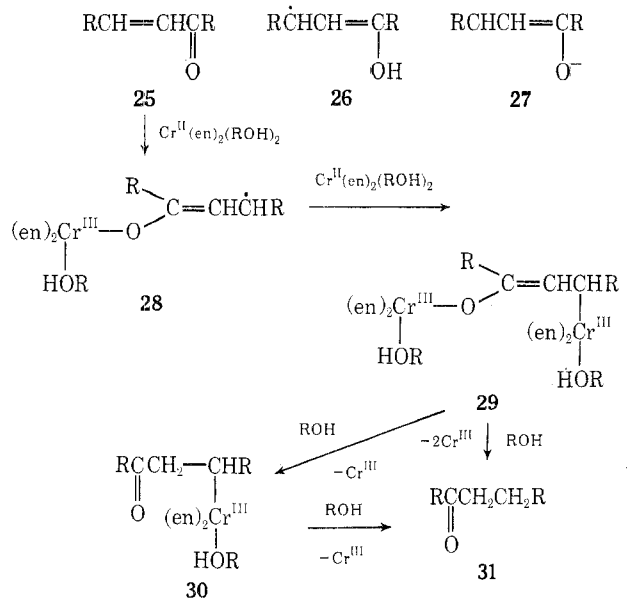


Table I
Polarographic Reduction Potentials of the Enones Studied

Ketone	Reduced with $Cr^{II}(en_2)$	$E_{1/2}$, V *vs.* sce: In DMF[a]	$E_{1/2}$, V *vs.* sce: In MeOH[a]
7	Yes	−2.22	−1.76
10	Yes	−2.24[b]	−1.65
11	Yes	−2.15	−1.67
12	Yes	−2.1[c]	−1.57
13	Yes	−2.1[c]	−1.56
20	No	−2.43	−1.92

[a] *n*-$Bu_4N^+BF_4^-$ (0.5 *M*) was employed as the supporting electrolyte. [b] When 0.1 *M* H_2O was present, the $E_{1/2}$ value was −2.19 V. [c] Estimated value; see ref 8c.

Scheme III

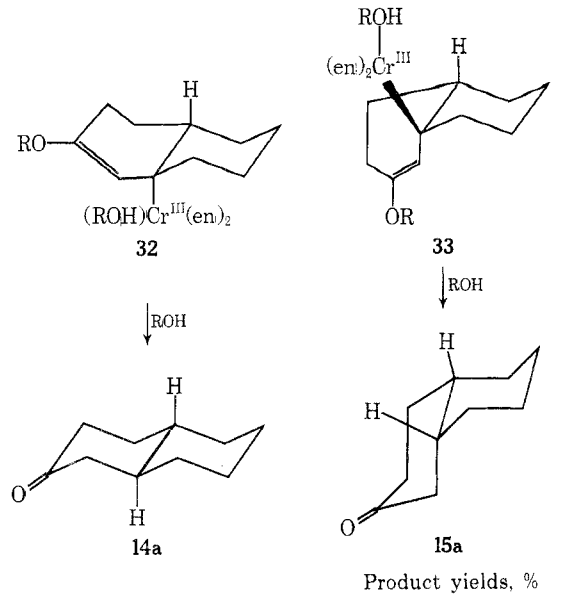


duction potentials (*ca.* 0.5 V or 12 kcal/mol) of the Cr(III) species and the enones (*e.g.*, **25**, Scheme III) is sufficient to exclude the reaction proceding by transfer of only an electron from the Cr(II) species (an outer-sphere electron transfer) to the enone to form directly either the anion radical **27** (as from electrochemical reduction in DMF) or the protonated anion radical **26** (as from electrochemical reduction in MeOH).

Instead, it seems most likely that the initial electron transfer involves the enone **25** entering the coordination sphere of the Cr(II) (an inner-sphere electron transfer) as indicated in Scheme III to form the Cr(III) species **28** (where ROH is MeOH or HOAc). This species **28**, an allylic radical, would be expected to react with a second $(en)_2Cr(II)$ ion to form the alkyl-Cr(III) intermediate **29** in a reaction analogous to that observed[2b,4,11] with alkyl radicals and Cr(II) complexes. The further hydrolysis (or alcoholysis) of the intermediate **29** [or the related β-keto alkyl-Cr(III) intermediate **30**] would then yield the reduced product **31**. This reaction path (Scheme III), which is in many respects analogous to the scheme operative in the reduction of alkyl halides with Cr(II) complexes,[2b,4] accounts for the spectroscopically observed alkyl-Cr(III) intermediate, for the formation of β-deuterio ketones **8b**, **14b**, and **15b** in those reactions where part of the proton donor present was replaced with D_2O, and for the ability of the Cr(II) complex to reduce enones with reduction potentials more negative than that of the corresponding Cr(III) complex. The suggested reaction path is also consistent with the data obtained from a kinetic study[6b] of the related reduction of acetylenedicarboxylic acid to fumaric acid with aquated chromium(II) ion. This study[6b] provided kinetic evidence for the reaction of the unsaturated carbonyl compound with 2 mol of the solvated chromium(II) ion to form an organochromium intermediate that hydrolyzed to form the reduced product and chromium(III) ion.

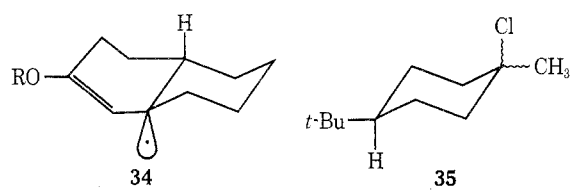
In many respects the reaction pathway suggested in Scheme III also parallels the pathway suggested for the reductions of enones with alkali metals in liquid NH_3 or other solvents[8a,b,16] in that an intermediate enol derivative with an ionic or covalent carbon–metal bond at the β carbon appears to be involved. In this context, the Cr(II) reduction of enones represents a special case of an enone dissolving-metal reduction in which the intermediate **29** (or **30**) possesses a carbon–metal bond that is relatively

Scheme IV



Product yields, %

Reaction conditions	14a	15a
$Cr^{II}(en)_2$, HOAc, MeOH	16	13
$Cr^{II}(en)_2$, MeOH, HOAc, *n*-PrSH	57	11

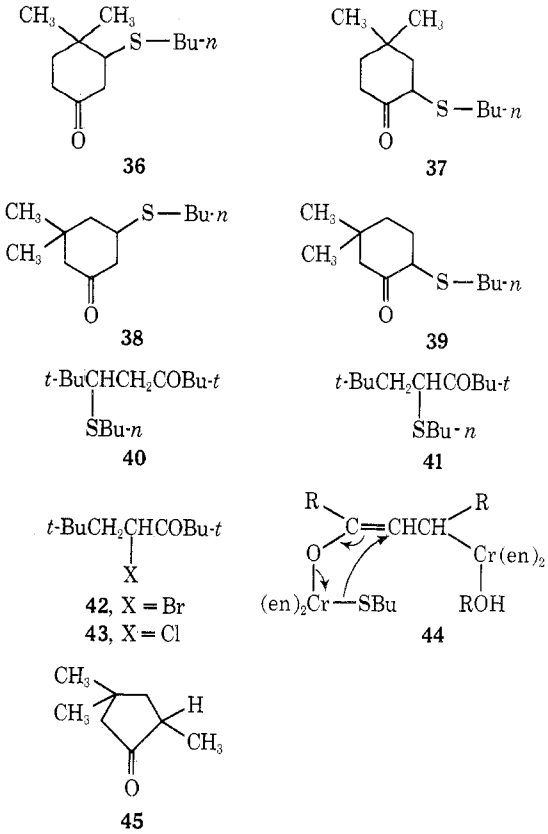


stable even in proton-donating media. For this reason, it was of interest to examine the stereochemistry of the reduction of the octalone **11**, since in typical alkali metal reductions more than 98% of the reduced product is the trans isomer **14a**.[8b,16] However, if relatively stable β-ketoalkyl-Cr(III) intermediates such as **32** and **33** (Scheme IV) are produced, the formation of the intermediate **33** with the bulky Cr(III) group in an equatorial conformation rather than an axial conformation (as in **32**) should be more favorable. Subsequent protonolysis of the carbon–metal bond with retention of configuration should then increase substantially the proportion of the cis ketone **15a** in the reduction product. In fact, the decalone mixture obtained from reduction of the octalone **11** with $Cr^{II}(en_2)$ in MeOH containing HOAc contains 55% of the trans (**14a**) and 45% of the cis (**15a**) ketones.

Although these results support the idea of an intermediate alkyl-Cr(III) intermediate such as **29** or **30** in the reduction sequence, the yields of monomeric reduction products (*e.g.*, **14**, **15**, **16**, **21**, and **23**) from the corresponding enones were often disappointingly low (15–40%; the reduction of enone **7** to **8** in 81% yield was exceptional). In most cases the low yields were the result of two competing side reactions. One side reaction was the competing dimerization of an intermediate radical species (*e.g.*, **28**) to form mixtures of diastereoisomeric dihydro dimers such as **17**, **22**, and **24**. This side reaction, which presumably occurs because the rate of dimerization of the radical **28** is competitive with the trapping of this radical by a second molecule of the Cr(II) complex, is reminiscent of a common side reaction (dimerization of **26**) observed in the electrochemical reduction of enones.[8a,b]

A second, less well-defined competing process involved reaction of the starting enone with the diamine ligand **1** to form one or more basic products that were soluble in

Scheme V



aqueous acid. Although our efforts to isolate and characterize pure substances from these crude basic products were not productive, control experiments in the absence of Cr(II) indicated that a substantial fraction of the unhindered enones (*e.g.*, **12**) was consumed in such competing reactions.

In an effort to overcome these yield-lowering side reactions, we explored the addition to the reaction mixture of various efficient H-atom donors that might serve to intercept the intermediate radical **28**.[4b,c] Among the H-atom donors examined (see Experimental Section), the mercaptans *n*-PrSH and *n*-BuSH proved to be especially effective and completely eliminated the formation of the dihydro dimers **17**, **22**, and **24**. With a reaction mixture composed of 1 molar equiv of the enone, 3–4 molar equiv of the Cr(II) complex **9b**, 3 molar equiv of *n*-BuSH (or *n*-PrSH), and 5 molar equiv of HOAc in MeOH solution, the yields of monomeric, saturated ketonic products were improved substantially in all cases. With the α,β-unsaturated ketones **10** and **11** possessing two β-alkyl substituents, the yields (68–79%) of reduction products **14–16** were sufficient to make this reduction procedure preparatively useful. The change in stereochemical results (85% trans ketone **14a** and 15% cis ketone **15a**) obtained from the reduction of the octalone **11** in the presence of *n*-PrSH suggests that at least part of the increased yield in these cases is attributable to trapping the intermediate *tert*-alkyl radical (*e.g.*, **34**) by an axial H-atom transfer from the mercaptan to form additional trans ketone **14a**. This stereochemical change is analogous to that seen in the reduction of either stereoisomer of the *tert*-alkyl chloride **35** with $(en)_2Cr(ClO_4)_2$ in the presence or absence of *n*-BuSH[4f] in that H-atom transfer to a cyclohexyl radical from an axial direction was favored. Although we were unable to obtain evidence supporting the view, it is possible that part of the increased yield of monomeric reduction products in the presence of mercaptans is attributable to a more rapid reduction by a Cr(II) species with the mercaptan as one of the ligands.

Although the addition of *n*-BuSH also improved the yields of saturated ketones **21** and **23** obtained from the enones **12** and **13**, in each of the Cr(II) reductions of an α,β-unsaturated ketone **7**, **12**, and **13** with a single β-alkyl substituent, a new set of side reactions was observed when *n*-BuSH was added. From each of these reactions, two new thio ether products **36–41** (Scheme V) appeared as by-products. Appropriate control experiments indicated that the β-keto sulfides **36**, **38**, and **40** could arise by at least two likely processes. In the presence of the basic diamine **1** (but not in neutral solution), *n*-BuSH added to each of the enones **7**, **12**, and **13** to form the corresponding β-keto sulfide in a reaction that is very likely a Michael addition of the *n*-BuS^- anion. Each enone also underwent a slow addition of *n*-BuSH to form only the corresponding β-keto sulfide in a free-radical chain reaction[17] catalyzed by azoisobutyronitrile. However, neither of these processes accounts for the formation of the minor α-keto sulfides **37**, **39**, and **41**. An appropriate control experiment also indicated that formation of the α-keto sulfide **41** could not be attributed to addition of *n*-BuSH to the enone **7** in a reaction catalyzed[18] by the Cr(III) species generated by the reduction. It therefore appears that some intermediate formed during the reduction process is responsible for the formation of the α-keto sulfide by-products. One possibility is that illustrated in structure **44**, in which the intermediate chromium enolate serves to transfer a mercaptide group to the α-carbon atom. In any case, the presence of these thio ether by-products clearly makes this procedure [Cr(II) complex + *n*-BuSH] an unattractive method for the reduction of relatively unhindered α,β-unsaturated ketones containing a single β-alkyl substituent.

Finally, we wish to note one other minor by-product, the cyclopentanone **45** (Scheme V), that was observed in the reduction of the enone **13** with the Cr(II) complex **9b** in the absence of *n*-BuSH. This enone reduction with accompanying rearrangement has been observed previously during the reduction of enones with metals in acidic media (*e.g.*, the Clemmensen reduction).[19,20]

Experimental Section[21]

Preparation of the Chromium(II) Reagents. Aqueous solutions of $Cr(ClO_4)_2$ were prepared by stirring excess Cr with aqueous 1.4 *M* $HClO_4$ at 35–40° for 8 hr.[3b,4b] The resulting deep blue solutions were siphoned from the excess Cr and stored under N_2. Aliquots of these solutions were standardized as previously described;[3b,22] the concentration of $Cr(ClO_4)_2$ was 0.490–0.720 *M*. The quantity of Cr(III) salts in these solutions was determined by passing standardized solutions of $Cr(ClO_4)_2$ through a column of amalgamated zinc [a Jones reductor[3a,12] to reduce any Cr(III) to Cr(II)[5]]. Typically, a passage of aqueous 0.720 *M* $Cr(ClO_4)_2$ over zinc amalgam followed by titration indicated the total Cr(II) concentration to be 0.768 *M*, corresponding to 0.048 *M* Cr(III) salts in the stock solution.

The relatively insoluble $Cr(OAc)_2 \cdot H_2O$ was obtained by a modification of previous procedures[12] in which aqueous $Cr(ClO_4)_2$ was treated with boiling aqueous NaOAc in a flask fitted with a coarse sintered glass disk. The mixture was agitated with N_2 passed through the sintered glass disk; then the solid $Cr(OAc)_2 \cdot H_2O$ was collected on the sintered glass and washed successively with three portions of H_2O, two portions of EtOH, and Et_2O, all under N_2. Finally, the sample was dried under reduced pressure and stored under nitrogen. In a typical preparation, the $Cr(OAc)_2 \cdot H_2O$ was obtained as a bright red solid in 94% yield. Although this product dissolved in DMSO to form a purple solution (*ca.* 1 *M*), it was not soluble in preparatively useful concentrations in any of the following solvents: H_2O, MeOH, EtOH, *i*-PrOH, *t*-BuOH, acetone, MeCN, DMF, or HMPA. However, when amounts of the diamine **1** greater than 2 mol/mol $Cr(OAc)_2$ were added, purple solutions of the complex **9b** were obtained in all of the previous solvents except acetone, MeCN, and HMPA.

In MeOH and in *i*-PrOH, it was necessary to add 2.4 molar equiv of the diamine **1** to form 1 *M* solutions of the Cr(II) complex **9b**; in DMF a 3 *M* solution was obtained by the addition of 3.3 molar equiv of the diamine **1**. Complexes soluble in MeOH were not obtained with either of the ligands, the amino alcohol **4** or the diamine **3**. However, a purple solution was obtained from 6.4 mmol of $Cr(OAc)_2$, 3.5 ml of MeOH, and 31 mmol of the amino alcohol **2**. Also, the addition of 66 mmol of aqueous 28% NH_3 to 6.4 mmol of $Cr(OAc)_2$ and 3.5 ml of MeOH afforded a deep blue solution of the corresponding complex.

A solution of the complex **9b** in MeOH exhibited λ_{max} 552 mμ (ε 32) [lit.[4c] in H_2O–DMF λ_{max} 550 mμ (ε 25)]. After exposure to air for 1 hr the resulting $Cr^{III}(en)_2$ solution exhibited maxima at 384 (ε 51) and 520 mμ (ε 69) [lit.[4c] in DMF–H_2O λ_{max} 380 (ε 59) and 510 mμ (ε 75)]. In DMF solution the maximum for the Cr(II) complex **9b** was at 520 mμ (ε 45), and, after air oxidation, the Cr(III) complex had maxima at 380 (ε 50) and 520 mμ (ε 54). A similar solution prepared from $Cr(ClO_4)_2$ and 3 equiv of the diamine **1** in DMF containing 0.5 *M* H_2O exhibited a maximum at 538 mμ (ε 51); after air oxidation to Cr(III) the maxima were at 386 (ε 80) and 534 mμ (ε 93). When a 0.045 *M* solution of this complex **9b** in MeOH was treated with the relatively unhindered ketone **13** (0.022 *M*), a new, more intense absorption appeared with maxima at 378 (ε ~400) and 516 mμ (ε ~130) corresponding to the species $RCr^{III}(en)_2$ [lit.[4c] in DMF–H_2O λ ~400 mμ (ε ~500)]. From a comparable experiment in DMF solution, maxima were observed at 380 (ε ~250) and 536 mμ (ε ~100). In MeOH solution these new peaks slowly disappeared and after several hours the spectrum of the solution corresponded to $Cr^{III}(en)_2$. Comparable spectral changes were observed when $CH_3COCH{=}CH_2$ was added to a solution of the complex **9b** and less intense but related spectral changes were seen upon addition of the complex to the hindered enones **7**, **10**, and **12**. Although the intensities of the new $RCr^{III}(en)_2$ absorptions decayed only over a period of hours in MeOH solution with or without added *n*-BuSH, this absorption was discharged rapidly by the addition of HOAc.

Polarographic Measurements. The measurements of oxidation and reduction potentials by polarography (at a dropping Hg electrode) and by cyclic voltammetry (at a spherical Hg-coated Pt electrode) were obtained with the apparatus and reference electrodes (saturated calomel with intermediate salt bridges containing aqueous 1 *M* $NaNO_3$ and 0.5 *M* $Et_4N^+BF_4^-$ in DMF) described previously.[23] The supporting electrolytes and solvents were either 0.5 *M* *n*-$Bu_4N^+BF_4^-$ in purified[23] DMF or 0.5 *M* *n*-$Bu_4N^+BF_4^-$ in purified[24] MeOH. In DMF solution, the $E_{1/2}$ values (*vs.* sce) measured polarographically for the various enones follow: **10** (2.3 m*M*), −2.24 V (α*n* = 1.2, i_d = 17.4 μA); **11**, −2.15 V;[8c] **7**, −2.22 V;[8] **14**, −2.43 V.[8c] Repetition of this measurement for ketone **10** (2.4×10^{-3} *M*) in DMF containing 0.1 *M* H_2O gave an $E_{1/2}$ value of −2.19 V (α*n* = 0.9, i_d = 19 μA). The $E_{1/2}$ values (*vs.* sce) determined polarographically in MeOH solution follow: **10** (8.8–10.1 m*M*), −1.65 V (α*n* = 0.9, i_d = 5.3–6.6 μA); **11** (11.5–15.5 m*M*), −1.67 V (α*n* = 0.7, i_d = 6.5–11 μA); **7** (4.3–5.6 m*M*), −1.76 V (α*n* = 0.7, i_d = 2.7–3.5 μA); **13** (4.7–6.4 m*M*), −1.56 V (α*n* = 0.9, i_d = 3.2–3.4 μA); **12** (2.9–4.6 m*M*), −1.57 V (α*n* = 0.9, i_d = 1.8–3.1 μA); **14** (7.8–8.3 m*M*), −1.92 V (α*n* = 0.9, i_d = 5.5–7.6 μA). Thus, the reduction potentials of all these ketones are *ca.* 0.5 V less negative in MeOH than in DMF solution.

Polarographic reduction of a DMF solution containing 0.5 *M* *n*-Bu_4NBF_4, 4.9 m*M* Cr(II) and Cr(III) species [from $Cr(ClO_4)_2$], and 0.5 *M* H_2O gave $E_{1/2}$ = −1.51 V (*vs.* sce, α*n* = 0.6, i_d = 13 μA). The irreversible nature of this reduction was indicated by cyclic voltammetry ($E_{1/2} \cong -1.60$ V) since no oxidation peak was observed. The corresponding polarographic reduction of a DMF solution containing 0.5 *M* *n*-Bu_4NBF_4, 4.9 m*M* $(en)_2Cr(II)$ and $(en)_2Cr(III)$ species [from $Cr(ClO_4)_2$ and 3 molar equiv of the diamine **1**] and 0.5 *M* H_2O gave $E_{1/2}$ = −1.89 V (*vs.* sce, α*n* = 1.0, i_d = 11 μA). When the latter measurement was repeated with the mole ratios Cr(II):diamine **1** equal to 1.0, 2.0, and 4.0, the corresponding $E_{1/2}$ values were −1.85, −1.86, and −1.93 V. Solutions of the complex **9b** [6.6 m*M* from $Cr(OAc)_2 \cdot H_2O$ and 3 molar equiv of the diamine **1**] and 0.5 *M* *n*-Bu_4NBF_4 in MeOH and in DMF were also measured.

In DMF solution a reversible wave [Cr(III) ⇄ Cr(II)] for the complex **9b** was observed at −1.77 V (α*n* = 0.8, i_d = 2.0 μA) followed by an irreversible wave [presumably Cr(II) → Cr(0)] at −2.13 V (α*n* = 0.5, i_d = 5.6 μA). The nature and reversibility of the first wave were substantiated by cyclic voltammetry, since the locations of the peak currents, i_{pa} and i_{pc}, were the same with solutions containing (spectrophotometric analysis) the Cr(II) and Cr(III) species and the ratio i_{pc}/i_{pa} did not vary with scan rate. When the DMF solution of the complex **9b** was obtained from 0.027 *M* $Cr(OAc)_2$ and 0.081 *M* diamine **1**, cyclic voltammetry indicated an $E_{1/2}$ value of −1.64 V; a similar measurement with a solution obtained from 0.017 *M* $Cr(OAc)_2$ and 0.81 *M* diamine **1** gave an $E_{1/2}$ value of −1.59 V. The second reduction wave (at −2.13 V) exhibited no current peak on reoxidation and the peak reduction current, i_{pc}, rapidly diminished on repetitive scans. In MeOH solution, a 12 m*M* solution of the Cr(II) complex **9b** exhibited an oxidation wave at *ca.* −1.07 V. These measurements in MeOH were complicated by erratic behavior of the dropping Hg electrode. The $E_{1/2}$ value was better determined by cyclic voltammetry where reversible behavior was observed with solutions containing (spectrophotometric analysis) either complexes of Cr(II) or complexes of Cr(III). With a MeOH solution obtained from 0.026 *M* $Cr(OAc)_2$ and 0.078 *M* diamine **1**, the $E_{1/2}$ value was −1.10 V; when the concentrations were 0.026 *M* $Cr(OAc)_2$ and 0.78 *M* diamine **1**, the $E_{1/2}$ value was −1.17 V.

Reduction of Isophorone (10). A. General Procedure in MeOH Solution. When a suspension of 32.0 g (175 mmol) of $Cr(OAc)_2 \cdot H_2O$ in 100 ml of MeOH was treated with 24.5 g (405 mmol, 2.3 molar equiv) of the diamine **1**, the Cr(II) salt dissolved and the solution (which initially warmed to 55°) was stirred at 50° for 10 min. (If the precaution of stirring this solution for 10 min to complete the formation of the Cr(II) complex **9b** before adding the remaining reactants was not observed, substantial amounts of the subsequently described by-products **19a** and **19b** were present in the final product.) The resulting solution was treated with 13.5 g (16.3 ml, 150 mmol) of *n*-BuSH, cooled to 30°, treated with 15.0 g (250 mmol) of HOAc, and again cooled to 28°. To the resulting purple solution was added, with stirring and external cooling, 7.00 g (51 mmol) of isophorone (**10**) and the reddish-purple reaction mixture was stirred at 25° for 24 hr. The resulting magenta-colored solution was treated with 200 g of ice and 200 ml of H_2O and then acidified to pH 2–3 with aqueous 6 *M* HCl, saturated with NaCl, and extracted with five 75-ml portions of Et_2O. The Et_2O extract was washed successively with aqueous $NaHCO_3$ and H_2O and then dried and concentrated to leave 12.3 g of crude product as a colorless liquid containing (glpc, Carbowax 20 M on Chromosorb P) *n*-BuSH (retention time 1.9 min), the saturated ketone **16** (9.1 min), *n*-BuSSBu-*n* (16.9 min), and a small amount of the starting ketone **10** (19.5 min) as well as several minor unidentified components. Fractional distillation separated 0.61 g of a fraction, bp 25–27° (14 mm), containing (glpc) mainly *n*-BuSH, 5.39 g of the saturated ketone **16**, bp 78–82° (6 mm), $n^{25}D$ 1.4452 [lit.[25] bp 73–74° (14 mm), $n^{20}D$ 1.4461], and 2.70 g of a fraction, bp 75–77° (1.6 mm), containing (glpc) mainly *n*-BuSSBu-*n* accompanied by lesser amounts of ketones **10** and **16**. Redistillation of the latter fraction separated an additional 0.21 g of the saturated ketone **16** (total yield 5.60 g, 79%); this product was identified with an authentic sample by comparison of glpc retention times and ir and nmr spectra. Various related reductions of the enone **10**, summarized in Table II, were performed in which the mode of formation of the complex **9b** was varied and in which no *n*-BuSH was added. When the amount of *n*-BuSH was lowered from the usual 3–5 mol/mol of enone **10** to 1.2 mol of *n*-BuSH/mol of **10**, the yield of the reduction product **16** was lowered to 40%. For glpc analysis (Carbowax 20 M on Chromosorb P), the crude products were mixed with *n*-$C_{15}H_{32}$ (internal standard) and analyzed on equipment calibrated with known mixtures of authentic samples. In a mixture containing the ether **19b**, the glpc retention times follow: ether **19b** (8.0 min), ketone **16** (13.3 min), *n*-BuSSBu-*n* (24.5 min), and ketone **10** (28.2 min). Collected (glpc) samples of the ketones **10** and **16** were identified with authentic samples by comparison of glpc retention times and ir spectra. A collected (glpc) sample of *n*-BuSSBu-*n* was obtained as a colorless liquid: ir (CCl_4) no peaks in the 3- or 6-μ regions attributable to OH, C=O, or C=C; nmr (CCl_4) δ 2.3–2.8 (4 H, m, CH_2S), 1.1–2.0 (8 H, m, CH_2), and 0.7–1.1 (6 H, m, CH_3); mass spectrum *m/e* (rel intensity) 180 (32), 179 (38), 178 (M^+, 100), 124 (29), 122 (78), 89 (20), 88 (32), 87 (34), 79 (29), 59 (31), 57 (78), 55 (36), 47 (28), 45 (24), 44 (28), 42 (34), and 41 (47). *Anal.* Calcd for $C_8H_{18}S_2$: mol wt, 178.0850. Found: 178.0875.

An authentic sample of *n*-BuSSBu-*n*, prepared in 63% yield by a published procedure,[26] was obtained as a colorless liquid, bp 84–85° (4 mm), $n^{25}D$ 1.4910 [lit.[26] bp 120–123° (25 mm), $n^{20}D$ 1.4926], that was identified with the previously described material by comparison of ir and nmr spectra and glpc retention times.

A collected (glpc) sample of the ether **19b** was obtained as a colorless liquid: ir (CCl_4) 1635 and 1670 cm^{-1} (weak, C=C); nmr

Table II
Reduction of α,β-Unsaturated Ketones with Various Chromium(II) Compounds

Ketone (mmol)	Cr(II) salt (mmol)	Diamine 1, mmol	Additives (mmol)	Solvent (ml)	Reaction time, hr	Reaction temp, °C	Products (yield, %)
10 (51)	$Cr(OAc)_2$ (175)	405	*n*-BuSH (150) + HOAc (250)	MeOH (100)	24	25	*n*-BuSSBu-*n*[a] + **16** (79%)[b]
10 (11)	$Cr(OAc)_2$ (35)	81	*n*-BuSH (30) + HOAc (50)	MeOH (20)	24	25[c]	*n*-BuSSBu-*n*[a] + **16** (84)[a]
10 (25)	$Cr(OAc)_2$ (75)	203	*n*-BuSH (75) + HOAc (125)	MeOH (45)	12	25[d]	*n*-BuSSBu-*n*[a] + **16** (61)[a] + **19b**[a]
10 (87)	$Cr(OAc)_2$ (304)	705	HOAc (435)	MeOH (175)	4	25	**16** (1.2)[a] + **19a**[a] + **19b** (~6)[a] + **17** (2)[b]
10 (22)	$Cr(ClO_4)_2$ (64)	192		DMF (75) + H_2O (150)	3	25	**16** (26)[a] + **17** (5)[b]
11 (21)	$Cr(OAc)_2$ (69)	162	*n*-PrSH (60) + HOAc (90)	MeOH (35)	24	25	*n*-PrSSPr-*n*[a] + **14a** (48)[b] + **15a** (8)[b]
11 (6.7)	$Cr(OAc)_2$ (23)	54	*n*-PrSH (20) + HOAc (33)	MeOH (15)	2	28–35	*n*-PrSSPr-*n*[a] + **14a** (57)[a] + **15a** (11)[a]
11 (2.6)	$Cr(OAc)_2$ (12)	28	HOAc (18)	MeOH (7)	24[e]	0–5	**14a** (16)[a] + **15a** (13)[a] + **18**[a,f]
11 (6.7)	$Cr(ClO_4)_2$ (21)	60		DMF (25) + H_2O (50)	20	25	**14a** (23)[a] + **15a** (19)[a]
7 (18)	$Cr(OAc)_2$ (84)	195	HOAc (90)	MeOH (40)	24	25	**8a** (81)
7 (18)	$Cr(OAc)_2$ (63)	54	*n*-BuSH (54) + HOAc (90)	MeOH (40)	24	25	**8a** (23)[b] + *n*-BuSSBu-*n*[a] + **40**[a] + **41**[a]
7 (1.07)	$Cr(ClO_4)_2$ (2.6)	8.2		DMF (15) + H_2O (5)	0.3	25	**8a** (72)[a]
13 (40)	$Cr(OAc)_2$ (144)	324	HOAc (200)	MeOH (82)	3.5	25	**23** (4)[a] + **24** (3)[b] + **45** (0.4)[a]
13 (24)	$Cr(OAc)_2$ (84)	194	*n*-BuSH (72) + HOAc (120)	MeOH (50)	23	25	*n*-BuSSBu-*n*[a] + **23** (18)[b] + **38**[a] + **39**[a]
20 (20)	$Cr(OAc)_2$ (70)	160	*n*-PrSH (60) + HOAc (100)	MeOH (35)	24	25	**20** (86% recovery)[a]
12 (32)	$Cr(OAc)_2$ (113)	261	HOAc (160)	MeOH (65)	14	25	**21** (20)[b] + **22** (2)[b]
12 (32)	$Cr(OAc)_2$ (113)	261	*n*-BuSH (97) + HOAc (160)	MeOH (65)	23	25	*n*-BuSSBu-*n*[a] + **21** (47)[b] + **36**[a] + **37**[a]

[a] Determined by glpc analysis. [b] Determined by isolation. [c] In this experiment the complex **9b** was formed at temperatures below 25°. [d] In this experiment the reactants were all added rapidly with cooling without allowing an initial 10-min reaction period to form the complex **9b**. [e] This reaction was performed in the dark. [f] The identification of these alcohol by-products **18** is only tentative.

(CCl_4) δ 5.4 (1 H, broad, vinyl CH), 3.5–3.8 (1 H, m, allylic CHO), 3.25 (3 H, s, OCH_3), 1.1–2.0 (7 H, m, CH_2 and allylic CH_3), 0.99 (3 H, s, CH_3), and 0.89 (3 H, s, CH_3); mass spectrum *m/e* (rel intensity 154 (M^+, 20), 139 (100), 107 (35), 99 (32), 84 (35), 83 (35), 58 (35), and 41 (80). *Anal.* Calcd for $C_{10}H_{18}O$: mol wt, 154.1358. Found: 154.1366. Isophorone (**10**) was reduced with $LiAlH_4$ as previously described[27] to yield 94% of the allylic alcohol **19a** as a colorless liquid: bp 93–94° (15 mm); $n^{25}D$ 1.4705 [lit.[27] bp 95–100° (25 mm), $n^{24}D$ 1.4731]; ir (CCl_4) 3600, 3340 (OH), and 1670 cm^{-1} (weak, C=C); nmr (CCl_4) δ 5.4 (1 H, broad, vinyl CH), 4.1 (1 H, broad, allylic CHO), 3.20 (1 H, OH, exchanged with D_2O), 1.1–2.1 (7 H, m, CH_2 and vinyl CH_3), 1.00 (3 H, s, CH_3), and 0.89 (3 H, s, CH_3); mass spectrum *m/e* (rel intensity), 122 (49), 107 (100), 105 (20), 91 (55), 79 (28), 58 (41), 44 (25), and 43 (57). When a solution of 1.00 g of this alcohol **19a** in 15 ml of MeOH was diluted with 200 ml of H_2O, acidified to pH 2 with HCl, and subjected to the previously described isolation procedure used in the Cr(II) reductions, the crude product recovered (0.96 g) corresponded (nmr analysis) to a mixture of the alcohol **19a** and the ether **19b**. The glpc curve of the mixture exhibited two rapidly eluted peaks (presumably dienes from elimination in the injection port) and a peak corresponding in glpc retention time to the ether **19b**.

In an experiment where no *n*-BuSH was added, the crude product was distilled to separate a fraction [bp 56–62° (6 mm)] containing the ketone **16**, the alcohol **19a**, and the ether **19b**. The residue from the distillation was triturated with hexane to separate 152 mg (2%) of a mixture of dihydro dimers **17**, mp 154–162°. Fractional crystallization from EtOH separated 111 mg of the higher melting isomer, mp 163–164.5° (lit.[28] mp 163°), and 10 mg of the lower melting isomer, mp 121–123° (lit.[28] mp 123–124°). Each of these materials was identified with an authentic sample by a mixture melting point determination and by comparison of ir spectra. Authentic samples of the two diastereoisomeric dihydro dimers **17** were obtained by the previously described procedure.[28] The isomer, mp 164–164.5°, had the following spectra properties: ir (CCl_4), 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.2–2.6 (12 H, m, including one resolved AB quartet with J = 14 Hz at *ca.* 1.42 and 1.80, CH_2), 1.09 (12 H, s, CH_3), and 1.04 (6 H, s, CH_3); mass spectrum *m/e* (rel intensity) 139 (100), 125 (30), 83 (53), and 55 (36). The spectral properties of the isomer, mp 120–121°, are ir (CCl_4) 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.2–2.6 (12 H, m, including a resolved AB quartet with J = 14 Hz at *ca.* 1.45 and 1.82, CH_2), and 1.09 (18 H, s, CH_3).

B. General Procedure with DMF and Other Solvents. Although a variety of attempts to reduce various cyclohexenone derivatives with solutions of $Cr(ClO_4)_2$ in aqueous DMF without added nitrogen-containing ligands resulted in no evidence of reduction,[9] these reductions were at least partially successful in the presence of added diamine **1**. For example, a solution of 64 mmol of $Cr(ClO_4)_2$ in 150 ml of H_2O and 75 ml of deoxygenated DMF was treated with 11.5 g (192 mmol) of the diamine **1** and the resulting violet solution was treated with 3.0 g (22 mmol) of isophorone (**10**). After the mixture had been stirred at 25° for 3 hr, it was subjected to the usual isolation procedure to separate 1.32 g of crude product as a pale yellow liquid from which the crystalline dihydro dimer **17** separated. Trituration with hexane separated 0.15 g (5%) of the crude dihydro dimer **17**, mp 159.5–161°. Recrystallization (EtOH) afforded the one epimer of the dihydro dimer **17** as white plates, mp 166.5–167°, identified by comparison of ir and nmr spectra. The mother liquors remaining after separation of the dimer **17** contained (glpc) a mixture of the ketones **10** (7% recovery) and **16** (26% yield) as well as a number of minor unidentified components. A collected (glpc) sample of the ketone **16** was identified with an authentic sample by comparison of glpc retention times and mass spectra. A comparable result was ob-

tained when the reduction of ketone **10** was performed with $Cr(ClO_4)_2$, and the diamine **1** in aqueous THF. An attempt to reduce isophorone (**10**) with a solution of $Cr(OAc)_2$ in DMSO[29] resulted only in recovery of the unchanged ketone **10.** A series of reductions of isophorone (**10**) with the Cr(II) complex **9b** in the solvents DMF, DMSO, HOAc, PhOH, *i*-PrOH, or an *i*-PrOH–HOAc mixture and with the complex formed from $Cr(OAc)_2$ and the triamine **6** in MeOH gave results similar to the previously described reduction in MeOH with no added *n*-BuSH in that low yields (5–10%) of mixtures of reduction products **16** and **17** were obtained. Similar poor yields of reduction products were obtained from reductions of isophorone (**10**) with solutions obtained from $Cr(OAc)_2$ and excess NH_3[5b] either in H_2O or in H_2O–DMSO mixtures.

We explored several hydrogen atom donors other than *n*-BuSH, including H_3PO_2 and $HSCH_2COOH$; H_3PO_2 was without substantial benefit and we were unable to maintain the Cr reagent in solution when $HSCH_2CO_2H$ was added. A series of reductions were performed with solutions of the Cr complex **9b** in *i*-PrOH with 5 mol of *n*-BuSH added/mol of ketone **10** reduced. In the absence of added HOAc, the yield of reduced ketone **16** was in the range of 8–18%. When 5 mol of HOAc/mol of ketone **10** was added without *n*-BuSH, the yield of ketone **16** was 40%. Similar observations were made for reductions performed in EtOH solution, the yield of ketone **16** under optimum conditions (with both *n*-BuSH and HOAc) being 70%. With both solvents, EtOH and *i*-PrOH, the reactions employing 1 *M* solutions of the Cr complex **9b** were frequently complicated by precipitation of a substantial fraction of the Cr complex as a reaction progressed with the result that reduction was incomplete. This difficulty was avoided by the use of MeOH as the reaction solvent.

Reduction of the Octalone 12. A. In MeOH Solution. The crude product, from reduction of 3.00 g (21 mmol) of the octanone **11** with the Cr complex **9b** in MeOH containing HOAc and *n*-PrSH[30] as summarized in Table II, was obtained as a pale yellow liquid containing (glpc, Carbowax 20 M on Chromosorb P) *n*-PrSSPr-*n* (retention time 3.1 min), the trans decalone **14a** (12.0 min), and the cis decalone **15a** (14.5 min). Distillation of this mixture in a short-path still separated 0.21 g of a fraction, bp 79–82° (2.5 mm), containing (glpc) primarily the decalones **14** and **15** with some *n*-PrSSPr-*n*, and 7.61 g (54%) of the decalones **14** and **15,** bp 82–89° (2.5 mm), containing (glpc) 85% of the trans isomer **14a** and 15% of the cis isomer **15a.** Various modifications of this reduction procedure are also summarized in Table II. For the glpc analysis of these compounds, naphthalene was employed as an internal standard and the glpc apparatus was calibrated with known mixtures of authentic samples. On one glpc column (Carbowax 20 M on Chromosorb P) the retention times follow: naphthalene (17.8 min), trans decalone **14a** (22.0 min), cis decalone **15a** (27.7 min), and octalone **11** (34.9 min). On a second glpc column (silicone SE-52 on Chromosorb P) the retention times follow: naphthalene (9.7 min), trans decalone **14a** (17.0 min), cis decalone **15a** (19.7 min), and octalone **11** (27.2 min). Collected (glpc) samples of the cis ketone **15a** ($n^{25}D$ 1.4905) and the trans ketone **14a** ($n^{25}D$ 1.4814) were identified with authentic samples by comparison of glpc retention times and ir and nmr spectra. A collected (glpc) sample of *n*-PrSSPr-*n* was identified with a subsequently described authentic sample by comparison of glpc retention times and ir and mass spectra.

An authentic sample of *n*-PrSSP-*n* was obtained in 53% yield as previously described,[26] and was separated as a colorless liquid: bp 190–191°; $n^{25}D$ 1.4961 [lit.[31] bp 69–70° (10 mm), $n^{20}D$ 1.4940]; ir (CCl_4), no peaks in the 3- or 6-μ regions attributable to OH, C=O, or C=C; nmr (CCl_4) δ 2.63 (4 H, t, J = 7 Hz, CH_2S), 1.69 [4 H, sextet (J = 7 Hz) with additional fine splitting apparent, CH_2], 1.00 (6 H, t, J = 7 Hz, with additional fine splitting, CH_3); mass spectrum *m/e* (rel intensity) 150 (M^+, 30), 108 (25), and 43 (100). *Anal.* Calcd for $C_6H_{14}S_2$: mol wt, 150.0537. Found: 150.0534.

When the octalone **11** was reduced with the Cr(II) complex in the dark and in the absence of added *n*-PrSH (see Table II), the crude product contained, in addition to two rapidly eluted components having the same retention times as the alcohols **18,** the trans decalone **14a** (16% yield), the cis decalone **15a** (13% yield), and the octalone **11** (10% recovery); thus, the mixture of decalones **14** and **15** was composed of 55% **14a** and 45% **15a.** When the same reaction was repeated at 25° without deliberate exclusion of light, the ratio of isomers, 60% **14a** and 40% **15a,** remained about the same but the yields, 7% of **14a** and 5% of **15a,** were lower. When the same reaction was run at −70 to −78° for 12 hr, the crude product again contained (glpc) two rapidly eluted components (retention times 4.3 and 4.8 min) corresponding to the epimeric alcohols **18** as well as the trans ketone **14a** (15.9 min, 5% yield), the cis ketone **15a** (19.6 min, 4% yield), and the enone **11** 35.6 min, 14% recovery).

B. In DMF Solution. As summarized in Table II, reduction of the octalone **11** with the $Cr(ClO_4)_2$–diamine **1** complex in aqueous DMF yielded 23% of the trans isomer **14a** and 19% of the cis isomer **15a,** corresponding to a decalone mixture containing 58% **14a** and 42% **15a.** Collected (glpc) samples of the two decalones **14** and **15** were identified with authentic samples by comparison of the glpc retention times and ir spectra. Repetition of this reaction with added H_3PO_2 or Ph_3SiH as possible hydrogen-atom donors did not significantly improve the yield of the decalones **14** and **15.** When comparable reactions were done in other solvents, the following yields were obtained: THF, 13% **14a** and 10% **15a;** *t*-BuOH, 20% **14a** and 17% **15a;** *i*-PrOH, 24% **14a** and 20% **15a.** Thus, in all of these cases where there was no mercaptan in the reaction mixture, 54–60% of the decalone product was the trans isomer **14a.**

A 0.65 *M* solution of $Cr(ClO_4)_2$ in D_2O was prepared by the previously described reaction of excess Cr with 28.7 g of aqueous 70% $HClO_4$ in 200 ml of D_2O. Following previous procedures a portion of this solution containing 12 mmol of $Cr(ClO_4)_2$ in 20 ml of DMF and 18 ml of D_2O was treated successively with 36 mmol of diamine **1** and 3.81 mmol of the octalone **11** and then stirred at 25° for 8 hr. The crude reaction product (264 mg) contained (glpc) 55% of **14** and 45% of **15.** Collected (glpc) samples of each decalone isomer were passed three times through a glpc column packed with 10% KOH and 10% Carbowax 20 M suspended on Chromosorb P[32] to exchange for hydrogen any deuterium bound to carbons α to the carbonyl group of the decalones **14** and **15.**[33] The resulting cis isomer **15** contained (mass spectral analysis) 60% d_0 species, 39% d_1 species, and 1% d_2 species. The trans isomer **14** contained (mass spectral analysis) 57% d_0 species, 41% d_1 species, and 2% d_2 species.

Reduction of the Ketone 7. A. In MeOH Solution. Table II summarizes the reduction of 3.00 g (18 mmol) of the enone **7** with a MeOH solution of the complex **9b** and HOAc. The crude product (2.63 g) was distilled to separate 2.43 g (81%) of ketone **8a,** bp 87.5–88° (10 mm), $n^{25}D$ 1.4223 (lit.[8a] $n^{25}D$ 1.4217), that was identified with an authentic sample by comparison of ir spectra. None of the corresponding dihydro dimer[8a] was detected (glpc). For analysis of reaction mixtures in this case, cumene was employed as an internal standard. The glpc (Carbowax 20 M on Chromosorb P) retention times follow: cumene, 13.6 min; ketone **8a,** 21.3 min; and ketone **7,** 25.1 min.

A comparable reduction of 3.00 g (18 mmol) of the enone **7,** in the presence of *n*-BuSH (Table II) yielded 3.80 g of a crude product that contained (glpc, Carbowax 20 M on Chromosorb P) *n*-BuSH (retention time 2.0 min), the ketone **8a** (5.2 min), *n*-BuSSBu-*n* (17.0 min), the ketone **41** (32.0 min), and the ketone **40** (36.3 min). Partial distillation of this mixture in a short-path still separated 0.71 g (23%) of the ketone **8a,** identified with an authentic sample by comparison of ir, nmr, and mass spectra. The residue (2.60 g) from this distillation contained (glpc) the two ketones **41** (~45%) and **40** (~55%) but none of the dihydro dimer was detected. Collected (glpc) samples of the ketones **40** and **41** were identified with subsequently described authentic samples by comparison of ir and nmr spectra. As a control experiment, a solution of the enone **7,** the diamine **1,** *n*-BuSH, and HOAc in MeOH was stirred at 25° for 13 hr and then subjected to the usual isolation and analysis. The crude neutral product contained the starting enone **7,** *n*-BuSSBu-*n,* and the β-keto sulfide **40,** but none of the α-keto sulfide **41** was detected. A collected (glpc) sample of the sulfide **40** was identified with a subsequently described sample by comparison of glpc retention times and ir and mass spectra. To be certain that the α-keto sulfide **41** present in the reaction mixtures did not result from a Cr(III)-catalyzed addition of *n*-BuSH to the enone **14,**[18] a solution of 1.5 mmol of the enone **7,** the complex **9b** from 3.0 mmol of $Cr(OAc)_2$ and 8.0 mmol of the diamine **1,** and 7.4 mmol of HOAc in 4 ml of MeOH was stirred at 25° for 9 hr. The resulting solution of reduced ketone **8a** and Cr(III) species was treated with 4.4 mmol of *n*-BuSH, 3.3 mmol of HOAc, 1.5 mmol of enone **7,** and 2 ml of MeOH and then stirred for 13 hr at 25°. After the usual isolation procedure, the crude neutral product contained (glpc) the ketone **8a,** the enone **7,** *n*-BuSSBu-*n,* and the β-keto sulfide **40** but none of the α-keto sulfide **41** was detected.

B. In DMF Solution. A reduction of the enone **7** with the $Cr(ClO_4)_2$–diamine **1** complex in aqueous DMF (Table II) afford-

ed a mixture of the ketone **8a** (72% yield) and the enone **7** (4% recovery). Collected (glpc) samples of ketones **7** and **8a** were identified with authentic samples by comparison of glpc retention times and ir spectra. When a comparable reduction was attempted in the absence of the diamine **1**, 91% of the enone **7** was recovered and no reduced ketone **8a** was detected.[9]

A similar reaction was performed with 0.97 mmol of ketone **7**, 2.6 mmol of $Cr(ClO_4)_2$, 6.57 mmol of *N,N*-diethylethanolamine (**5**), 5 ml of H_2O, and 15 ml of DMF. A green precipitate separated when the amino alcohol **5** was added. After the usual isolation, analysis (glpc) indicated a 96% yield of ketone **8a**. When the reaction was repeated with 1.05 mmol of ketone **7**, 2.60 mmol of $Cr(ClO_4)_2$, 5.7 mmol of *N,N,N',N'*-tetramethylenediamine (**3**), 5 ml of H_2O, and 22 ml of DMF, a brown precipitate was present throughout the reaction. Analysis (glpc) indicated the presence of the saturated ketone **8a** (24% yield) and the starting ketone **7** (71% recovery). In this case it seems likely that reduction is slow because of the insolubility of the Cr(II)–diamine **3** complex. A solution of 12 mmol of $Cr(ClO_4)_2$, 36 mmol of the diamine **1**, and 3.0 mmol of the enone **7** in 10 ml of DMF and 18 ml of D_2O was stirred at 25° for 2.5 hr and then subjected to the usual isolation procedure. Analysis (glpc with added cumene as an internal standard) indicated that the ketone **8** had been formed in 75% yield. The product was passed three times through a column packed with 10% KOH and 10% Carbowax 20 M on Chromosorb P^{32} to exchange for hydrogen any deuterium present α to the carbonyl group of the ketone **8**. The resulting ketone **8** contained (mass spectral analysis) 63% d_0 species, 36% d_1 species, and 1% d_2 species.

Preparation of the Ketones 40 and 41. A mixture of 1.00 g (6.0 mmol) of the enone **7**, 5.4 g (60 mmol) of *n*-BuSH, and 0.33 (2 mmol, added in portions during the reaction) of azoisobutyronitrile was stirred at 25° and irradiated with a 150-W incandescent bulb. After a reaction period of 72 hr, analysis (glpc, Carbowax 20 M on Chromosorb P) indicated that all the enone **7** had been consumed and the mixture contained *n*-BuSH (retention time 1.9 min), *n*-BuSSBu-*n* (9.6 min), and the ketone **40** (18.8 min); none of the isomeric ketone **41** was detected. When a neutral MeOH solution of the enone **7** and *n*-BuSH was stirred at 25° without an added radical initiator, none of either ketone **40** or **41** was detected. A collected (glpc) sample of the ketone **40** was obtained as a colorless liquid: $n^{25}D$ 1.4648; ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4), δ 2.3–3.1 (5 H, m, CH_2CO, CH_2SCH) and 0.8–1.7 [(25 H, m, aliphatic CH including two 9 H singlets at 0.98 and 1.13 (*t*-Bu)]; mass spectrum *m/e* (rel intensity) 258 (M^+, <1), 111 (32), 95 (45), 58 (100), 57 (78), 43 (65), and 41 (26).

Anal. Calcd for $C_{15}H_{30}OS$: C, 69.76; H, 11.70. Found: C, 69.66; H, 11.64.

To a refluxing solution of 3.80 g (17 mmol) of powdered $CuBr_2$ in 18 ml of EtOAc was added a solution of 1.70 g (10 mmol) of the ketone **8a** in 8 ml of $CHCl_3$.[34] This addition was accompanied by separation of a white precipitate (CuBr). After the mixture had been refluxed with stirring for 3 hr, analysis (glpc, Carbowax 20 M on Chromosorb P) indicated the presence of both the ketone **8a** (retention time 3.3 min) and the bromo ketone **42** (8.5 min). An additional 0.67 g (3 mmol) of $CrBr_2$ was added and refluxing and stirring were continued for an additional 1 hr. The reaction mixture was filtered, and the filtrate was decolorized with charcoal, diluted with Et_2O, washed successively with aqueous $NaHCO_3$ and H_2O, dried, and concentrated. The residual liquid was distilled to separate 1.85 g (75%) of the bromo ketone **42** as a colorless liquid: bp 74–75° (3.5 mm); $n^{25}D$ 1.4602; ir (CCl_4) 1715 cm^{-1} C=O); nmr (CCl_4) δ 4.73 (1 H, d of d, J = 7.4 and 4.9 Hz, CHBr), 2.40 (1 H, d of d, J = 15.2 and 7.4 Hz, one of CH_2 protons), 2.12 (1 H, d of d, J = 15.2 and 4.9 Hz, one of CH_2 protons), 1.30 (9 H, s, *t*-Bu), and 0.95 (9 H, s, *t*-Bu); mass spectrum *m/e* (rel intensity), 251 and 249 (M^+, <1), 85 (30), 58 (33), 57 (92), and 43 (100).

Anal. Calcd for $C_{11}H_{21}BrO$: C, 53.02; H, 8.50; Br, 32.07. Found: C, 52.91; H, 8.49, Br, 31.91.

To a warm (80°) solution of 0.64 g (15 mmol) of LiCl and 5.11 g (30 mmol) of $CuCl_2 \cdot H_2O$ in 10 ml of DMF was added 2.00 g (12 mmol) of the ketone **8a**.[35] The resulting solution was heated to 80–90° for 5 hr and then partitioned between H_2O and Et_2O. The ethereal extract was washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated. Distillation separated 1.01 g of a fraction, bp 71–73° (5 mm), containing (glpc, Carbowax 20 M on Chromosorb P) the chloro ketone **43** (retention time 6.5 min) contaminated with a small amount of starting ketone **8a** (3.0 min) and a second fraction, bp 73–74° (5 mm), $n^{25}D$ 1.4420, containing (glpc) the pure chloro ketone **43**: ir (CCl_4) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 4.64 (1 H, d of d, J = 5.6 and 6.8 Hz, CHCl), 1.5–2.4 (2 H, m, CH_2), 1.23 (9 H, s, *t*-Bu), and 0.96 (9 H, s, *t*-Bu); mass spectrum *m/e* (rel intensity), 206 and 204 (M^+, <1), 85 (13), 58 (14), 57 (100), 43 (35), and 41 (13).

Anal. Calcd for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34; Cl, 17.32. Found: C, 64.54; H, 10.33; Cl, 17.25.

To a boiling solution of 0.81 g (9 mmol) of *n*-BuSH and 0.32 g (8 mmol) of NaOH in 7 ml of EtOH was added, dropwise and with stirring, 1.00 g (5 mmol) of the chloro ketone **43**. The resulting mixture, from which a white precipitate separated, was refluxed with stirring for 10 min and then partitioned between saturated aqueous NaCl and Et_2O. The Et_2O solution was dried and concentrated to leave 1.24 g of crude product as a pale yellow liquid containing (glpc, Carbowax 20 M on Chromosorb P) the ketone **41** (retention time 17.2 min) accompanied by minor amounts of the ketone **8a** (3.1 min) and *n*-BuSSBu-*n* (5.2 min). A collected (glpc) sample of the ketone **41** was obtained as a colorless liquid: $n^{25}D$ 1.4642; ir (CCl_4), 1690 cm^{-1} (C=O); nmr (CCl_4) δ 3.66 (1 H, d of d, J = 3.4 and 1.2 Hz, CHS), 1.2–2.6 (17 H, m, CH_2 and *t*-Bu singlet at 1.24), 0.7–1.0 (12 H, CH_3 and *t*-Bu singlet at 0.85); mass spectrum *m/e* (rel intensity) 258 (M^+, 3), 173 (16), 117 (65), 58 (40), 57 (57), and 43 (100).

Anal. Calcd for $C_{15}H_{30}OS$: C, 69.76; H, 11.70; S, 12.41. Found: C, 69.88; H, 11.84; S, 12.31.

Repetition of this reaction with the bromo ketone **42** afforded a crude product containing (glpc, Carbowax 20 M on Chromosorb P) primarily the ketone **8a** (retention time 3.0 min) and *n*-BuSSBu-*n* (9.5 min) accompanied by minor amounts of the starting bromo ketone **42** (8.5 min) and the ketone **41** (16.8 min). Collected (glpc) samples of *n*-BuSSBu-*n* and the ketones **8a** and **41** were identified with authentic samples by comparison of glpc retention times and mass spectra.

Reduction of the Ketone 13. A. Catalytic Hydrogenation. A MeOH solution of the ketone **13** was hydrogenated for 1 hr at 25° and 1 atm H_2 pressure over a 5% Pt/C catalyst to yield 94% of the ketone **23**: bp 74–74.5° (16 mm); $n^{25}D$ 1.4458 [lit.[36] bp 80.5° (30 mm)]; ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4), δ 1.4–2.4 (8 H, m, CH_2), and 0.98 (6 H, s, CH_3); mass spectrum *m/e* (rel intensity) 126 (M^+, 30), 83 (100), 57 (33), 55 (51), 43 (35), and 41 (23).

B. With the Cr Complex 9b. Reduction of 5.0 g (40 mmol) of the enone **13** with a MeOH solution of Cr complex **9b** and HOAc (Table II) afforded 430 mg of crude neutral product as a yellow oil that was diluted with hexane and cooled to separate 85 mg of the crude solid dihydro dimer **24**. Recrystallization from hexane afforded 68 mg (2.7%) of one epimer of the dihydro dimer **24** as white prisms: mp 144–145°; recrystallization raised the melting point to 144.5–146.5°; ir (CCl_4), 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.3–2.7 (14 H, m, CH and CH_2), 1.12 (6 H, s, CH_3), and 0.92 (6 H, s, CH_3); mass spectrum *m/e* (rel intensity), 250 (M^+, <1), 58 (49), and 43 (100). *Anal.* Calcd for $C_{16}H_{26}O_2$: mol wt, 250.1933. Found: 250.1931.

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.46; H, 10.41.

A portion of the crude neutral reaction product (mixed with 1-phenyloctane as an internal standard) contained (glpc, Carbowax 20 M on Chromosorb P, apparatus calibrated with known mixtures) ketone **45** (retention time 5.0 min, 0.4% yield), ketone **23** (8.4 min, 4% yield), unchanged enone **13** (11.3 min, 0.9% recovery), and 1-phenyloctane (25.8 min). A collected (glpc) sample of the ketone **23** was identified with an authentic sample by comparison of glpc retention times and ir spectra and a collected (glpc) sample of ketone **45** was identified with an authentic sample by comparison of glpc retention times and mass spectra: *m/e* (rel intensity) 126 (M^+, 83), 111 (28), 83 (100), 69 (80), 57 (32), 56 (72), 55 (55), 42 (51), and 41 (60).

A comparable reduction of 3.00 g (24 mmol) of the enone **13** in the presence of *n*-BuSH (Table II) afforded a crude product containing (glpc, Carbowax 20 M on Chromosorb P) the ketone **23** (retention time 10.0 min) and *n*-BuSSBu-*n* (15.5 min); neither of the ketones **13** nor **45** (4.8 min) was detected in the crude product. Fractional distillation of the crude product separated 0.54 g (18%) of the ketone **23**, bp 64–64.5° (5 mm), $n^{25}D$ 1.4458, that was identified with the previously described sample by comparison of glpc retention times and ir and nmr spectra. The residue (1.42 g) from this distillation contained (glpc, Carbowax 20 M on Chromosorb P) two higher boiling components, a minor component thought to be ketone **39** (*ca.* 3%, retention time 23.2 min), and the ketone **38** (*ca.* 97%, 35.5 min). A collected (glpc) sample of the

minor component **39** had the following mass spectrum: *m/e* (rel intensity) 214 (M^+, 8), 126 (41), 70 (13), 68 (15), 58 (61), 55 (17), 43 (100), and 41 (16). Attempts to collect (glpc) a pure sample of the ketone **38** afforded a mixture (ir and nmr analysis) of the ketone **38** and the unsaturated ketone **13** (from elimination of *n*-BuSH from **38**): ir (CCl_4) 1715 (C=O) and 1680 cm^{-1} (conjugated C=O). Comparison of the ir, nmr, and mass spectra of this collected material with the spectra of the subsequently described authentic ketone **38** provided compelling evidence for the presence of ketone **38** in the reaction mixture.

To obtain an authentic sample of the ketone **38**, a mixture of 2.00 g (16 mmol) of the ketone **13**, 14.40 g (160 mmol) of *n*-BuSH, and 0.82 g (5 mmol) of azoisobutyronitrile was stirred at 25° and irradiated with a 150-W incandescent bulb for 72 hr. The resulting solution was concentrated under reduced pressure and then diluted with hexane and cooled at −78° to precipitate the unchanged azoisobutyronitrile. The supernatant liquid was concentrated and then fractionally distilled to separate 0.52 g of fractions, bp 84–100° (1 mm), $n^{25}D$ 1.4868–1.4895, followed by 0.65 g of the ketone **38**: bp 100–102° (1 mm); $n^{25}D$ 1.4906; ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 2.0–3.2 (7 H, m, CH_2COCH_2 and $CHSCH_2$), 1.2–2.0 (6 H, m, CH_2), and 0.8–1.2 (9 H, m, CH_3 groups including singlets at 0.89 and 1.10); mass spectrum *m/e* (rel intensity) 214 (M^+, 37), 125 (85), 83 (35), 69 (70), 58 (54), 56 (20), 55 (52), 43 (100), and 41 (40). *Anal.* Calcd for $C_{12}H_{22}OS$: mol wt, 214.1391. Found: 214.1396.

Anal. Calcd for $C_{12}H_{22}OS$: C, 67.23; H, 10.35; S, 14.96. Found: C, 67.16; H, 10.33; S, 14.87.

Reduction of the Ketone 12. Reduction of 4.00 g (32 mmol) of the enone **12** with a MeOH solution of the Cr complex **9b** and HOAc (Table II) gave a crude neutral product containing (glpc, Carbowax 20 M on Chromosorb P) the ketone **21** (retention time 7.5 min) and a small amount of the starting ketone **12** (9.5 min). Fractional distillation separated 0.80 g (20%) of the ketone **21**, bp 80–81.5° (12 mm) (lit.[36] bp 173–176°), that solidified on standing: mp 41–42° (lit.[36] mp 43–44.5°); ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 2.28 (4 H, t, J = 7.5 Hz, CH_2CO), 1.66 (4 H, t, J = 7.5 Hz, CH_2), and 1.10 (6 H, s, CH_3); mass spectrum *m/e* (rel intensity) 126 (M^+, 2), 72 (4), 58 (40), 43 (100), and 42 (6).

The residue from this distillation was triturated with hexane to separate 85 mg (2%) of one epimer of the dihydro dimer **22**, mp 127–133°. Recrystallization from hexane afforded the pure epimer of diketone **22** as white needles: mp 137–138°; ir (CCl_4) 1715 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.0–2.8 (8 H, m, CH_2CO), 1.2–2.0 (6 H, m, CH_2 and CH), 1.17 (6 H, s, CH_3), and 1.13 (6 H, s, CH_3); mass spectrum *m/e* (rel intensity) 250 (M^+, 24), 179 (17), 126 (45), 125 (100), 97 (25), 83 (72), 70 (54), 69 (46), 67 (22), 56 (48), 55 (77), 53 (23), 43 (31), and 41 (37).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.71; H, 10.53.

Repetition of this reaction in the presence of *n*-BuSH (Table II) gave a crude product containing (glpc, Carbowax 20 M on Chromosorb P) *n*-BuSH (retention time 2.0 min), the ketone **21** (8.3 min), a very small amount of the starting ketone **12** (10.5 min) and *n*-BuSSBu-*n* (13.6 min). Fractional distillation of the crude product separated 1.87 g (47%) of the ketone **21**, bp 74–75.5° (10 mm), contaminated (glpc) with *ca.* 5% of *n*-BuSSBu-*n*. The residue (1.56 g) from this distillation contained (glpc, Carbowax 20 M on Chromosorb P) a component believed to be ketone **37** (*ca.* 15%, retention time 30.6 min) and the ketone **36** (*ca.* 85%, 44.5 min). A collected (glpc) sample of the minor component **37** had the following spectral properties: ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 1.3–3.7 (13 H, m, CH and CH_2) and 0.9–1.3 (9 H, m, CH_3 including two 3 H singlets at 1.12 and 1.18); mass spectrum *m/e* (rel intensity) 214 (M^+, 7), 127 (40), 75 (30), 63 (48), 60 (16), 43 (100), and 41 (16). Attempts to collect (glpc) the major product afforded a mixture (ir and nmr analysis) of the ketone **36** and the unsaturated ketone **12** (from elimination of *n*-BuSH), ir (CCl_4) 1710 (C=O) and 1685 cm^{-1} (conjugated C=O). Comparison of the ir, nmr, and mass spectra of this collected material with the spectra of the subsequently described authentic sample of the ketone **36** has led us to conclude that the ketone **36** is present in the reaction mixture.

An authentic sample of ketone **36** was obtained by the previously described procedure using 3.00 g (24 mmol) of the ketone **12**, 21.0 g (240 mmol) of *n*-BuSH, and 1.31 g (8 mmol) of azoisobutyronitrile. Fractional distillation of the crude product separated 1.14 g of fractions, bp 45–122° (1.8 mm), and 1.15 g of a fraction, bp 122–126° (1.8 mm), $n^{25}D$ 1.4920, containing (ir analysis) mainly the ketone **36**. Redistillation afforded the pure ketone **36**: bp 114–115° (1.4 mm); $n^{25}D$ 1.4961; ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 2.1–2.9 (7 H, m, $CHSCH_2$ and CH_2COCH_2), 1.3–1.9 (6 H, m, CH_2), and 0.9–1.3 (9 H, m, CH_3 including singlets at 1.10 and 1.18); mass spectrum *m/e* (rel intensity) 214 (M^+, 13), 125 (30), 58 (50), and 43 (100). *Anal.* Calcd for $C_{12}H_{22}OS$: mol wt, 214.1391. Found: 214.1396.

Anal. Calcd for $C_{12}H_{22}OS$: C, 67.23; H, 10.35; S, 14.96. Found: 67.04; H, 10.31; S, 14.82.

After a solution of the Cr(II)–NH_3 complex, from 56 mmol of $Cr(OAc)_2$ and 560 mmol of aqueous 28% NH_3, and 16 mmol of the ketone **12** in 44 ml of MeOH had been stirred at 25–30° for 3.5 hr, it was subjected to the usual isolation procedure. Distillation afforded 0.61 g (30%) of a mixture (glpc) of ketones **21** (*ca.* 68%) and **12** (*ca.* 32%). The residue from this distillation was triturated with hexane to separate 0.11 g (5%) of the crude dihydro dimer **22**, mp 128–131°. When this reaction was performed with 56 mmol of $Cr(OAc)_2$, 16 mmol of ketone **12**, and 50 ml of aqueous 28% NH_3, with no added cosolvent (MeOH),[5b] the volatile materials in the crude product (1.12 g) were the ketones **21** (*ca.* 37%) and **12** (*ca.* 63%); 92 mg of the crude dihydro dimer **22**, mp 130–132°, was also isolated.

To learn how rapidly the ketone **12** reacted with the nitrogen-containing ligands in the absence of Cr salts, a solution of 1.24 g (10 mmol) of the ketone **12**, 4.86 g (81 mmol) of the diamine **1**, and 319 mg of 1-phenyloctane (an internal standard) in 20 ml of MeOH was stirred at 25° for 30 min and subjected to the usual isolation procedure. The recovered neutral material contained (glpc, Carbowax 20 M on Chromosorb P) the enone **12** (retention time 6.7 min, 31% recovery) and 1-phenyloctane (12.7 min). When the same experiment was performed with 1.24 g (10 mmol) of the ketone **12**, 15 g of aqueous 28% NH_3, and 1-phenyloctane in 10 ml of MeOH, 45% of the ketone **12** was recovered.

A solution of 520 mmol of the diamine **1**, 190 mmol of *n*-BuSH, 320 mmol of HOAc, and 64 mmol of the enone **12** in 128 ml of MeOH was stirred at 25° for 12 hr and then subjected to the usual isolation procedure. The crude neutral product contained (glpc) the enone **12**, *n*-BuSSBu-*n*, and the β-keto sulfide **36**, but none of the component believed to be the α-keto sulfide **37** was detected. Fractional distillation separated 0.83 g of early fractions, bp 90–132° (3.5 mm), containing the three components noted above and 11.2 g of fractions, bp 132–134.5° (3.5 mm), that contained (glpc and ir analysis) the pure β-keto sulfide **36**.

Registry No.—7, 1653-94-7; **8a,** 40239-53-0; **10,** 78-59-1; **11,** 1196-55-0; **12,** 1073-13-8; **13,** 4694-17-1; **14a,** 700-77-6; **15a,** 1579-21-1; **17** isomer A, 50987-69-4; **17** isomer B, 4994-12-1; **19a,** 470-99-5; **19b,** 50987-46-7; **20,** 15466-96-3; **21,** 4255-62-3; **22,** 5020-04-2; **23,** 2979-19-3; **24,** 50987-47-8; **36,** 50987-48-9; **37,** 50987-49-0; **38,** 50987-50-3; **40,** 50987-51-4; **41,** 50987-43-4; **42,** 50987-44-5; **43,** 50987-45-6; **45,** 4694-12-6; *n*-BuSSBu-*n*, 629-45-8; *n*-PrSSPr-*n*, 629-19-6.

References and Notes

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(14) Although it is clear from earlier studies[4c,10] that the Cr(II) species is present as a bis en complex, the Cr(III) species may be present as either $Cr(en)_3^{3+}$ or $Cr(en)_2(ligand)_2^{3+}$, since the bis and tris en complexes of Cr(III) appear to be of comparable stability [see C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 196, 200 (1946)]. Earlier polarographic studies[10c] of reduction of $Cr(en)_3^{3+}$ in aqueous solution have indicated that electrode process observed is $Cr(en)_3^{3+} + e \rightleftarrows Cr(en)_3^{2+} \rightleftarrows Cr(en)_2(ligand)_2^{2+} + en$. This process exhibited "pseudo-reversible" behavior in alkaline solution at relatively high en concentrations. In our studies starting with preformed $Cr(en)_2(ligand)_2$ and low concentrations of en we believe we are observing only the reversible electron transfer process: $Cr(en)_2(ligand)_2^{2+} \rightleftarrows Cr(en)_2(ligand)_2^{3+} + e$.
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A New Ring Expansion Procedure. VI. The Decomposition of the Magnesium Salts of Some 1-(α-Bromobenzyl)-1-cycloalkanols and Bicycloalkanols

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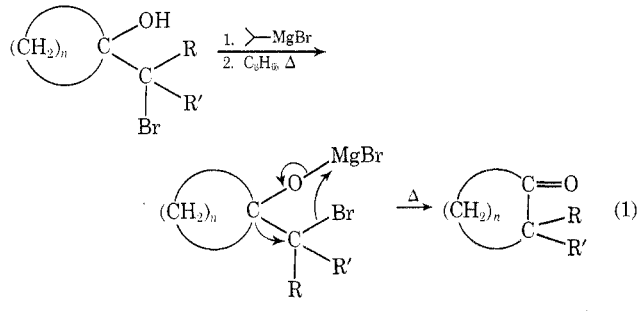
The results of the new ring expansion procedure applied to 2-methylcyclopentanone, 2-methylcyclohexanone, camphor, and bicyclo[2.2.2]octanone-2 are presented and discussed. Particular attention is afforded to the factors affecting product distribution. Each ketone was converted to its corresponding 2-phenyl-substituted ring-enlarged ketone by the decomposition of the magnesium salt from the 1-(α-bromobenzyl)-1-cycloalkanol.

Previously published papers[1] describe a new and relatively simple procedure by which one may achieve a ring enlargement (eq 1). The bromohydrins were prepared from olefins by treatment with aqueous *N*-bromosuccinimide, or ketones by reaction with benzylmagnesium chloride followed by a free-radical bromination.[1] Ring-enlarged ketones of reasonable purity were obtained in overall fair yields.



(1)

$n = 4, 5, 6, 7$; R = H; R′ = CH_3, Ph; R = R′ = CH_3

The studies of Geissman and Akawie[2] have mechanistically classed the rearrangement as a pinacol type involving a migration to an incipient electron-deficient carbon atom produced from an electrophilic attack by magnesium on the halogen atom (eq 1). A high degree of carbonium ion character is involved in the transition state, since they observed that secondary and tertiary halides rearrange regardless of the migrating group but primary halides only rearrange when a good migrating group is involved.

The results of the ring-enlargement procedure applied to 2-methylcyclopentanone, 2-methylcyclohexanone, camphor, and bicyclo[2.2.2]octanone-2 are presented and dis-