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

DEN-ICHI MOMOSE, KAZUO IGUCHI, TOSHIKAZU SUGIYAMA,
and YASUJI YAMADA*

*Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji,
Tokyo 192-03, Japan*

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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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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.[1] 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.[2] 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.[3,4] Cleavage of the cobalt–carbon bond leads to the formation of a carbon–carbon bond.[5,6] Rearrangement mediated by a trivalent cobalt intermediate is also recognized in important biological reactions.[7] 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.*[8] Although the use of the reagent in organic synthesis has so far been limited to dimerization of olefins,[9] 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.[10] For the reductive coupling of benzylic halides, low-valent transition metal reagents such as Cr(II),[11] V((II),[12] W(0),[13] Fe(0)[14] and Co(0)[15] are frequently employed. Our studies demonstrated that $CoCl(Ph_3P)_3$ 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 I. Reductive Coupling of Benzylic Halides

Benzylic halide	Reaction conditions[a]	Product	Yield (%)[b]
Benzyl chloride	RT 1.5 h	1,2-Diphenylethane	70
Benzyl bromide	RT 5 min	1,2-Diphenylethane	69
1-Chloro-1-phenylethane	RT 1 h	2,3-Diphenylbutane[c]	69
1-Chloro-1-phenylbutane	RT 2 h	4,5-Diphenyloctane[d]	75
2-Chloro-2-phenylpropane	RT 2 h	2,3-Dimethyl-2,3-diphenylbutane	83
Chlorodiphenylmethane	RT 17 h	1,1,2,2-Tetraphenylethane	67
Benzal bromide	50 °C 24 h	(*E*)-Stilbene	68
Benzotrichloride	50 °C 24 h	(*E*)-1,2-Dichloro-1,2-diphenylethane	66
Benzotribromide	60 °C 6 h	Diphenylacetylene	65

a) Carried out in benzene. *b*) Isolated yield.
c) Both *meso* (mp 124—125 °C) and *dl* (oil) isomers were formed in a ratio of 1 : 1.
d) Both *meso* (mp 96—97 °C) and *dl* (oil) isomers were formed in a ratio of 2 : 3.
RT = room temperature.

The results of the reductive coupling of benzylic halides are shown in Table I.

Benzylic 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 wihin 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, $Co_2(CO)_8$, 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[16)] 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 $CoCl(Ph_3P)_3$ 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 benzylic to the homobenzylic position in the initially formed homobenzyl radical intermediate giving rise to the benzylic radical.[17)]

Coupling of a benzylic geminal dibromide with $CoCl(Ph_3P)_3$ leads to the formation of a carbon–carbon double bond. Benzal bromide (**1**) was treated with $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$. 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 benzylic radical intermediate (Chart 2). The relatively stable benzylic 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 acetylenic bond was accomplished by the reaction of benzotribromide with $CoCl(Ph_3P)_3$, giving diphenylacetylene in a 65% yield. A similar reaction of benzo-

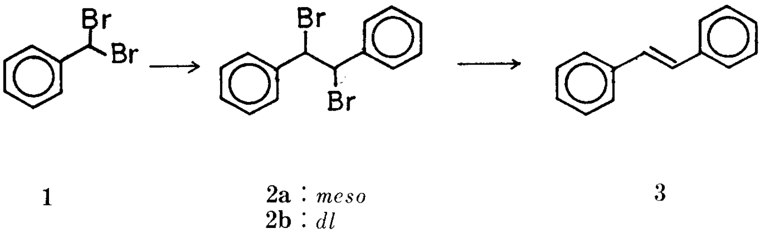


Chart 1

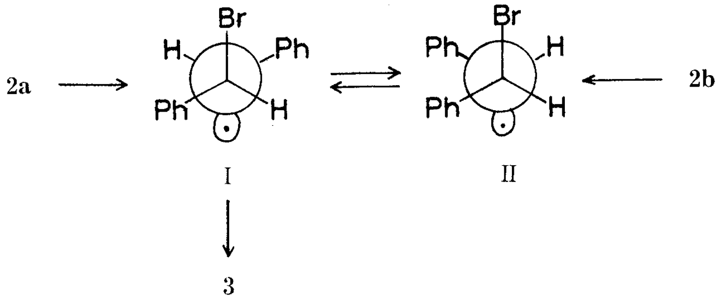


Chart 2

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 $CoCl(Ph_3P)_3$.

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 $CoCl(Ph_3P)_3$ was carried out in benzene, and the results are summarized in Table II.

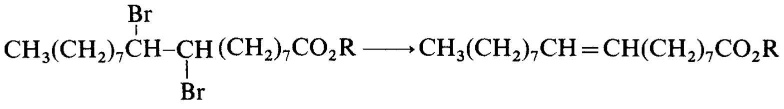
In every case, dehalogenation took place cleanly at room temperature to give olefins **5** in 81—91% yields. The *erythro* isomer of the carboxylic acid (**4a**) gave the *E* olefin exclusively, whereas the *threo* isomer **4b** afforded a mixture of *E* and *Z* olefins. In the case of the corresponding 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 $CoCl(Ph_3P)_3$ 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-dibromocholestanol and 5β,6α-dibromocholestanol with $CoCl(Ph_3P)_3$ (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



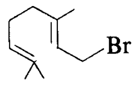
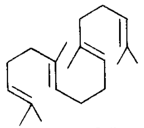
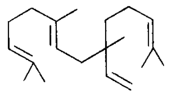
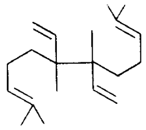
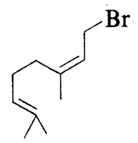
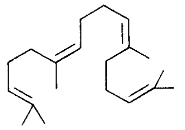
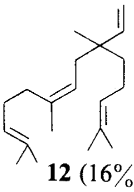
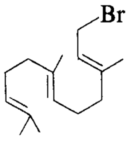
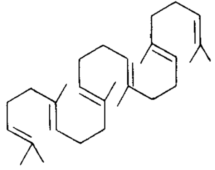
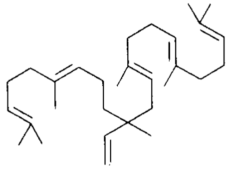
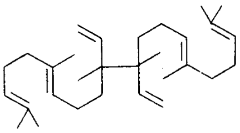
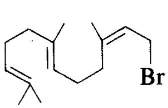
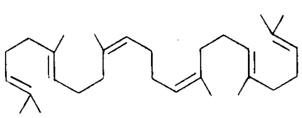
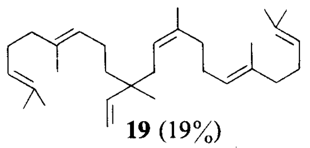
$$\mathrm{CH_3(CH_2)_7\underset{\substack{|\\ }}{\overset{\substack{Br\\|}}{C}}H\text{-}\underset{\substack{|\\ Br}}{C}H(CH_2)_7CO_2R \longrightarrow CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2R}$$

4a: R = H (*erythro*) **5**
4b: R = H (*threo*)
4c: R = Me (*erythro*)
4d: R = Me (*threo*)

Dibromide	Yield (%)[a]	*E*/*Z* Ratio of olefin[b]
4a	82	100: 0
4b	86	43:57
4c	86	85:15
4d	88	88:12
4c	91	94: 6[c]
4d	81	35:65[c]

a) Isolated yield.
b) Determined by NMR of the epoxides obtained from the olefins by treatment with *m*-CPBA.
c) Reaction in the presence of acetic acid.

Table III. Coupling of Allylic Bromides Using $\mathrm{CoCl(Ph_3P)_3}$

Allylic bromide	Products (yield)[a]
 **6**	 **7** (66%) +  **8** (16%) +  **9** (7%)
 **10**	 **11** (63%) +  **12** (16%) + **9** (9%)
 **13**	 **14** (55%) +  **15** (22%) +  **16** (12%)
 **17**	 **18** (51%) +  **19** (19%) + **16** (8%)

a) 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,[11,20] and in some cases transition metal carbonyls[14,21] and lanthanoid compounds[22] were also used. However, few examples of allylic coupling promoted by low-valent cobalt are available.[23]

Reductive coupling of terpenoid allylic halides with $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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 benzylic 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 $CoCl(Ph_3P)_3$ 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 (^{1}H-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-Markownikoff manner followed by hydrogen abstraction from the solvent.

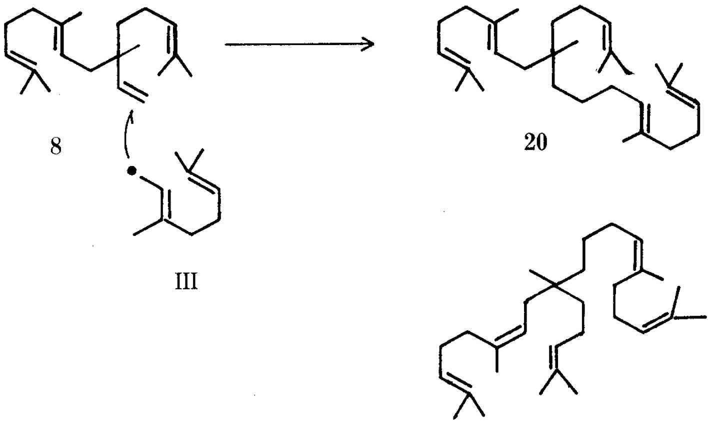


Chart 3

Reaction of farnesyl bromide (**13**) and the geometrical isomer **17** with $CoCl(Ph_3P)_3$ in benzene at room temperature for 3 h afforded (*E*,*E*,*E*,*E*)-squalene (**14**) (55% yield) and (6*E*,10*Z*,14*Z*,18*E*)-squalene (**18**) (51% yield), respectively, with the concomitant formation of their regioisomers, in a stereospecific manner. This method provides an efficient synthesis of squalene.[20d,24]

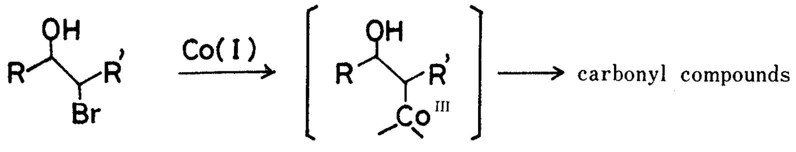
The characteristic feature of the allylic coupling is that the reaction proceeds with retention of the stereochemistry of the carbon–carbon double bond of the allylic halides used, and that the reaction provides the tail-to-tail coupling product with high regioselectivity. The reason for retention of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

Conversion of Bromohydrins to Ketones

Nucleophilic addition of monovalent cobalt to bromohydrins leads to β-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_{12}.[7)]

The reaction of methyl 11-bromo-10-hydroxyundecanoate (**22**) and 2-bromo-cyclododecanol (**26**) with $CoCl(Ph_3P)_3$ was carried out by different procedures, and the results are summarized in Table IV.

Treatment of **22** with $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ in the presence of triethylamine gave **27** (66% yield), **28** (19% yield) and **29** (11% yield) (entry 6). Use of *N*,*N*-diisopropylethylamine, 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



IV

Chart 4

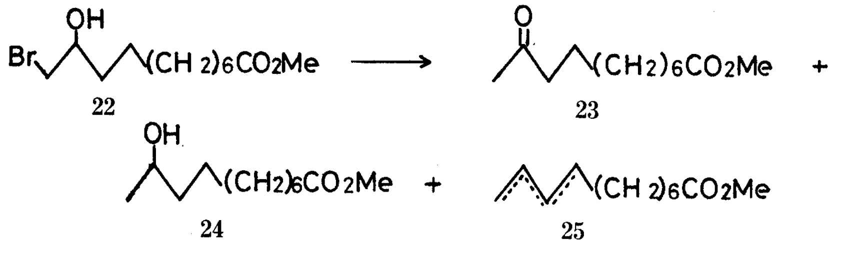
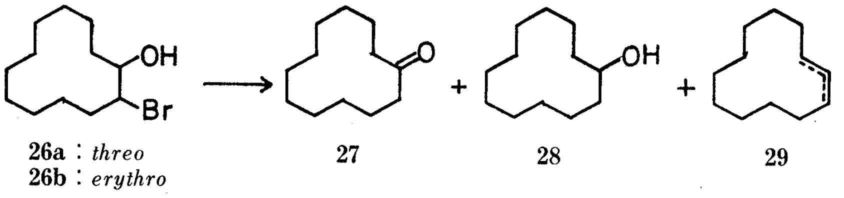


Chart 5



26a : *threo*
26b : *erythro*
27 **28** **29**

Chart 6

Table IV. Product Yields in the Reaction of Bromohydrins with $CoCl(Ph_3P)_3$

Entry	Bromohydrin	Additive	Product yield (%)[a]		
			Ketone	Alcohol	Olefin
1	**22**		44	42	10[b]
2	**26a**		40	42	10
3	**26b**		40	39	10
4	**22**	Et_3N	51	35	7[b]
5[c]	**22**	Et_3N	85	9	
6	**26a**	Et_3N	66	19	11
7[c]	**26a**	Et_3N	90		
8	**26a**	Cyclohexene	64	26	5
9[c]	**26a**	Cyclohexene	80	5	

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 $CoCl(Ph_3P)_3$ to a mixture of the bromohydrin and the additive.

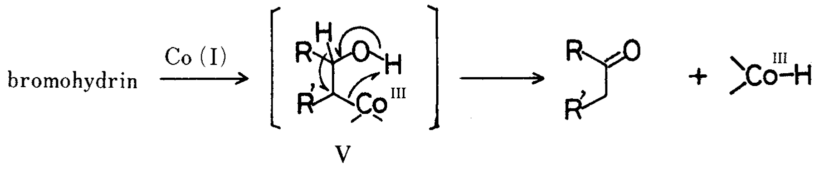


Chart 7

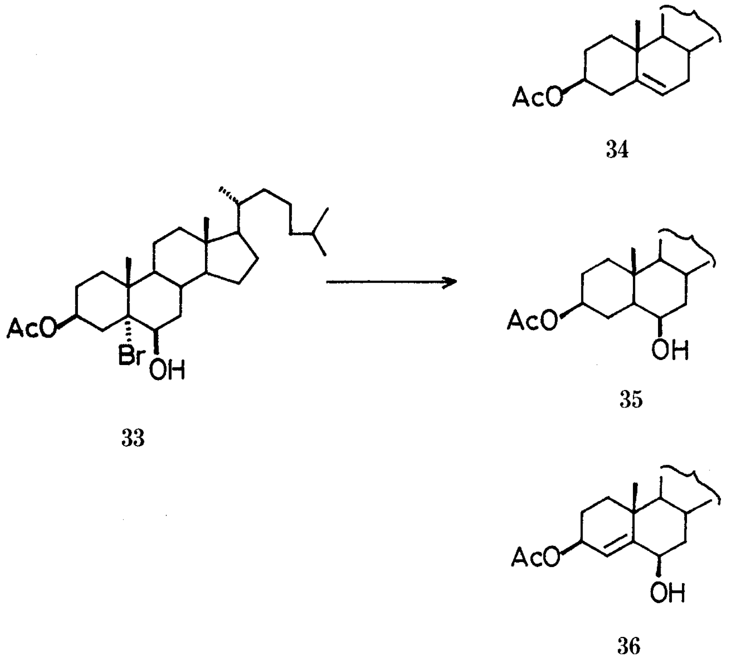


Chart 8

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 β-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 deuterated bromohydrin. The reaction of 1-D-2-bromocyclododecanol with $CoCl(Ph_3P)_3$ in benzene afforded 2-D-cyclododecanone (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*-diaxial 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 hydroxyl 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.7)

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 $CHCl_3$ 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 $CDCl_3$. Chemical shifts (δ) were recorded relative to $(CH_3)_4Si$ 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 $CoCl(Ph_3P)_3$ 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 Na_2SO_4. 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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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 ($CDCl_3$) 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 $CoCl(Ph_3P)_3$ 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-diphenyloctane as a colorless oil and 75 mg (29% yield) of *meso*-4,5-diphenyloctane as colorless crystals. *dl*-4,5-Diphenyloctane: 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-Diphenyloctane: 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 $CoCl(Ph_3P)_3$ 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

(83% yield) of 2,3-dimethyl-2,3-diphenylbutane as colorless crystals: NMR δ 6.98 (10H, m), 1.30 (12H, s); MS m/z 238 (M^+).

Reductive Coupling of Chlorodiphenylmetane——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 $CoCl(Ph_3P)_3$ 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 1,1,2,2-tetraphenylethane as colorless crystals: mp 205—207 °C (lit.[12b)] 212 °C); NMR δ 7.30—6.95 (20H, m), 4.80 (2H, s); MS m/z 334 (M^+).

Reductive Coupling of Benzal Bromide (1)——Benzal bromide (500 mg, 2.0 mmol) was added to a stirred suspension of 5.29 g (6.0 mmol) of $CoCl(Ph_3P)_3$ 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^+).

Debromination 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 $CoCl(Ph_3P)_3$ 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.

Debromination 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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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 iodide[32)] (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 Benzyl Chloride in Toluene——Benzyl chloride (127 mg, 1.0 mmol) was added to a stirred suspension of 1.06 g (1.2 mmol) of $CoCl(Ph_3P)_3$ 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 Benzyl Chloride in Ethyl Acetate——Benzyl 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 $CoCl(Ph_3P)_3$ 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 Benzyl Chloride in 1,2-Dimethoxyethane (DME)——Benzyl 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 $CoCl(Ph_3P)_3$ 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 Benzyl Chloride in Acetone——Benzyl 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 $CoCl(Ph_3P)_3$ 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 Benzyl Chloride in Acetonitrile——Benzyl 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 $CoCl(Ph_3P)_3$ 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 Benzyl Chloride in DMF——Benzyl 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 $CoCl(Ph_3P)_3$ 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 Na_2SO_4 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 $CoCl(Ph_3P)_3$ 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 iodide[32)] 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-diphenylethylene as colorless crystals: mp 140—142 °C (lit.[33)] 152 °C); NMR δ 7.15 (10H, s); MS m/z 248 (M^+).

Reductive Coupling of Benzotribromide——A mixture of 120 mg (0.36 mmol) of benzotribromide and 1.45 g

(1.65 mmol) of $CoCl(Ph_3P)_3$ 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.34) 59—60 °C); MS *m/z* 178 (M^+).

Debromination of *erythro*-9,10-Dibromooctadecanoic Acid (4a)——A mixture of 210 mg (0.47 mmol) of *erythro*-9,10-dibromooctadecanoic acid (**4a**) and 1.0 g (1.14 mmol) of $CoCl(Ph_3P)_3$ 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) at 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.35) 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 CH_2Cl_2 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.36)

Dehalogenation of *threo*-9,10-Dibromooctadecanoic Acid (4b)——A mixture of 274 mg (0.62 mmol) of *threo*-9,10-dibromooctadecanoic acid (**4b**) and 1.31 g (1.48 mmol) of $CoCl(Ph_3P)_3$ in 13 ml of dry benzene was stirred at room temperature for 1.5 h under Ar. Wrok-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*-epoxide36)) 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-Dibromooctadecanoic Acid Methyl Ester (4c)——A mixture of 180 mg (0.39 mmol) of *erythro*-9,10-dibromooctadecanoic acid methyl ester (**4c**) and 0.83 g (0.94 mmol) of $CoCl(Ph_3P)_3$ 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-octadecenoic 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 *threo*-9,10-Dibromooctadecanoic Acid Methyl Ester (4d)——A mixture of 203 mg (0.45 mmol) of *threo*-9,10-dibromooctadecanoic acid methyl ester (**4d**) and 941 mg (1.07 mmol) of $CoCl(Ph_3P)_3$ 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 *etythro*-9,10-Dibromooctadecanoic Acid Methyl Ester (4c) in the Presence of Acetic Acid——A mixture of 200 mg (0.44 mmol) of **4c**, 1.16 g (1.32 mmol) of $CoCl(Ph_3P)_3$ 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 *threo*-9,10-Dibromooctadecanoic 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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ (1.08 g, 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 column 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**.

738): 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).

839): 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 $C_{20}H_{34}$: 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 $CoCl(Ph_3P)_3$ 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**.

11[38]: 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).

12[40]: colorless oil; IR 910 cm^{-1}; MS *m/z* 274 (M^+); NMR δ 5.75 (1H, dd), 5.20—4.75 (5H, m), 2.05 (6H, m), 1.69 (9H, s), 1.60 (6H, s), 0.95 (3H, 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 $CoCl(Ph_3P)_3$ 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,E*)-squalene (**14**), 88 mg (22% yield) of **15** and 47 mg (12% yield) of **16**.

14[38]: colorless oil; IR 1445, 1360 cm^{-1}; MS *m/z* 410 (M^+); NMR δ 5.10 (6H, m), 2.05 (20H, m), 1.69 (6H, s), 1.60 (18H, s).

15: colorless oil; IR 910 cm^{-1}; MS *m/z* 410 (M^+); NMR δ 5.75 (1H, dd), 5.20—4.80 (7H, m), 2.00 (18H, m), 1.69 (6H, s), 1.60 (15H, s), 0.92 (3H, s); *Anal.* Calcd for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.96; H, 12.32.

16: colorless oil; IR 910 cm^{-1}; MS *m/z* 410 (M^+); NMR δ 5.75 (2H, dd), 5.20—4.80 (8H, m), 2.00 (12H, m), 1.69 (6H, s), 1.60 (12H, s), 0.93 (6H, s); *Anal.* Calcd for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.95; H, 12.56.

Reductive Coupling of (2*Z*,6*E*)-Farnesyl Bromide (17)——(2*Z*,6*E*)-Farnesyl bromide (**17**) (856 mg, 3.0 mmol) was added to a suspension of 2.91 g (3.3 mmol) of $CoCl(Ph_3P)_3$ 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 (6*E*,10*Z*,14*Z*,18*E*)-squalene (**18**), 115 mg (19% yield) of **19** and 50 mg (8% yield) of **16**.

18[38]: colorless oil; IR 1445, 1360 cm^{-1}; MS *m/z* 410 (M^+); NMR δ 5.10 (6H, m), 2.05 (20H, m), 1.69 (12H, s), 1.61 (12H, s).

19: colorless oil; IR 910 cm^{-1}; MS *m/z* 410 (M^+); NMR δ 5.75 (1H, dd), 5.20—4.80 (7H, m), 2.00 (18H, m), 1.69 (9H, s), 1.60 (12H, s), 0.92 (3H, s); *Anal.* Calcd for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.86; H, 12.48.

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 $CoCl(Ph_3P)_3$ 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 Na_2SO_4 and concentrated under reduced pressure. The residue 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 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**.

20: colorless oil; IR 1450, 1380 cm^{-1}; NMR δ 5.15 (5H, m), 2.20—1.80 (14H, m), 1.69 (9H, s), 1.60 (15H, s), 1.22 (6H, m), 0.90 (3H, s); high resolution MS Calcd (M^+) *m/z* 412.4066. Found 412.4049.

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 $CoCl(Ph_3P)_3$ 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**.

21: colorless oil; IR 1450, 1380 cm^{-1}; NMR δ 5.15 (5H, m), 2.20—1.80 (14H, m), 1.69 (15H, s), 1.60 (9H, s), 1.22 (6H, m), 0.90 (3H, s); high resolution MS Calcd (M^+) *m/e* 412.4066. Found 412.4049.

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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ 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[32] 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 : 10) 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**.

23: colorless oil[41]; IR 1715, 1735 cm^{-1}; MS *m/z* 214 (M^+).

24[42]: colorless oil; IR 3500, 1735 cm^{-1}.

25: colorless oil; MS *m/z* 198 (M^+); NMR δ 5.40 (2H, m, $C{-}C\underline{H}{=}C\underline{H}{-}C$), 5.25—4.95 (3H, m, $C{-}C\underline{H}{=}C\underline{H}_2$), 0.95 (3H, t, $C\underline{H}_3{-}CH_2CH{=}C$). Mixture of methyl 8-undecenoate, methyl 9-undecenoate and methyl 10-undecenoate in a ratio of 5 : 3 : 2.

Reaction of *threo*-2-Bromocyclododecanol (26a) (Entry 2)——A mixture of 358 mg (1.36 mmol) of *threo*-2-bromocyclododecanol (**26a**) and 1.80 g (2.04 mmol) of $CoCl(Ph_3P)_3$ in 15 ml of dry benzene was stirred at room temperarure 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.[43] 59 °C).

28: colorless crystals; mp 79 °C (lit.[44] 79 °C).

29: colorless oil; MS *m/z* 166 (M^+).

Reaction of *erythro*-2-Bromocyclododecanol (26b) (Entry 3)——A mixture of 259 mg (0.98 mmol) of *erythro*-2-bromocyclododecanol (**26b**) and 1.30 g (1.48 mmol) of $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ in the Presence of Triethylamine (Entry 4)——A mixture of 350 mg (1.19 mmol) of **22**, 1.58 g (1.79 mmol) of $CoCl(Ph_3P)_3$ and 0.86 ml (6.0 mmol) of Et_3N 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 $CoCl(Ph_3P)_3$ 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 Et_3N (4.8 mmol) in 100 ml of dry solvent (C_6H_6–Et_2O, 1 : 1) was placed in a 200 ml round-bottomed flask equipped with a Soxlet extractor filled with 2.10 g of $CoCl(Ph_3P)_3$ (2.4 mmol). The mixture was gently refluxed for 48 h under Ar. At the end of the reaction, the $CoCl(Ph_3P)_3$ 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-Bromocyclododecanol (26a) with $CoCl(Ph_3P)_3$ in the Presence of Triethylamine (Entry 6)——A mixture of 200 mg (0.76 mmol) of **26a**, 1.04 g (1.13 mmol) of $CoCl(Ph_3P)_3$ and 0.4 ml (2.3 mmol) of Et_3N 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-Bromocyclododecanol (26a) with $CoCl(Ph_3P)_3$ in the Presence of Triethylamine (Entry 7)——A solution of 1.23 g of $CoCl(Ph_3P)_3$ (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 Et_3N (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 $CoCl(Ph_3P)_3$ in the Presence of Cyclohexene (Entry 8)——A mixture of 228 mg (0.87 mmol) of **26a**, 1.15 g (1.31 mmol) of $CoCl(Ph_3P)_3$ 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 $CoCl(Ph_3P)_3$ in the Presence of Cyclohexene (Entry 9)——A solution of 1.62 g (1.84 mmol) of $CoCl(Ph_3P)_3$ 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-Bromocyclododecanol (30)——A mixture of 407 mg of *erythro*-2-bromocyclododecanol (**26b**) (1.55 mmol) and 500 mg of pyridiniumchlorochromate (PCC) (2.3 mmol) in 50 ml CH_2Cl_2 was stirred at room temperature for 15 h. The mixture was filtered through a short silica gel column with CH_2Cl_2 as the eluent. The eluate was concentrated under reduced pressure to afford crude 2-bromocyclododecanone as a colorless oil. The oil was dissolved in 15 ml of EtOH, and 130 mg of $NaBD_4$ (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 Et_2O. The ether solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Flash chromatography of the residue afforded 220 mg of *threo*-1-D-bromocyclododecanol (**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.* Calcd for $C_{12}H_{22}DBrO$: 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 $CoCl(Ph_3P)_3$——A mixture of 80 mg of **30** (0.30 mmol) and 400 mg of $CoCl(Ph_3P)_3$ (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-cyclododecanone (**31**) (25% yield) and 22 mg of 1-D-cyclododecanol (**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 cyclododecanone); *Anal.* Calcd for $C_{12}H_{21}DO$: 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.* Calcd for $C_{12}H_{23}DO$: C, 78.19; H, 13.13. Found: C, 77.95; H, 12.99.

Reaction of 3β-Acetoxy-5α-bromocholestan-6β-ol (33)——A mixture of 326 mg (0.62 mmol) of 3β-acetoxy-5α-bromocholestan-6β-ol and 928 mg (1.05 mmol) of $CoCl(Ph_3P)_3$ 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[32] 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 (0.5 H, 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 $CHCl_3$, and 275 mg of MnO_2 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^+).

37: colorless crystals; mp 103—104 °C (lit.[47] 108—109 °C); IR 1725, 1710, 1635 cm^{-1}; NMR δ 6.05 (1H, m), 4.62 (1H, m), 1.98 (3H, s); MS *m*/*z* 442 (M^+).

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