Reaction of Organic Halides with Chlorotris-(triphenylphosphine)cobalt(I)

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Reaction of various types of organic halides with a monovalent cobalt complex, chlorotris(triphenylphosphine)cobalt(I) is described. Reaction of benzylic monohalides, dihalides and trihalides with CoCl(Ph₃P)₃ gave a coupling product with formation of a carbon–carbon single bond, double bond and triple bond, respectively, under mild and non-basic conditions. Dehalogenation of non-benzylic vicinal dihalides with the reagent took place cleanly to give an olefin in high yield. Reductive coupling of allylic halides using the reagent afforded regioselectively a 1,5-diene with retention of the stereochemistry of the carbon–carbon double bond of the allylic halides used. By using this reaction, (E,E,E,E)-squalene was stereospecifically synthesized from (E,E)-farnesyl bromide. Reaction of halohydrins with CoCl(Ph₃P)₃ gave exclusively a ketone in the presence of an amine or olefin through an alkylcobalt intermediate. A 1,2-hydrogen shift is involved in this reaction.

Keywords—chlorotris(triphenylphosphine)cobalt(I); coupling reaction; benzylic halides; allylic halides; synthesis of 1,5-diene; squalene; halohydrin; ketone synthesis

Recently synthetic organic reactions using low-valent transition metal reagents have been extensively studied. During the course of our investigation on the reaction of organic halides with the monovalent cobalt complex, chlorotris(triphenylphosphine)cobalt(I), we achieved the coupling of organic halides such as benzylic and allylic halides, and the efficient conversion of halohydrins to ketones, as reported in preliminary communications. This paper presents the full details of these reactions together with additional findings.

Monovalent cobalt such as cob(I)alamin or cobaloxime(I) is known to show nucleophilic properties and reacts with alkyl halides giving trivalent alkylcobalt compounds. Cleavage of the cobalt–carbon bond leads to the formation of a carbon–carbon bond. Rearrangement mediated by a trivalent cobalt intermediate is also recognized in important biological reactions. Because of the chemical and biological interest of trivalent alkylcobalt compounds, we studied the reaction of organic halides with chlorotris(triphenylphosphine)cobalt(I), a fairly stable monovalent cobalt complex prepared by Aresta et al. Although the use of the reagent in organic synthesis has so far been limited to dimerization of olefins, the reagent appears to be convenient in practice for organic reactions since the crystalline complex is easy to manipulate and can be stored for several months under argon.

Reductive Coupling of Benzylic Halides

Coupling of organic halides is an important synthetic reaction forming carbon–carbon bonds. For the reductive coupling of benzylic halides, low-valent transition metal reagents such as Cr(II), V(II), W(0), Fe(0) and Co(0) are frequently employed. Our studies demonstrated that CoCl(Ph₃P)₃ also effects the coupling of various types of benzylic halides with the advantages that the reaction can be carried out under mild and non-basic conditions and can be accomplished in various organic solvents.
Table 1. Reductive Coupling of Benzyl Halides

<table>
<thead>
<tr>
<th>Benzyl halide</th>
<th>Reaction conditions</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl chloride</td>
<td>RT 1.5 h</td>
<td>1,2-Diphenylethane</td>
<td>70</td>
</tr>
<tr>
<td>Benzyl bromide</td>
<td>RT 5 min</td>
<td>1,2-Diphenylethane</td>
<td>69</td>
</tr>
<tr>
<td>1-Chloro-1-phenylethane</td>
<td>RT 1 h</td>
<td>2,3-Diphenylbutane</td>
<td>69</td>
</tr>
<tr>
<td>1-Chloro-1-phenylbutane</td>
<td>RT 2 h</td>
<td>4,5-Diphenylcyclohexane</td>
<td>75</td>
</tr>
<tr>
<td>2-Chloro-2-phenylpropane</td>
<td>RT 2 h</td>
<td>2,3-Dimethyl-2,3-diphenylbutane</td>
<td>83</td>
</tr>
<tr>
<td>Chlorodiphenylethane</td>
<td>RT 17 h</td>
<td>1,1,2,2-Tetraphenylethane</td>
<td>67</td>
</tr>
<tr>
<td>Benzal bromide</td>
<td>50 °C 24 h</td>
<td>(E)-Stilbene</td>
<td>68</td>
</tr>
<tr>
<td>Benzetrichloride</td>
<td>50 °C 24 h</td>
<td>(E)-1,2-Dichloro-1,2-diphenylethane</td>
<td>66</td>
</tr>
<tr>
<td>Benzotritylboride</td>
<td>60 °C 6 h</td>
<td>Diphenylacetylene</td>
<td>65</td>
</tr>
</tbody>
</table>

a) Carried out in benzene.  b) Isolated yield.

The results of the reductive coupling of benzyl halides are shown in Table I. Benzyl monochlorides including primary, secondary and tertiary chlorides are smoothly coupled to give 1,2-diphenylethanes in good yields. In the case of benzyl bromide, the reaction was completed within 5 minutes, faster than that of the corresponding chloride under the same reaction conditions, giving 1,2-diphenylethane in a similar yield. The reaction can be carried out in toluene, 1,2-dimethoxyethane, ethyl acetate, acetone, acetonitrile and N,N-dimethylformamide; benzyl chloride was converted to 1,2-diphenylethane in 60—70% yields. Racemic 1-chloro-1-phenylethane and 1-chloro-1-phenylbutane gave corresponding coupling products consisting of meso and dl isomers in ratios of 1:1 and 2:3, respectively. Similar results were reported for the reaction of the former compound using cobalt(0) carbonyl complex, Co₂(CO)₈, under phase transfer conditions; the reaction was postulated to proceed through a radical mechanism.₁⁶

Formation of meso and dl isomers from the coupling of the racemic halide in nearly the same ratio strongly suggests that the coupling proceeds via a radical species derivatives derived from the initially formed trivalent alkylcobalt intermediate by homolytic cleavage of the cobalt-carbon bond. The involvement of the radical process was also supported by the reaction of homobenzyl bromide, phenethyl bromide, with CoCl(Ph₃P)₃ affording 2,3-diphenylbutane in 40% yield as a mixture of meso and dl isomers in a ratio of 3:2. The reaction involves a 1,2-shift of hydrogen from the benzyl to the homobenzyl position in the initially formed homobenzyl radical intermediate giving rise to the benzyl radical.₁⁷

Coupling of a benzyl geminal dibromide with CoCl(Ph₃P)₃ leads to the formation of a carbon–carbon double bond. Benzyl bromide (I) was treated with CoCl(Ph₃P)₃ in benzene at 50 °C to give exclusively (E)-stilbene (3) in 68% yield. The formation of 3 was assumed to proceed through intramolecular reductive coupling of the initially formed 1,2-dibromo-1,2-diphenylethane (2) since the dibromide 2a and 2b were formed as minor products on treatment of 1 with 0.5 eq of CoCl(Ph₃P)₃. This was proved by the finding that the reaction of both 2a and 2b with the complex gave 3 in 94 and 91% yields, respectively. The exclusive formation of 3 can be explained by consideration of the initially formed benzyl radical intermediate (Chart 2). The relatively stable benzyl radicals [(I) from 2a and (II) from 2b] can equilibrate in favor of (I) rather than (II), and (I) leads to the olefin 3 by a subsequent one-electron trans-elimination process.₁⁸

Formation of an acetylene bond was accomplished by the reaction of benzotribromide with CoCl(Ph₃P)₃, giving diphenylacetylene in a 65% yield. A similar reaction of benzo-
trichloride did not afford diphenylacetylene but gave \((E)-1,2\)-dichloro-1,2-diphenylethene.

In conclusion, formation of a carbon–carbon single bond, double bond and triple bond was accomplished by the reductive coupling of benzylic mono-, di- and trihalides with CoCl(Ph₃P)₃.

**Dehalogenation of Vicinal Dihalides**

Formation of the aforementioned carbon–carbon double bond led us to investigate the dehalogenation of non-benzylic vicinal dihalides in which the intermediate radical species is not stabilized by phenyl substitution.

Reaction of 9,10-dibromooctadecanoic acids and their methyl esters with CoCl(Ph₃P)₃ was carried out in benzene, and the results are summarized in Table II.

In every case, dehalogenation took place cleanly at room temperature to give olefins 5 in 81—91% yields. The erythro isomer of the carboxylic acid (4a) gave the \(E\) olefin exclusively, whereas the threo isomer 4b afforded a mixture of \(E\) and \(Z\) olefins. In the case of the corresponding methyl esters (4c and 4d), the ratios of the olefins obtained were essentially the same. However, on treatment of the methyl esters 4c and 4d with CoCl(Ph₃P)₃ in the presence of acetic acid in benzene, the ratios of the products became close to those in the case of carboxylic acids 4a and 4b. The observation that nearly the same products ratio is obtained in the case of both erythro 4c and threo 4d esters suggests a radical process similar to that in the case of 2 for dehalogenation of the esters 4c and 4d in the absence of acetic acid. In the reaction of carboxylic acids and their esters in the presence of an acid, a remarkable difference was observed between erythro and threo isomers, suggesting an alternative reaction process for these dehalogenations; this remains to be investigated.

Reaction of 5α,6β-dibromocholesterol and 5β,6α-dibromocholesterol with CoCl(Ph₃P)₃ (40 °C, 4 h) afforded cholesterol in 75 and 70% yields, respectively. It is of interest that neither diaxial nor diequatorial nature of the two bromine atoms affected the reaction.¹⁹

**Reductive Coupling of Allylic Halides**

Coupling of allylic halides is a useful synthetic reaction forming a 1,5-diene system, which is frequently encountered in the structures of natural products. Recently low-valent transition
TABLE II. Dehalogenation of Vicinal Dibromides

\[
\begin{align*}
\text{Br} \\
\text{CH}_2(\text{CH}_2)_2\text{CH-CH(CH}_2\text{)_2CO}_2\text{R} & \longrightarrow \text{CH}_2(\text{CH}_2)_2\text{CH=CH(CH}_2\text{)_2CO}_2\text{R} \\
\text{Br} \\
4a: & \text{ R} = \text{H (erythro)} \\
4b: & \text{ R} = \text{H (threo)} \\
4c: & \text{ R} = \text{Me (erythro)} \\
4d: & \text{ R} = \text{Me (threo)} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Dibromide</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>E/Z Ratio of olefin&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>82</td>
<td>100 : 0</td>
</tr>
<tr>
<td>4b</td>
<td>86</td>
<td>43 : 57</td>
</tr>
<tr>
<td>4c</td>
<td>86</td>
<td>85 : 15</td>
</tr>
<tr>
<td>4d</td>
<td>88</td>
<td>88 : 12</td>
</tr>
<tr>
<td>4e</td>
<td>91</td>
<td>94 : 6&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4f</td>
<td>81</td>
<td>35 : 65&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by NMR of the epoxides obtained from the olefins by treatment with m-CPBA.

<sup>c</sup> Reaction in the presence of acetic acid.

TABLE III. Coupling of Allylic Bromides Using CoCl(Ph₃P)₃

<table>
<thead>
<tr>
<th>Allylic bromide</th>
<th>Products (yield)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Br</td>
<td>7 (66%) + 8 (16%) + 9 (7%)</td>
</tr>
<tr>
<td>10</td>
<td>11 (63%) + 12 (16%) + 9 (9%)</td>
</tr>
<tr>
<td>13 Br</td>
<td>14 (55%) + 15 (22%) + 16 (12%)</td>
</tr>
<tr>
<td>17 Br</td>
<td>18 (51%) + 19 (19%) + 16 (8%)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield.

metal compounds have been widely used for the coupling of allylic halides as in the case of benzylic halides. In many cases, higher-valent transition metal compounds with reducing agents were employed for such coupling reactions, and in some cases transition metal carboxyls and lanthanoid compounds were also used. However, few examples of allylic
coupling promoted by low-valent cobalt are available.23)

Reductive coupling of terpenoid allylic halides with CoCl(Ph₃P)₃ afforded 1,5-dienes in good yields. The results are summarized in Table III.

The reactions of geranyl bromide (6) and its geometrical isomer neryl bromide (10) with CoCl(Ph₃P)₃ in benzene at room temperature (0.5 h for 6 and 3 h for 10) both gave tail-to-tail coupling products (7 from 6 and 11 from 10) as the major product with regioselectivity of 70%. No geometrical isomers of the coupling products were formed in either reaction, showing that the geometry of the double bond of the allylic bromides was retained during the coupling reaction. The reaction of geranyl and neryl chlorides afforded the same coupling products with similar ratios and yields, although a longer reaction time was necessary (1 h for geranyl chloride and 17 h for neryl chloride).

For this coupling a wide variety of organic solvents can be employed, as in the case of benzylc coupling. Changing the reaction medium from benzene to n-hexane, toluene and 1,2-dimethoxyethane did not significantly affect the yield or distribution of the products. However, when the reaction was carried out in an aprotic polar solvent such as N,N-dimethylformamide (DMF) or hexamethylphosphoramide (HMPA), a trimer was newly formed in addition to the same dimeric coupled products but with a change in the product ratio. The reaction of 6 with CoCl(Ph₃P)₃ in DMF gave dimers 7 (53%), 8 (10%), and 9 (14%), and the trimer 20 (10%). Similar results were obtained in the reaction using HMPA. The structure of the trimer 20 was assigned on the basis of the mass spectrum [m/z 412 (M⁺)] and proton nuclear magnetic resonance (¹H-NMR) spectrum [δ 0.90 (3H, s), 1.21 (6H, m), 1.60 (15H, s), 1.69 (9H, s), 1.90—2.09 (14H, m) and 5.06 (5H, m) ppm]. In the reaction of 10 in DMF, the trimer 21 was also obtained in 11% yield in addition to the dimer 11 (48%), 12 (8%) and 9 (18%). Formation of the trimers can be explained by the addition of allylic radical species such as the geranyl radical (III), which is derived from a trivalent organocobalt intermediate, to the least hindered carbon–carbon double bond of the dimer 8 in an anti-

![Chart 3]

Markownikoff manner followed by hydrogen abstraction from the solvent.

Reaction of farnesyl bromide (13) and the geometrical isomer 17 with CoCl(Ph₃P)₃ in benzene at room temperature for 3 h afforded (E,E,E)-squalene (14) (55% yield) and (6E,10Z,14Z,18E)-squalene (18) (51% yield), respectively, with the concomitant formation of their regioisomers, in a stereospecific manner. This method provides an efficient synthesis of squalene.²⁴

The characteristic feature of the allylic coupling is that the reaction proceeds with retention of the stereochemistry of the carbon–carbon double bond of the allylic halides used,
and that the reaction provides the tail-to-tail coupling product with high regioselectivity. The reason for retention of the geometry of the olefinic bond may be the high rotational barrier about the double bond of the allylic radical.\textsuperscript{25}\textsuperscript{2}

**Conversion of Bromohydrins to Ketones**

Nucleophilic addition of monovalent cobalt to bromohydrins leads to $\beta$-hydroxyalkylcobalt (IV) as an intermediate from which formation of carbonyl compounds can be expected by homolytic cleavage of the cobalt–carbon bond followed by hydrogen migration as illustrated in Chart 4. The process is analogous to the biological transformation of 1,2-diols into carbonyl compounds catalyzed by diol dehydrase and vitamin B\textsubscript{12}.\textsuperscript{7}

The reaction of methyl 11-bromo-10-hydroxyundecanoate (22) and 2-bromo-cyclo-dodecanol (26) with CoCl(Ph\textsubscript{3}P)\textsubscript{3} was carried out by different procedures, and the results are summarized in Table IV.

Treatment of 22 with CoCl(Ph\textsubscript{3}P)\textsubscript{3} in benzene at room temperature for 6 h gave the ketone 23 (44\% yield) accompanied by an alcohol 24 (42\% yield) and the olefin 25 (10\% yield) (Chart 5). Similarly, reaction of both 26a (threo) and 26b (erythro) afforded 27, 28 and 29 in every case with nearly the same distribution as in the case of 22 (Chart 6). When the reaction was carried out in the presence of base or olefin, a considerable increase in the formation of the ketone was observed at the expense of the alcohol. For example, the reaction of 26a with CoCl(Ph\textsubscript{3}P)\textsubscript{3} in the presence of triethylamine gave 27 (66\% yield), 28 (19\% yield) and 29 (11\% yield) (entry 6). Use of $N$,\textsubscript{N}-disopropylethylamine, pyridine, imidazole, cyclohexene or 1-octene as an additive resulted in the formation of 27 in similar yield (for example, entry 8). Further improvement in formation of the ketone was achieved when the solution of reagent was added very slowly over a period of 6–48 h to a solution of the bromohydrin and
### Table IV. Product Yields in the Reaction of Bromohydrins with CoCl\(_2\)(Ph\(_3\)P)\(_3\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bromohydrin</th>
<th>Additive</th>
<th>Product yield (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ketone</td>
</tr>
<tr>
<td>1</td>
<td>22</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>26a</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>26b</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>Et(_2)N</td>
<td>51</td>
</tr>
<tr>
<td>5(^a)</td>
<td>22</td>
<td>Et(_2)N</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>26a</td>
<td>Et(_2)N</td>
<td>66</td>
</tr>
<tr>
<td>7(^a)</td>
<td>26a</td>
<td>Et(_2)N</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>26a</td>
<td>Cyclohexene</td>
<td>64</td>
</tr>
<tr>
<td>9(^a)</td>
<td>26a</td>
<td>Cyclohexene</td>
<td>80</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yield.
\(^b\) Mixture of methyl 8-undecenoate, methyl 9-undecenoate and methyl 10-undecenoate in a ratio of 5:3:2.
\(^c\) Reaction performed by slow addition of CoCl\(_2\)(Ph\(_3\)P)\(_3\) to a mixture of the bromohydrin and the additive.

![Chart 7](image)

![Chart 8](image)

Triethylamine or cyclohexene. By applying this procedure, conversion of 26a into 27 was effected exclusively as shown in entry 7.

A plausible reaction pathway for the formation of the ketones is illustrated in Chart 7. The \(\beta\)-hydroxyalkylcobalt intermediate (V) is initially formed by oxidative addition of
monovalent cobalt to the carbon–bromine bond of the bromohydrin. Cleavage of the cobalt–carbon bond followed by 1,2-hydrogen shift through a cyclic transition state gives rise to the ketone. The 1,2-hydrogen shift was proved by an experiment using deuterium bromohydrin. The reaction of 1-d-2-bromocycloclodecanol with CoCl(Ph3P)3 in benzene afforded 2-d-cycloclodecanone (75% D). The species of trivalent cobalt hydride generated during the reaction undergoes disproportionation with monovalent cobalt, yielding the divalent cobalt hydride, which might cause reduction of the bromohydrin to the alcohol. Such reduction was prevented by adding amine or olefin, which can trap the acidic cobalt hydride species.26 This reaction pathway was also supported by the following experiment. The reaction of 3β-acetoxy-5α-bromocholestan-6β-ol (33), whose hydroxyl group and bromine atom are fixed in a trans-diastereomeric form, afforded cholesteryl acetate (34), 3β-acetoxy-cholestan-6β-ol (35) and 3β-acetoxycholest-4-en-6β-ol (36) without any ketone. This result suggests that both the bromine and hydride group must be in close proximity for the formation of the ketone. It is noteworthy that 1,2-hydrogen shift in a β-hydroxyalkylcobalt intermediate (V) is also known in the biological transformation of diols into carbonyl compounds.27

In conclusion, the present reaction provides a useful synthetic method for formation of ketones from olefins via bromohydrins. A similar conversion of bromohydrin to ketones catalyzed by Pd(OAc)2 was recently reported by Tsuji et al.27

Experimental

Melting points are uncorrected. Infrared (IR) spectra were taken in CHCl3 solution with a Hitachi 215 spectrometer. 1H-NMR spectra were taken on a Varian T-60 (60 MHz), Varian EM-390 (90 MHz) or Varian XL-200 (200 MHz) spectrometer and were recorded in CDC13. Chemical shifts (δ) were recorded relative to (CH3)2Si as an internal standard. Mass spectra were measured with a Hitachi M-80 spectrometer. Elemental analyses were performed by the Analytical Center, Tokyo College of Pharmacy. All solvents used in the reaction were purified and degassed.

Reductive Coupling of Benzyl Chloride—Benzyl chloride (396 mg, 3.0 mmol) in 5 ml of dry benzene was added to a stirred suspension of 3.17 g (3.6 mmol) of CoCl(Ph3P)3 in 25 ml of dry benzene at room temperature under Ar. The mixture turned blue after stirring for 1.5 h. Insoluble material was filtered off, and the filtrate was washed with water and brine and dried over anhydrous Na2SO4. Removal of the solvent under reduced pressure gave a pale yellow oil. This was subjected to flash column chromatography28 on a silica gel column (E. Merck, Art 9385) eluted with n-hexane to give 192 mg (70% yield) of 1,2-diphenylethane as colorless crystals: mp 52°C (lit.11 52°C); NMR δ 7.18 (10H, s), 2.90 (4H, s); MS m/z 182 (M+).

Reductive Coupling of Benzyl Bromide—A stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry benzene was treated with 171 mg (1.0 mmol) of benzyl bromide in 2 ml of benzene at room temperature under Ar, and the mixture was stirred for 5 min. Work-up as described for benzyl chloride gave 63 mg (69% yield) of 1,2-diphenylethane as colorless crystals.

Reductive Coupling of 1-Chloro-1-phenylethane—1-Chloro-1-phenylethane (141 mg, 1.0 mmol) in 2 ml of benzene was added to a stirred suspension of 1.05 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 1 h. Work-up as described for benzyl chloride gave 35 mg (34% yield) of dl-2,3-diphenylbutane as a colorless oil and 37 mg (35% yield) of meso-2,3-diphenylbutane as colorless crystals. dl-2,3-Diphenylbutane: NMR (CDCl3) δ 6.95 (10H, m), 2.85 (2H, m), 1.24 (6H, d); MS m/z 186 (M+), meso-2,3-Diphenylbutane: mp 124—125°C (lit.29 125—126°C); NMR δ 7.12 (10H, m), 2.70 (2H, m), 0.96 (6H, d); MS m/z 186 (M+).

Reductive Coupling of 1-Chloro-1-phenylbutane—1-Chloro-1-phenylbutane (337 mg, 2.0 mmol) in 5 ml dry benzene was added to a stirred suspension of 2.13 g (2.4 mmol) of CoCl(Ph3P)3 in 15 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 2 h. Work-up as described for benzyl chloride gave 125 mg (46% yield) of dl-4,5-diphenylpentane as a colorless oil and 75 mg (29% yield) of meso-4,5-diphenylpentane as colorless crystals. dl-4,5-Diphenylpentane: NMR δ 7.2—6.6 (10H, m), 2.70 (2H, m), 1.8—0.75 (14H, m); MS m/z 266 (M+), meso-4,5-Diphenylpentane: mp 94—95°C (lit.30 96°C); NMR δ 7.35—7.00 (10H, m), 2.65 (2H, m), 2.45—0.56 (14H, m), MS m/z 266 (M+).

Reductive Coupling of 2-Chloro-2-phenylpropane—2-Chloro-2-phenylpropane (250 mg, 1.7 mmol) in 5 ml dry benzene was added to a stirred suspension of 3.16 g (3.6 mmol) of CoCl(Ph3P)3 in 25 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 2 h. Work-up as described for benzyl chloride gave 295 mg
Reductive Coupling of Chlorodiphenylmethane — Chlorodiphenylmethane (203 mg, 1.0 mmol) in 2 ml of benzene was added to a stirred suspension of 1.65 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 17 h. Work-up as described for benzyl chloride gave 112 mg (67% yield) of 1,2,2-tetraphenylethane as colorless crystals: mp 205—207°C (lit.126 212°C); NMR δ 7.30—6.95 (20H, m), 4.80 (2H, s); MS m/z 334 (M+).

Reductive Coupling of Benzenal Bromide (I) — Benzenal bromide (500 mg, 2.0 mmol) was added to a stirred suspension of 5.29 g (6.0 mmol) of CoCl(Ph3P)3 in 10 ml of dry benzene at 50°C under Ar, and the mixture was stirred at 50°C for 24 h. Work-up as described for benzyl chloride gave 123 mg (68% yield) of (E)-stilbene (3) as colorless crystals: mp 123—125°C (lit.31 122—124°C); NMR δ 7.5—7.0 (10H, m), 6.94 (2H, s); MS m/z 180 (M+).

Dekbromination of meso-1,2-Dibromo-1,2-diphenylethane (2a) — meso-1,2-Dibromo-1,2-diphenylethane (2a) (340 mg, 1.0 mmol) was added to a stirred suspension of 2.12 g (2.4 mmol) of CoCl(Ph3P)3 in 20 ml of dry benzene at 40°C under Ar, and the mixture was stirred at 40°C for 3 h. Work-up as described for benzyl chloride gave 169 mg (94% yield) of (E)-stilbene.

Dekbromination of dl-1,2-Dibromo-1,2-diphenylethane (2b) — dl-1,2-Dibromo-1,2-diphenylethane (2b) (340 mg, 1.0 mmol) was added to a stirred suspension of 2.12 g (2.4 mmol) of CoCl(Ph3P)3 in 20 ml of dry benzene at 40°C under Ar, and the mixture was stirred at 40°C for 3 h. Work-up as described for benzyl chloride gave 164 mg (91% yield) of (E)-stilbene.

Reductive Coupling of Phenethyl Bromide — Phenethyl bromide (555 mg, 3.0 mmol) was added to a stirred suspension of (3.6 mmol) of CoCl(Ph3P)3 in 25 ml of dry benzene at 40°C under Ar, and the mixture was stirred at 40°C for 8 h. The reaction mixture was filtered and the insoluble material was filtered off. Methyl iodide231 (15 ml) was added to the filtrate and the mixture was refluxed for 1 h. Precipitates were filtered off, and the filtrate was concentrated under reduced pressure. The residue was subjected to flash column chromatography on a silica gel column (E. Merck, Art 9358) eluted with n-hexane to give 48 mg (15% yield) of dl-2,3-diphenylbutane as a colorless oil and 79 mg (25% yield) of meso-2,3-diphenylbutane as colorless crystals: mp 124—125°C.

Reductive Coupling of Benzy1 Chloride in Toluene — Benzy1 chloride (127 mg, 1.0 mmol) was added to a stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 10 ml of dry toluene at room temperature under Ar, and the mixture was stirred for 3 h. Work-up as in the case of the reaction in benzene gave 58 mg (64% yield) of 1,2-diphenylethane.

Reductive Coupling of Benzy1 Chloride in Ethyl Acetate — Benzy1 chloride (132 mg, 1.0 mmol) in 2 ml of ethyl acetate was added to a stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry ethyl acetate at 50°C under Ar, and the mixture was stirred at 50°C for 15 min. Work-up as in the case of the reaction in benzene gave 63 mg (70% yield) of 1,2-diphenylethane.

Reductive Coupling of Benzy1 Chloride in 1,2-Dimethoxyethane (DME) — Benzy1 chloride (132 mg, 1.0 mmol) in 2 ml of DME was added to a stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry DME at room temperature under Ar, and the mixture was stirred for 15 h. Ethyl acetate (15 ml) was added to the reaction mixture, and work-up as in the case of the reaction in benzene gave 64 mg (70% yield) of 1,2-diphenylethane.

Reductive Coupling of Benzy1 Chloride in Acetone — Benzy1 chloride (132 mg, 1.0 mmol) in 2 ml of acetone was added to a stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry acetone at room temperature under Ar, and the mixture was stirred for 4 h. Work-up as in the case of the reaction in DME gave 64 mg (70% yield) of 1,2-diphenylethane.

Reductive Coupling of Benzy1 Chloride in Acetonitrile — Benzy1 chloride (132 mg, 1.0 mmol) in 2 ml of acetonitrile was added to a stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry acetonitrile at room temperature under Ar, and the mixture was stirred at 50°C for 2 h. Work-up as in the case of the reaction in DME gave 54 mg (60% yield) of 1,2-diphenylethane.

Reductive Coupling of Benzy1 Chloride in DMF — Benzy1 chloride (132 mg, 1.0 mmol) in 2 ml of DMF was added to a stirred suspension of 1.06 g (1.2 mmol) of CoCl(Ph3P)3 in 8 ml of dry DMF at 40°C under Ar, and the mixture was stirred at 40°C for 2 h. The mixture was poured into 30 ml of water and extracted with 30 ml of n-hexane. The n-hexane solution was washed with water and brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was subjected to flash column chromatography on a silica gel column eluted with n-hexane to give 55 mg (60% yield) of 1,2-diphenylethane.

Reductive Coupling of Benzotrichloride — Benzotrichloride (391 mg, 2.0 mmol) was added to a stirred suspension of 6.35 g (7.2 mmol) of CoCl(Ph3P)3 in 20 ml of dry benzene at room temperature under Ar, and the mixture was stirred at 50°C for 20 h. Insoluble material was filtered off, and 15 ml of methyl iodide232 was added to the filtrate. The mixture was stirred at room temperature for 1 h, and the precipitates were filtered off. The filtrate was concentrated under reduced pressure, and the residue was subjected to flash column chromatography on a silica gel column eluted with n-hexane to give 163 mg (66% yield) of (E)-1,2-dichloro-1,2-diphenylethane as colorless crystals: mp 140—142°C (lit.33 152°C); NMR δ 7.25 (10H, s); MS m/z 248 (M+).

Reductive Coupling of Benzo1tribromide — A mixture of 120 mg (0.36 mmol) of benzo1tribromide and 1.45 g
(1.65 mmol) of CoCl(Ph3P)3 in 3.6 ml of dry benzene was stirred at 60 °C for 6 h under Ar. Work-up as in the case of benzotrichloride gave 22 mg (65% yield) of diphenylacetylene as colorless crystals: mp 60 °C (lit.59—60 °C); MS m/z 178 (M+).

**Debromination of erythro-9,10-Dibromo-octadecanoic Acid (4a)** — A mixture of 210 mg (0.47 mmol) of erythro-9,10-dibromo-octadecanoic acid (4a) and 1.0 g (1.14 mmol) of CoCl(Ph3P)3 in 10 ml of dry benzene was stirred at room temperature for 30 min. The reaction mixture was filtered and the filtrate was treated with 5 ml of methyl iodide32 to room temperature for 30 min. Precipitates were filtered off, and the filtrate was concentrated under reduced pressure. The residue was subjected to flash column chromatography on a silica gel column eluted with AcOEt-n-hexane (1:10) to give 110 mg (82% yield) of the olefin 5 as colorless crystals: mp 40 °C (lit.38 44—45 °C); NMR δ 5.25 (2H, m), 2.23 (2H, t), 1.90 (4H, m), 1.70—1.10 (22H, br s), 0.84 (3H, t); MS m/z 282 (M+). The E/Z ratio of the product could not be determined directly. However, formation of the E-olefin was confirmed by converting the olefin 5 into the corresponding epoxide: 5 was oxidized with m-chloroperbenzoic acid (m-CPBA) in CH2Cl2 at room temperature for 4 h to give an epoxide, whose NMR spectrum showed a signal at 2.70 ppm due to the protons attached to the E-epoxide ring.366

**Dehalogenation of theo-9,10-Dibromo-octadecanoic Acid (4b)** — A mixture of 274 mg (0.62 mmol) of theo-9,10-dibromo-octadecanoic acid (4b) and 1.31 g (1.48 mmol) of CoCl(Ph3P)3 in 13 ml of dry benzene was stirred at room temperature for 1.5 h under Ar. Work-up as described for 4a gave 150 mg (86% yield) of the olefin 5 as a colorless oil: NMR δ 5.25 (2H, m); MS m/z 282 (M+). The E/Z ratio of the olefin was determined in the same way as for 4a. The NMR spectrum of the resulting epoxides showed signals at 2.85 ppm (proton attached to the Z-epoxide350) and 2.70 ppm (proton attached to the E-epoxide) in a ratio of 57:43, indicating that the product was a 57:43 mixture of Z- and E-olefins.

**Dehalogenation of erythro-9,10-Dibromo-octadecanoic Acid Methyl Ester (4c)** — A mixture of 180 mg (0.39 mmol) of erythro-9,10-dibromo-octadecanoic acid methyl ester (4c) and 0.83 g (0.94 mmol) of CoCl(Ph3P)3 in 8 ml of dry benzene was stirred at room temperature for 2 h under Ar. Work-up as described for 4a gave 100 mg (86% yield) of 9-octadecanoic acid methyl ester as a colorless oil: NMR δ 5.25 (2H, m), 3.70 (3H, s), MS m/z 296 (M+). The E/Z ratio of the olefin was determined in the same way as for 4a. The NMR spectrum of the epoxides showed signals at 2.70 and 2.85 ppm in a ratio of 85:15, indicating that the E/Z ratio of the olefin was 85:15.

**Dehalogenation of theo-9,10-Dibromo-octadecanoic Acid Methyl Ester (4d)** — A mixture of 203 mg (0.45 mmol) of theo-9,10-dibromo-octadecanoic acid methyl ester (4d) and 941 mg (1.07 mmol) of CoCl(Ph3P)3 in 9 ml of dry benzene was stirred at room temperature for 2 h under Ar. Work-up as described for 4a gave 116 mg (88% yield) of olefin. The E/Z ratio of the olefin was 88:12.

**Dehalogenation of erythro-9,10-Dibromo-octadecanoic Acid Methyl Ester (4e) in the Presence of Acetic Acid** — A mixture of 200 mg (0.44 mmol) of 4e, 1.16 g (3.12 mmol) of CoCl(Ph3P)3 and 0.6 ml (10.5 mmol) of acetic acid in 11 ml of dry benzene was stirred at room temperature for 1 h under Ar. Work-up as described for 4a gave 118 mg (91% yield) of the olefin 5. The E/Z ratio of the olefin was 94:6.

**Dehalogenation of theo-9,10-Dibromo-octadecanoic Acid Methyl Ester (4d) in the Presence of Acetic Acid** — A mixture of 210 mg (0.46 mmol) of 4d, 1.21 g (1.37 mmol) of CoCl(Ph3P)3 and 0.7 ml (11 mol) of acetic acid in 12 ml of dry benzene was stirred at room temperature for 1.5 h under Ar. Work-up as described for 4a gave 126 mg (81% yield) of the olefin 5. The E/Z ratio of the olefin was 35:65.

**Dehalogenation of 5α,6β-Dibromocholestanol** — A mixture of 858 mg (1.58 mmol) of 5α,6β-dibromocholestanol and 3.33 g (3.77 mmol) of CoCl(Ph3P)3 in 30 ml of dry benzene was stirred at 40 °C for 4 h under Ar. Work-up as described for 4a gave 426 mg (70% yield) of cholesterol as colorless crystals: mp 148 °C (lit.37 148—149 °C).

**Dehalogenation of 5β,6α-Dibromocholestanol** — A mixture of 400 mg (0.73 mmol) of 5β,6α-dibromocholestanol and 1.54 g (1.74 mmol) of CoCl(Ph3P)3 in 13 ml of dry benzene was stirred at 40 °C for 4 h under Ar. Work-up as described for 4a gave 210 mg (74% yield) of cholesterol.

**Reductive Coupling of Geranyl Bromide (6)** — Geranyl bromide (6) (242 mg, 1.1 mmol) was added to a stirred suspension of CoCl(Ph3P)3 (1.08, 1.2 mmol) in 11 ml of dry benzene under Ar. The mixture was filtered, and the filtrate was treated with methyl iodide (5 ml)32 for 10 min at room temperature. Precipitates were filtered off and the filtrate was concentrated under reduced pressure. Flash chromatography of the residue on a silica gel column using n-hexane as an eluent afforded 100 mg (66% yield) of 7, 24 mg (16% yield) of 8 and 10 mg (7% yield) of 9.

7: colorless oil; IR 1440, 1360 cm−1; MS m/z 274 (M+); NMR δ 5.15 (4H, m), 2.01 (12H, m), 1.69 (6H, s), 1.60 (12H, s).
8: colorless oil; IR 910 cm−1; MS m/z 274 (M+); NMR δ 5.75 (1H, dd), 5.20—4.80 (5H, m), 2.05 (6H, m), 1.69 (6H, s), 1.60 (9H, s), 0.95 (3H, s).
9: colorless oil; IR 910 cm−1; MS m/z 274 (M+); NMR δ 5.75 (1H, dd), 5.20—4.75 (6H, m), 1.69 (6H, s), 1.60 (6H, s); Anal. Calcd for C28H54O2: C, 87.51; H, 12.49. Found: C, 87.67; H, 12.76.

**Reductive Coupling of Neryl Bromide (10)** — Neryl bromide (10) (210 mg, 0.97 mmol) was added to a stirred suspension of 0.94 g (1.07 mmol) of CoCl(Ph3P)3 in 10 ml of dry benzene under Ar, and the mixture was stirred at room temperature for 3 h. Work-up as described for 6 gave 83 mg (63% yield) of 11, 21 mg (16% yield) of 12 and 12 mg (9% yield) of 9.
colorless oil; IR 1440, 1360 cm⁻¹; MS m/z 274 (M⁺); NMR δ 5.15 (4H, m), 2.01 (12H, m), 1.69 (12H, s), 1.60 (6H, s).

Reductive Coupling of (E,E)-Farnesyl Bromide (13) — (E,E)-Farnesyl bromide (13) (571 mg, 2.0 mmol) was added to a stirred suspension of 1.94 g (2.2 mmol) of CoCl₂·P₃ in 20 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 3 h. Work-up as described for 6 gave 223 mg (55% yield) of (E,E,E)-squalene (14), 88 mg (22% yield) of 15 and 47 mg (12% yield) of 16.

Reductive Coupling of (2Z,6E)-Farnesyl Bromide (17) — (2Z,6E)-Farnesyl bromide (17) (856 mg, 3.0 mmol) was added to a suspension of 2.91 g (3.3 mmol) of CoCl₂·P₃ in 30 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 3 h. Work-up as described for 6 gave 310 mg (51% yield) of (6E,10Z,14Z,18E)-squalene (18), 115 mg (19% yield) of 19 and 50 mg (8% yield) of 16.

Reductive Coupling of Geranyl Bromide (6) in DMF — Geranyl bromide (6) (267 mg, 1.23 mmol) was added to a stirred suspension of 1.44 g (1.64 mmol) of CoCl₂·P₃ in 12 ml of dry DMF at room temperature under Ar, and the mixture was stirred for 6 h. The reaction mixture was poured into 50 ml of water and extracted with 50 ml of n-hexane. The n-hexane solution was washed with water and brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was treated with methyl iodide (5 ml) for 10 min at room temperature. Precipitates were filtered off and the filtrate was concentrated under reduced pressure. Flash chromatography on a silica gel column gave 90 mg (53% yield) of 7, 18 mg (11% yield) of 8, 24 mg (14% yield) of 9 and 17 mg (10% yield) of trimer 20.

Reductive Coupling of Neryl Bromide (10) in DMF — Neryl bromide (10) (212 mg, 0.98 mmol) was added to a stirred suspension of 1.29 g (1.47 mmol) of CoCl₂·P₃ in 10 ml of dry DMF at room temperature under Ar, and the mixture was stirred for 9 h. Work-up as described for 6 gave 65 mg (48% yield) of 11, 11 mg (8% yield) of 12, 24 mg (18% yield) of 13 and 15 mg (11% yield) of trimer 21.

Reductive Coupling of Geranyl Chloride — Geranyl chloride (375 mg, 2.0 mmol) in 5 ml of benzene was added to a stirred suspension of 1.94 g (2.2 mmol) of CoCl₂·P₃ in 15 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 1 h. Work-up as described for 6 gave 157 mg (57% yield) of 7, 54 mg (20% yield) of 8 and 10 mg (4% yield) of 9.

Reductive Coupling of Neryl Chloride — Neryl chloride (375 mg, 2.0 mmol) in 5 ml of benzene was added to a stirred suspension of 1.94 g (2.2 mmol) of CoCl₂·P₃ in 15 ml of dry benzene at room temperature under Ar, and the mixture was stirred for 17 h. Work-up as described for 6 gave 165 mg (60% yield) of 11, 37 mg (17% yield) of 12 and 12 mg (5% yield) of 9.

Reaction of Methyl 11-Bromo-10-hydroxyundecanoate (22) (Entry 1) — A mixture of 240 mg (0.81 mmol) of 11-bromo-10-hydroxyundecanoate (22) and 1.08 g (1.23 mmol) of CoCl₂·P₃ in 20 ml of dry benzene was stirred at 60 °C for 7.5 h under Ar. Insoluble material was filtered off and the filtrate was treated with 5 ml of methyl iodide for 10 min at room temperature. Precipitates were filtered off and the filtrate was concentrated under reduced pressure. The residue was subjected to flash chromatography on a silica gel column using AcOEt-n-hexane (1:1) as an eluent to give 73 mg (44% yield) of the ketone 23, 70 mg (42% yield) of the alcohol 24 and 15 mg (10% yield) of the olefin 25.

Reduction of three-2-Bromocyclooctadecanol (26a) (Entry 2) — A mixture of 358 mg (1.36 mmol) of three-2-bromocyclooctadecanol (26a) and 1.80 g (2.04 mmol) of CoCl₂·P₃ in 15 ml of dry benzene was stirred at room
temperature for 5 h under Ar. Work-up as in the case of entry 1 gave 100 mg (40% yield) of the ketone 27, 105 mg (42% yield) of the alcohol 28 and 22 mg (10% yield) of the olefin 29.

27: colorless crystals; mp 57—58 °C (lit. 59 °C).
28: colorless crystals; mp 79 °C (lit. 79 °C).
29: colorless oil; MS m/z 166 (M+).

**Reaction of erythro-2-Bromocyclodecaneol (26b)**

A mixture of 259 mg (0.98 mmol) of erythro-2-bromocyclodecaneol (26b) and 1.30 g (1.48 mmol) of CoCl(Ph3P)3 in 10 ml of dry benzene was stirred at room temperature for 3 h under Ar. Work-up as in the case of entry 1 gave 71 mg (40% yield) of the ketone 27, 70 mg (39% yield) of the alcohol 28 and 16 mg (10% yield) of the olefin 29.

**Reaction of Methyl 11-Bromo-10-hydroxyundecanoate (22) with CoCl(Ph3P)3 in the Presence of Triethylamine (Entry 4)**

A mixture of 350 mg (1.19 mmol) of 22, 1.58 g (1.79 mmol) of CoCl(Ph3P)3 and 0.86 ml (6.0 mmol) of Et3N in 20 ml of dry benzene was stirred at 50 °C for 8 h under Ar. Work-up as in the case of entry 1 gave 131 mg (51% yield) of the ketone 23, 91 mg (35% yield) of the alcohol 24 and 16 mg (7% yield) of the olefin 25.

**Reaction of Methyl 11-Bromo-10-hydroxyundecanoate (22) with CoCl(Ph3P)3 in the Presence of Triethylamine (Entry 5)**

A mixture of 141 mg (0.48 mmol) of methyl 11-bromo-10-hydroxyundecanoate (22) and 0.66 ml of Et3N (4.8 mmol) in 100 ml of dry solvent (C6H6-Et2O, 1:1) was placed in a 200 ml round-bottomed flask equipped with a Soxlet extractor filled with 2.10 g of CoCl(Ph3P)3 (2.4 mmol). The mixture was gently refluxed for 48 h under Ar. At the end of the reaction, the CoCl(Ph3P)3 in the Soxlet extractor was completely dissolved. Work-up as in the case of entry 1 gave 87 mg (85% yield) of the ketone 23 and 9 mg (9% yield) of the alcohol 24.

**Reaction of threo-2-Bromocyclodecaneol (26a) with CoCl(Ph3P)3 in the Presence of Triethylamine (Entry 6)**

A mixture of 200 mg (0.76 mmol) of 26a, 1.04 g (1.13 mmol) of CoCl(Ph3P)3 and 0.4 ml (2.3 mmol) of Et3N in 32 ml of dry benzene was stirred at room temperature for 3 h under Ar. Work-up as in the case of entry 1 gave 91 mg (66% yield) of the ketone 27, 27 mg (19% yield) of the alcohol 28 and 9 mg (11% yield) of the olefin 29.

**Reaction of threo-2-Bromocyclodecaneol (26a) with CoCl(Ph3P)3 in the Presence of Triethylamine (Entry 7)**

A solution of 1.23 g of CoCl(Ph3P)3 (1.40 mmol) in 50 ml of benzene was added dropwise to a stirred solution of 184 mg of 26a (0.70 mmol) and 0.6 ml of Et3N (4.30 mmol) in 14 ml of dry benzene over a period of 6 h at 50 °C under Ar, and the mixture was stirred for 1 h. Work-up as in the case of entry 1 gave 115 mg (90% yield) of the ketone 27.

**Reaction of 26a with CoCl(Ph3P)3 in the Presence of Cyclohexene (Entry 8)**

A mixture of 228 mg (0.87 mmol) of 26a, 1.15 g (1.31 mmol) of CoCl(Ph3P)3 and 2 ml (20 mmol) of cyclohexene in 20 ml of dry benzene was stirred at room temperature for 7.5 h under Ar. Work-up as in the case of entry 1 gave 101 mg (64% yield) of the ketone 27, 42 mg (26% yield) of the alcohol 28 and 7 mg (5% yield) of the olefin 29.

**Reaction of 26a with CoCl(Ph3P)3 in the Presence of Cyclohexene (Entry 9)**

A solution of 1.62 g (1.84 mmol) of CoCl(Ph3P)3 in 100 ml of dry benzene was added dropwise to a stirred solution of 242 mg (0.92 mmol) of 26a and 1.70 ml (18.4 mmol) of cyclohexene in 20 ml of dry benzene over a period of 5 h at room temperature under Ar. The mixture was stirred for 3 h. Work-up as in the case of entry 1 gave 134 mg (80% yield) of the ketone 27 and 9 mg (5% yield) of the alcohol 28.

**Preparation of threo-1-d-2-Bromocyclodecaneol (30)**

A mixture of 407 mg of erythro-2-bromocyclodecaneol (26b) (1.55 mmol) and 500 mg of pyridiniumchlorochromate (PCC) (2.3 mmol) in 50 ml CH2Cl2 was stirred at room temperature for 15 h. The mixture was filtered through a short silica gel column with CH2Cl2 as the eluent. The eluate was concentrated under reduced pressure to afford crude 2-bromocyclodecaneol as a colorless oil. The oil was dissolved in 15 ml of EtOH, and 130 mg of NaBD4 (3.1 mmol, 98% D) was added. The mixture was stirred at room temperature for 1 h, then acidified with 10% HCl solution and extracted with Et2O. The ether solution was washed with water and brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. Flash chromatography of the residue afforded 220 mg of threo-1-d-2-bromocyclodecaneol (30) (54% yield) and 170 mg of erythro isomer (42% yield).

30: colorless crystals; mp 65 °C; IR 3570 cm−1; NMR δ 4.35 (1H, t), 2.20—1.70 (4H, m), 1.33 (16H, br s); Anal. Caled for C15H23DBrO: C, 54.75; H, 8.81; Br, 30.24. Found: C, 54.46; H, 8.80; Br, 30.09.

**Erythro Isomer: colorless crystals; NMR δ 4.36 (1H, t), 2.20—1.70 (4H, m).**

**Reaction of 30 with CoCl(Ph3P)3**

A mixture of 14 mg of 30 (0.30 mmol) and 400 mg of CoCl(Ph3P)3 (0.45 mmol) in 3 ml of dry benzene was stirred at room temperature for 9 h. Work-up as in the case of entry 1 gave 14 mg of 2-d-cyclodecaneone (31) (25% yield) and 22 mg of 1-d-cyclodecaneone (32) (40% yield).

31: IR 1700 cm−1; NMR δ 2.45 (3H, m), 1.70 (4H, m), 1.35 (14H, br s); MS m/z (relative intensity) 183 (95, M+), 182 (35, M+ of cyclodecaneone); Anal. Caled for C17H22DO: C, 79.06; H, 12.16. Found: C, 78.81; H, 12.06.

32: IR 3610, 1010 cm−1; NMR δ 1.80—1.20 (22H, m), 1.45 (1H, s); MS m/z 185 (M+); Anal. Caled for C12H12DO: C, 78.19; H, 13.13. Found: C, 77.95; H, 12.99.

**Reaction of 3β-Acetoxy-5z-bromocholestan-6β-ol (33)**

A mixture of 326 mg (0.62 mmol) of 3β-acetoxy-5z-bromocholastan-6β-ol and 928 mg (1.05 mmol) of CoCl(Ph3P)3 in 40 ml of dry benzene was stirred at room temperature for 17 h under Ar. The reaction mixture was filtered and the filtrate was treated with 5 ml of methyl iodide for 30 min at room temperature. Precipitates were filtered off and the filtrate was concentrated under reduced pressure. The residue was subjected to flash chromatography on a silica gel column using AcOEt–n-hexane.
(1:4) as the eluent, to afford 75 mg (25% yield) of cholesteryl acetate (34) and 150 mg (50% yield) of an inseparable (1:1) mixture of 35 and 36.

34: colorless crystals; mp 112 °C (lit.45 114—115 °C).
Mixture of 35 and 36: colorless crystals; NMR δ 5.47 (0.5H, m), 5.25 (0.5H, br), 4.75 (0.5H, br), 4.22 (0.5H, m), 3.80 (0.5H, m), 2.06 (1.5H, s) 2.0 (1.5H, s), MS m/z 444 (M⁺), 442 (M⁺).
Part of the mixture (55 mg) was dissolved in 5 ml of CHCl₃, and 275 mg of MnO₂ was added. The reaction mixture was stirred at room temperature for 17 h, then filtered and the filtrate was concentrated under reduced pressure. The residue was subjected to flash chromatography using AcOEt–n-hexane (1:4) to give 27 mg of 3β-acetoxycholest-4-en-6-one (37) and 17 mg of (35).

35: colorless crystals; mp 145—146 °C (lit.46 148—149 °C); IR 3600, 1725 cm⁻¹; NMR δ 5.53 (1H, m), 5.28 (1H, dd), 4.27 (1H, m), 2.10 (3H, s), MS m/z 442 (M⁺).

References and Notes

23) Coupling of allylic bromide using cobalt metal to give 1,5-hexadiene was reported, but details of the reaction conditions and the yield of the product were not given; R. D. Rieke, A. V. Kavaliunas, L. D. Rhyne, and D. J. Fraser, J. Am. Chem. Soc., 101, 246 (1979).
26) Page 67 in ref. 1.
32) To remove triphenylphosphine liberated during the reaction as methyltriphénylphosphonium iodide.
36) The chemical shift of the corresponding protons of elaicic acid epoxide and its methyl ester appeared at
2.70 ppm, while the values for oleic acid epoxide and its methyl ester were 2.85 ppm.