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Reaction of α-Halo Organoindium Reagents with Carbonyl Compounds and Electron-deficient Alkenes

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Abstract: A variety of α-halo organoindium reagents were prepared *in situ* from the reaction of *gem*-dihalo compounds with indium metal, and their reactions with carbonyl compounds and electron-deficient alkenes were examined. The reactions of simple 1,1-diiodoalkanes with indium metal gave no defined products but benzal iodide gave stilbene in a moderate yield. α-Halo organoindium reagents drived from α,α-dibromo carbonyl compounds gave oxiranes and cyclopropanes upon the reactions with aldehydes and alkenes, respectively. 3,3-Dichloropropenes reacted with aldehydes in the presence of indium metal to give the corresponding chlorohydrins and/or homoallylalcohols, depending on the structures of both the dichloropropenes and aldehydes employed.

INTRODUCTION

α-Halo organometallic compounds are an interesting family of organometallic reagents. They are generally referred to as metal carbenoids and used as precursors to carbenes.[1] Organoalkaline metals[2] and organomercuries[3] possessing halogen atom at the α-carbon are such examples. In some cases, on the other hand, they behave as α-halo carbanionic species and, by the reaction with electrophiles, they are used for various organic transformations; of which the typical examples are olefination, epoxidation, and cyclopropanation. To date, a variety of α-halo organometallic compounds have hitherto been synthesized and extensively studied in organic synthesis. Simmons-Smith cyclopropanation based on zinc carbenoids is a well-known example of the versatile reactions of such metal carbenoid reagents.

Indium-mediated reactions have recently emerged as a useful tool in organic synthesis.[4] We have previously reported that the organoindium compounds derived from dibromo-substituted active methylene compounds, such as dibromomalononitrile, and indium metal reacted with alkenes and carbonyl compounds to give cyclopropanes and oxiranes, depending on the nature of the reagents and substrates.[5] The most plausible intermediates of these reactions are considered to be α-halo organoindium reagents. This paper describes further reactions of *gem*-dihalo compounds with indium metal in the presence or absence of carbon electrophiles.

RESULTS

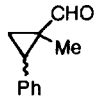
a. 1,1-Diiodoalkanes.

The reaction of 1,1-diiodoalkanes such as diiodomethane, 1,1-diiodooctane, and 1,1-diiodo-2,2-dimethylpropane with indium powder in *N*,*N*-dimethylformamide (DMF) was sluggish at room temperature.

At higher temperature (>100 °C) indium metal was consumed, but the reactions gave, after hydrolysis, only intractable polymeric materials. Even in the presence of electrophiles (aldehydes, acid chlorides, and electron-deficient alkenes), no products could be characterized.

b. Benzal iodide.

Benzal iodide was heated with indium in DMF at 60 °C for 1 h. Aqueous workup of the reaction mixture gave (*E*)- and (*Z*)-stilbene in 36% yield, together with benzaldehyde (17% yield) and benzoic acid (18%). The stilbene could be formed via indium-mediated deiodinative dimerization of benzal iodide, whereas the latter two are considered to be formed from the benzal iodide via hydrolysis and the subsequent autoxidation, respectively. The same reaction was examined in the presence of various kinds of electrophiles, but no cross-coupling was observed. Only with methacrolein, a low yield (7 %) of cyclopropane **1** could be isolated.

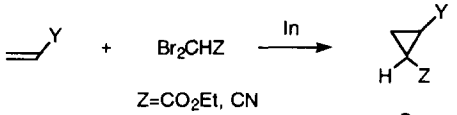


1

c. α,α-*Dibromo ester, nitrile, and ketone.*

The organoindium reagents derived from ethyl dibromoacetate and dibromoacetonitrile readily reacted with electron-deficient alkenes giving the corresponding cyclopropane **2** (Table 1). The yields are generally lower than those of the previously reported dibromo-substituted active methylene cases.[5] The resulting cyclopropanes were mixtures of *cis*- and *trans*-stereoisomers, indicating that the addition of the organoindium reagents is not stereoselective.

Table 1. Indium-mediated Reaction of Ethyl Dibromoacetate and Dibromoacetonitrile with Electron-deficient Alkenes



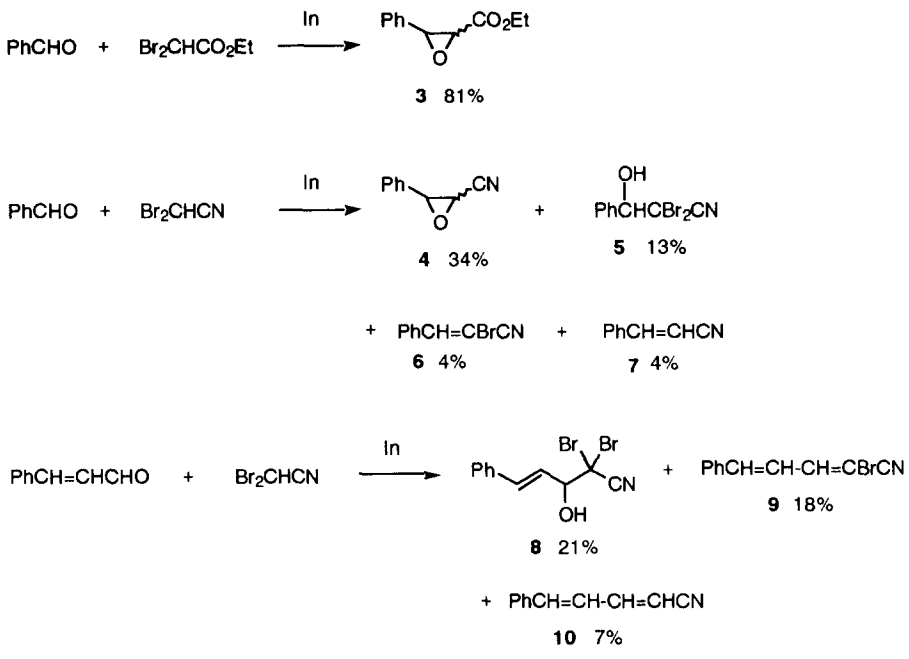
Z=CO_2Et, CN

2

Dibromo compound	Alkene	Product	Yield/%	*cis* : *trans*
Br_2CHCO_2Et	$PhCH{=}C(CN)_2$	**2a**	69	49 : 51
	$EtCH{=}CH(CN)CO_2Et$	**2b**	65	57 : 43
Br_2CHCN	$PhCH{=}C(CN)_2$	**2c**	60	17 : 83
	$EtCH{=}CH(CN)CO_2Et$	**2d**	42	44 : 56
	$CH_2{=}CHCO_2Et$	**2e**	15	— [a]

[a] Not determined.

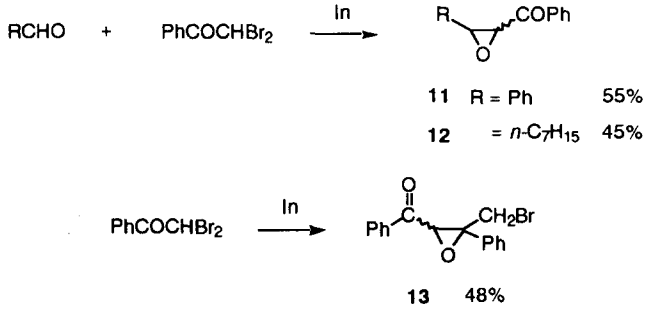
Ethyl dibromoacetate reacted with benzaldehhyde in the presence of indium metal to give a high yield of oxirane **3** (Scheme 1). On the other hand, the reaction of the α-bromoorganoindium reagent, derived from dibromoacetonitrile, with carbonyl compounds is rather complicated; benzaldehyde gave a low yield (34%)



Scheme 1

of oxirane **4**, together with bromohydrin **5**, 2-bromocinnamonitrile (**6**), and cinnamonitrile (**7**). The reaction with cinnamaldehyde gave bromohydrin **8** and dienes **9** and **10**. The dibromo alcohols **5** and **8** are considered to be formed via a condensation of the conjugate base of dibromoacetonitrile with the aldehydes.[6]

Upon treatment with indium powder, α,α-dibromoacetophenone reacted with benzaldehyde and octanal to give the corresponding oxiranes **11** and **12** in moderate yields (Scheme 2). Without aldehydes, the dibromide was dimerized to give epoxy ketone **13** in 48% yield. Interestingly, the dibromomethyl group of α,α-dibromoacetophenone was converted to a bromomethyl group in **13** during this reaction. The reaction mechanism is discussed later.

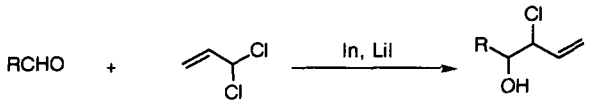


Scheme 2

d. 3,3-Dichloropropene.

Indium-mediated reaction of 3,3-dichloropropene with aldehydes in the presence of lithium iodide gave chlorohydrin **14** exclusively (Table 2). The products were mixtures of *syn*- and *anti*-stereoisomers. The stereochemical assignment was easily achieved by converting the chlorohydrin **14** to the corresponding oxirane which was analyzed by ^{1}H NMR analysis. This protocol provide a convenient route to substituted vinyloxiranes which are generally difficult to prepare.[7]

Table 2. Indium-mediated Reaction of 3,3-Dichloropropene with Aldehydes



14

Aldehyde	product	Yield/%	*syn* : *anti*
PhCHO	**14a**	93	78 : 22
4-MeOC$_6$H$_4$CHO	**14b**	72	84 : 16
PhCH=CHCHO	**14c**	55	59 : 41
Me(CH$_2$)$_2$CH=CHCHO	**14d**	42	65 : 35
Me(CH$_2$)$_6$CHO	**14e**	71	54 : 46

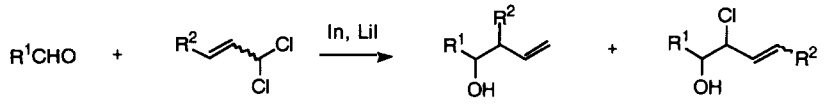
e. 1-Substituted 3,3-dichloropropenes.

3,3-Dichloro-1-phenylpropene reacted with aldehydes, in the presence of indium and lithium iodide, to give homoallylalcohol **15** as the major product together with small amounts of chlorohydrin **16** (Table 3). Interestingly, the ratio homoallylalcohol/chlorohydrin depends largely on the aldehydes employed; with increase the bulkiness of the aldehydes, the ratio increases; and octanal, benzaldehyde, and 2-hexenal gave the corresponding homoallylalcohols exclusively. Other 1-substituted 3,3-dichloropropenes gave similar results, though the yields are lower and the reactions required higher temperature (100 – 120 °C). It should be emphasized here that both the chlorine atoms in the starting 3,3-dichloropropenes are lost in homoallylalcohol **15**.

DISCUSSION

The α-haloorganoindium reagents derived from *gem*-dihalides and indium metal showed diverse reactivity toward electrophiles depending on the structures of the reagents. The presence of activating groups on the α-carbon, in particular electron-withdrawing substituents, increases the nucleophilicity of the indium carbenoids giving higher yields of coupling products with carbon electrophiles. Thus, the reactivity of the α-haloindium reagents derived from dibromoacetate, dibromoacetonitrile, and α,α-dibromoacetophenone is lower than that from dibromo-substituted active methylene compounds, generally giving lower yields of the corresponding cyclopropanes and oxiranes by the reaction with electron-deficient alkenes and carbonyl compounds, respectively. Benzal iodide scarecely reacted with such electrophiles, and simple 1,1-dihaloalkanes were failed to give any defined products.

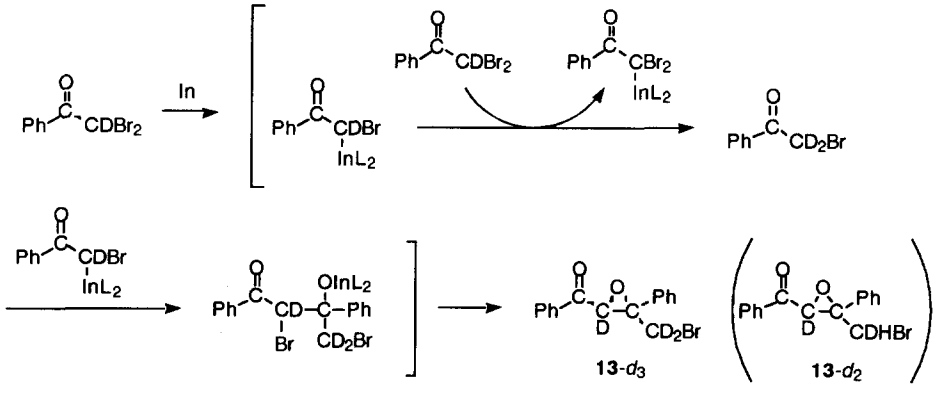
Table 3. Indium-mediated Reaction of 1-Substituted 3,3-Dichloropropene with Aldehydes



15 16

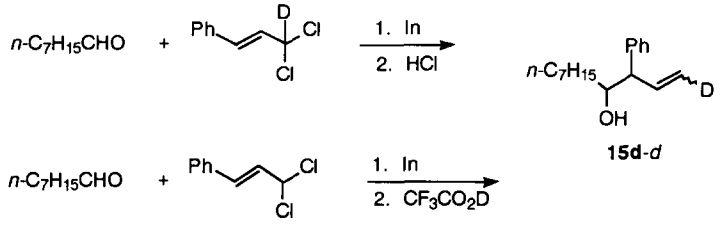
entry	R^1	R^2	Yield/% 15	16	entry	R^1	R^2	Yield/% 15	16
a	H	Ph	28	50	f	$Me(CH_2)_2CH=CH$	Ph	41	0
b	Et	Ph	69	10	g	Ph	Me	29	0
c	*n*-Pr	Ph	82	15	h	Ph	*n*-Pr	10	0
d	n-C_7H_{15}	Ph	50	0	i	n-C_7H_{15}	Me	27	0
e	Ph	Ph	75	0	j	n-C_7H_{15}	*n*-Pr	13	0

Indium-mediated self-condensation of α,α-dibromoacetophenone gave rise to **13** which bears a bromomethyl group in place of the original dibromomethyl group. One of possible mechanisms for the formation of **13** could be a dimerization of the α-bromoorganoindium reagent, α-bromo-α-indioacetophenone. However, quenching the reaction with trifluoroacetic acid-*d* resulted in no deuterium-incorporation; thus excluding the possibility of this process. Then, we prepared α,α-dibromo-α-deuterioacetophenone and subjected to the same reaction. When quenched with dil. HCl, the product was a mixture of **13**-d_2 (64%) and **13**-d_3 (36%) based on MS and ^{1}H NMR spectroscopy. The formation of **13**-d_3 is reasonably explained by Scheme 3: *e.g.*, intially produced α-bromo-α-indioacetophenone abstracts the acidic α-D of the starting α,α-dibromo-α-deuterioacetophenone to produce phenacyl bromide-α,α-d_2, which coupled with the indium carbenoid to furnish **13**-d_3.[8]

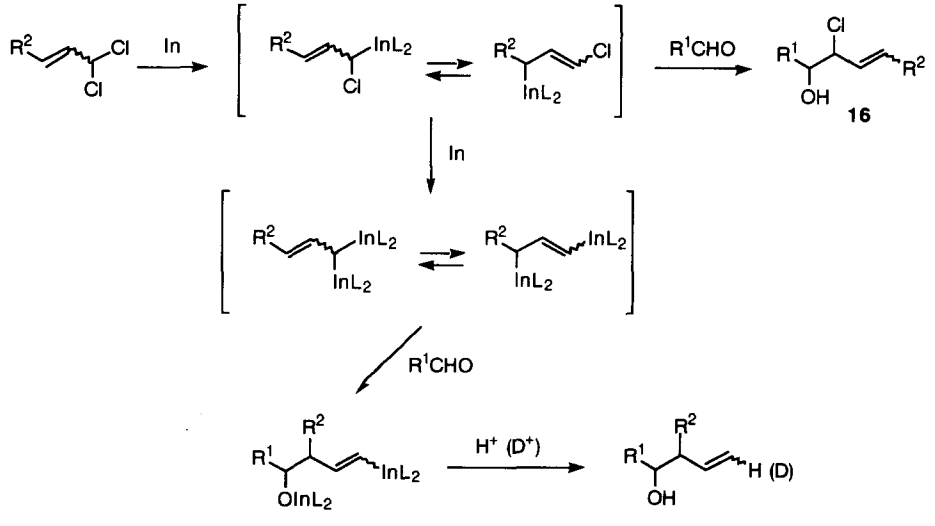


Scheme 3

The reaction of 1-substituted 3,3-dichloropropene with aldehydes gave homoallylalcohol **15** preferentially or, in some cases, exclusively. In order to rationalize the reaction mechanism, the reaction of 3,3-dichloro-3-deuterio-1-phenylpropene with octanal was examined (Scheme 4). The coupling reaction was carried out in a usual manner and the reaction was quenched with dil. HCl. The product **15d**-*d* ($E : Z$ = 2.5 : 1) was obtained in 50% yield without loss of D. When the reaction of non-deuterated 3,3-dichloro-1-phenylpropene with octanal was quenched with trifluoroacetic acid-*d*, the same compound **15d**-*d* with 70% D was produced. Based on these results, a plausible reaction sequence for the reaction of 1-substituted 3,3-dichloropropenes is illustrated in Scheme 5, which includes *gem*-bisindium species as a key intermediate. Reactive aldehydes such as formaldehyde readily react with allylic monoindium intermediate to give chlorohydrin **16**, whereas higher aldehydes react preferentially with more nucleophilic *gem*-bisindium reagent to furnish homoallyllic alcohol **15**. Recently, a variety of *gem*-bismetallic reagents are described in literature and atttract much attention;[9] however, this is the first example of *gem*-bisindium compounds.



Scheme 4



Scheme 5

EXPERIMENTAL

General. IR spectra were recorded on a JASCO IRA-102 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-90 spectrometer (90 MHz) or a Varian XL-200 spectrometer (200 MHz) with Me_4Si as internal standard; *J*-values are given in Hz. ^{13}C NMR spectra were measured for solutions in $CDCl_3$ with a Varian XL-200 spectrometer (50 MHz). Mass specta were measured on a Hitachi M-2000 spectrometer at 70 eV. Elemental analyses were done at the Elemental Analysis Centre of Kyoto University. All reactions were carried out under argon. Indium powder (99.99%), stabilized by 0.5% MgO, was obtained from Nacalai Tesque Co. Ltd. The following materials were synthesized according to the published methods: benzal iodide,[10] 1,1-diiodo-2,2-dimethylpropane,[11] 1,1-diiodooctane,[12] dibromoacetonitrile,[13] ethyl dibromoacetate,[14] 1,1-dibromoacetophenone,[15] 3,3-dichloropropene,[16] and 3,3-dichloro-1-phenylpropene.[17]

Reaction of benzal iodide with indium. Benzal iodide (0.34 g, 1.0 mmol) and indium powder (0.11 g, 1.0 mmol) were stirred in DMF (3.0 cm^3) at 60 °C for 1 h. The reaction mixture was cooled to room temperature and poured into water. The products were extracted with diethyl ether. The extracts were washed with brine and dried (Na_2SO_4). After the solvent was removed under reduced pressure, the residue was column chromatographed (silica gel; dichloromethane : hexane = 1 : 1) to give stilbene (*E/Z* mixture) (32 mg, 36%), benzaldehyde (18 mg, 17%), and benzoic acid (22 mg, 18%).

Indium-induced reaction of benzal iodide with methacrolein. A mixture of indium powder (0.11 g, 1.0 mmol), benzal iodide (0.35 g, 1.0 mmol), and methacrolein (0.83 cm^3, 1.0 mmol) in DMF (3.0 cm^3) was heated with stirring at 105 °C for 4 h. The reaction mixture was worked up as above to give stilbene (25 mg, 28%), benzaldehyde (16 mg, 15%), and 1-methyl-2-phenylcyclopropanecarboxyaldehyde (**1**)[18] (*cis* : *trans* = 13 : 87) (11 mg, 7%). The *cis/trans* ratio was determined based on the ^{1}H NMR.

Indium-mediated reaction of ethyl dibromoacetate and dibromoacetonitrile with electron-deficient alkenes. The following reaction of ethyl dibromoacetate with benzylidenemalononitrile represents the general procedure. A mixture of ethyl dibromoacetate (0.49 g, 2.0 mmol), benzylidenemalononitrile (0.15 g, 1.0 mmol), and indium powder (0.23 g, 2.0 mmol) in DMF (3.0 cm^3) was ultrasonicated for 2.5 h at room temperature. Usual aqueous workup and column chromatography on silica gel (dichloromethane : hexane = 4 : 1) gave ethyl 1,1-dicyano-2-phenylcyclopropanecarboxylate (**2a**) (*cis* : *trans* = 51 : 49) (0.17 g, 69%). Separation of the *cis*- and *trans*-isomers was achieved by careful column chromatography. Other reactions were similarly carried out and the results are summarized in Table 1.

Ethyl 1,1-dicyano-2-phenylcyclopropanecarboxylate (2a).[19] *cis*-Isomer: colourless needles; mp 75-78 °C ; *Rf* 0.51 (silica gel; dichloromethane : hexane = 4 : 1); IR (melt, cm^{-1}): 3065, 2995, 2255 (CN), 1743 (C=O), 1502, 1450, 1410, 1395, 1374, 1354, 1294, 1201, 1097, 1029, 972, 840, 739, 700; ^{1}H NMR (200 MHz): 1.20 (*t*, *J*=7.1, 3H, Me), 3.10 (*d*, *J*=10.5, 1H, C*H*CO_2Et), 3.59 (*d*, *J*=10.5, 1H, C*H*Ph), 4.20 (*q*, *J*=7.1, 2H, CH_2), 7.20-7.40 (*m*, 5H, Ph); MS: *m/z* (rel. intensity) 195 (M^+-OEt, 9), 168 (M^+-CO_2Et, 100). *trans*-Isomer: colourless crystals; mp 68-70 °C (*lit.*[19] mp 68-69 °C); *Rf* 0.63 (silica gel; dichloromethane : hexane = 4 : 1); ^{1}H NMR (200 MHz): 1.38 (*t*, *J*=7.1, 3H, Me), 3.14 (*d*, *J*=8.1, 1H, C*H*CO_2Et), 3.69 (*d*, *J*=8.1, 1H, C*H*Ph), 4.37 (*q*, *J*=7.1, 2H, CH_2), 7.25-7.38 (*m*, 2H, Ph), 7.40 - 7.50 (*m*, 3H, Ph).

Diethyl 1-cyano-3-ethyl-1,2-cyclopropanedicarboxylate (2b). cis-Isomer: IR (neat, cm^{-1}): 2985, 2245 (CN), 1736 (C=O), 1463, 1379, 1315, 1292, 1250, 1187, 1094, 1030, 848; ^{1}H NMR (200 MHz): 1.09 (*t*, *J*=7.2, 3H, CH_2CH_3), 1.31 (*t*, *J*=7.2, 3H, $CO_2CH_2CH_3$), 1.35 (*t*, *J*=7.2, 3H, $CO_2CH_2CH_3$), 1.79-2.03

(*m*, 2H, CH_2CH_3), 2.11 (*m*, 1H, CH), 2.71 (*d*, *J*=9.6, 1H, $CHCO_2Et$), 4.25 (*q*, *J*=7.2, 2H, $CO_2CH_2CH_3$), 4.29 (*q*, *J*=7.2, 2H, $CO_2CH_2CH_3$); MS: *m/z* (rel. intensity) 240 (M^++1, 1), 194 (M^+-OEt, 30), 166 (M^+-CO_2Et, 85), 138 (100). *trans*-Isomer: IR (neat, cm^{-1}): 2995, 2950, 2250 (CN), 1741 (C=O), 1462, 1443, 1371, 1301, 1292, 1260, 1185, 1399, 1038, 1020; ^1H NMR (200 MHz): 1.15 (*t*, *J*=7.4, 3H, CH_2CH_3), 1.26 (*t*, *J*=7.1, 3H, $CO_2CH_2CH_3$), 1.33 (*t*, *J*=7.1, 3H, $CO_2CH_2CH_3$), 1.56-1.83 (*m*, 2H, CH_2CH_3), 2.30 - 2.42 (*m*, 2H, CH x2), 4.17 (*q*, *J*=7.1, 2H, $CO_2CH_2CH_3$), 4.26 (*dq*, *J*=7.1, 2.1, 2H, $CO_2CH_2CH_3$); MS: *m/z* (rel. intensity) 240 (M^++1, 2), 194 (M^+-OEt, 42), 166 (M^+-CO_2Et, 95), 138 (100). Anal. (*cis/trans* mixture): calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.07; H, 7.04; N, 5.78.

3-Phenyl-1,1,2-cyclopropanetricarbonitrile (2c). *cis*-Isomer: colourless crystals; mp 156 °C (dec); IR (neat, cm^{-1}): 3050, 3025, 2255 (CN), 1603, 1502, 1449, 1341, 1276, 1094, 1013, 831, 768, 737, 698, 664, 658; ^1H NMR (200 MHz): 3.13 (*d*, *J*=9.6, 1H, CHCN), 3.57 (*d*, *J*=9.6, 1H, CH), 7.51 (*s*, 5H, Ph); MS: *m/z* (rel. intensity) 193 (M^+, 100). Anal: calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.90; H, 3.55; N, 21.99. *trans*-Isomer: pale yellow oil; bp 170 °C/ 3 Torr; IR (neat, cm^{-1}): 3045, 2255 (CN), 1601, 1586, 1505, 1450, 1403, 1208, 1085, 1002, 912, 784, 745, 698, 660; ^1H NMR (200 MHz): 3.08 (*d*, *J*=7.6, 1H, CHCN), 3.70 (*d*, *J*=7.6, 1H, CH), 7.32 (*m*, 2H, Ph), 7.45 (*m*, 3H, Ph); MS: *m/z* (rel. intensity) 193 (M^+, 100). Anal: calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.57; H, 3.44; N, 21.81.

Ethyl 1,2-dicyano-3-ethylcyclopropanecarboxylate (2d). *cis*-Isomer: colourless oil; IR (neat, cm^{-1}): 2980, 2945, 2050 (CN), 1744 (C=O), 1466, 1370, 1296, 1251, 1188, 1100, 1018, 857, 731; ^1H NMR (200 MHz): 1.21 (*t*, *J*=7.3, 3H, CH_2CH_3), 1.38 (*t*, *J*=7.3, 3H, $CO_2CH_2CH_3$), 1.80-1.96 (m, 2H, CH_2CH_3), 2.14 (m, 1H, CH), 2.65 (*d*, *J*=9.0, 1H, CHCN), 4.33 (*q*, *J*=7.3 Hz, 2H, $CO_2CH_2CH_3$); MS: *m/z* (rel. intensity) 164 (M^+-CO, 23), 123 (100), 119 (M^+-CO_2Et, 83). Anal: calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 61.80; H, 6.25; N, 14.43. *trans*-Isomer: colourless oil; IR (neat, cm^{-1}): 2978, 2945, 2252 (CN), 1748 (C=O), 1465, 1362, 1320, 1307, 1288, 1256, 1187, 1100, 1004, 856, 732; ^1H NMR (200 MHz): 1.17 (*t*, *J*=7.2, 3H, CH_2CH_3), 1.39 (*t*, *J*=7.2, 3H, $CO_2CH_2CH_3$), 1.61-1.87 (m, 2H, CH_2CH_3), 2.21 (*d*, *J*=7.4, 1H, CHCN), 2.42 (*q*, *J*=7.4, 1H, CH), 4.39 (*q*, *J*=7.4, 2H, $CO_2CH_2CH_3$); MS: *m/z* (rel. intensity) 193 (M^+, 100), 164 (M^+-CO, 62), 123 (98), 119 (M^+-CO_2Et, 100). Anal: calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 61.94; H, 6.29; N, 14.56.

Ethyl 2-cyanocyclopropanecarboxylate (2e).[20] ^1H NMR (90 MHz): 1.32 (*t*, *J*=7.2, 3H, CH_2CH_3), 1.70-3.00 (*m*, 4H, CH x 4), 4.28 (*q*, *J*=7.2, 2H, $CO_2CH_2CH_3$).

Indium-mediated reaction of ethyl dibromoacetate with benzaldehyde. A mixture of ethyl dibromoacetate (0.49 g, 2.0 mmol), benzaldehyde (0.10 cm^3, 1.0 mmol), and indium powder (0.23 g, 2.0 mmol) in DMF (3.0 cm^3) was ultrasonicated for 2 h at room temperature. Usual aqueous workup and column chromatography on silica gel (dichloromethane : hexane = 4 : 1) gave 2-ethoxycarbonyl-3-phenyloxirane (**3**)[21] (*cis* : *trans* = 55 : 45) (0.16 g, 81%). The *cis/trans* ratio was determined based on the ^1H NMR analysis.

Indium-mediated reaction of dibromoacetonitrile with benzaldehyde. This reaction was similarly carried out as above and the following products were isolated; 2-cyano-3-phenyloxirane (**4**)[22] (*cis* : *trans* = 67 : 33) (34% yield), 2,2-dibromo-3-hydroxy-3-phenylpropanenitrile (**5**) (13%), 2-bromo-3-phenylpropenenitrile (**6**) (4%), and 3-phenylpropenenitrile (**7**) (4%).

2,2-Dibromo-3-hydroxy-3-phenylpropanenitrile (5). IR (neat, cm^{-1}) 3465, 2250(CN), 1497, 1453, 1194, 1050, 1028, 772, 752, 712, 699; ^1H NMR (90 MHz): 3.26 (*s*, 1H, OH), 5.13 (*s*, 1H, CH), 7.33-7.69 (*m*, 5H, Ph); MS: *m/z* (rel. intensity) 201/199/197 (Br_2CHCN, 17), 107 (PhCHOH, 100); Anal: calcd for $C_9H_7Br_2NO$: C, 35.45; H, 2.31. Found: C, 35.46; H, 2.48.

2-Bromo-3-phenylpropenenitrile (6).[23] IR (neat, cm^{-1}): 2210 (CN), 1595, 1573, 1498, 1448, 1204, 995, 916, 760, 730, 688; ^1H NMR (90 MHz): 7.33-7.52 (*m*, 2H, Ph), 7.56 (*s*, 1H, =CH), 7.60-7.76 (*m*, 3H, Ph); MS: *m/z* (rel. intensity) 209/207 (M^+, 100).

Indium-mediated reaction of dibromoacetonitrile with cinnamaldehyde. This reaction was similarly carried out as above and the following products were isolated; 2,2-dibromo-3-hydroxy-5-phenyl-4-pentenenitrile (**8**) (21% yield), 2-bromo-5-phenyl-2,4-pentadienenirile (**9**) (18%), and 5-phenyl-2,4-pentadienenitrile (**10**) (7%).

2,2-Dibromo-3-hydroxy-5-phenyl-4-pentenenitrile (8). IR (neat, cm^{-1}): 3450, 3030, 2240 (CN), 1648 (C=C), 1495, 1447, 1397, 1290, 1122, 1040, 967, 751, 691; ^1H NMR (90 MHz): 2.97 (*s*, 1H, OH), 4.70 (*d*, *J*=6.0, 1H, C*H*OH), 6.33 (*dd*, *J*=15.6, 6.0, 1H, PhCH=C*H*), 6.97 (*d*, *J*=15.6, 1H, PhC*H*=CH), 7.38-7.57 (*m*, 5H, Ph); MS: *m/z* (rel. intensity) 333/331/329 (M^+, 28), 133 (M^+-CBr_2CN, 100); Anal: calcd for $C_{11}H_9Br_2NO$: C, 39.79; H, 3.04. Found: C, 40.06; H, 3.04.

2-Bromo-5-phenyl-2,4-pentadienenitrile (9).[24] ^1H NMR (90 MHz): 6.8-7.4 (*m*, 8H, Ph and =CH x 3); MS: *m/z* (rel. intensity) 235/233 (M^+, 75), 154 (M^+-Br, 100).

Indium-mediated reaction of α,α-dibromoacetophenone with benzaldehyde. A mixture of α,α-dibromoacetophenone (0.28 g, 1.0 mmol), benzaldehyde (0.10 cm^3, 1.0 mmol), and indium powder (0.23 g, 2.0 mmol) in DMF (3.0 cm^3) was ultrasonicated for 3 h at room temperature. Usual aqueous workup and column chromatography on silica gel (dichloromethane : hexane = 5 : 4) gave 2-benzoyl-3-phenyloxirane (**11**)[25] (*cis* : *trans* = 88 : 12) (0.13 g, 55%). The *cis/trans* ratio was determined based on the ^1H NMR analysis. The reaction with octanal was similarly carried out and 2-benzoyl-3-heptyloxirane (**12**) (*cis* : *trans* = 91 : 9) was obtained in 45% yield.

2-Benzoyl-3-heptyloxirane (12). IR (neat, cm^{-1}): 2935, 2855, 1687 (C=O), 1597, 1578, 1447, 1418, 1374, 1224, 960, 797; MS: *m/z* (rel. intensity) 246 (M^+, 3), 105 (PhCO, 100); ^1H NMR (200 MHz) for *cis*-isomer: 0.84 (*t*, 3H, *J*=6.9, Me), 1.13 - 1.54 (*m*, 12H, CH_2), 3.43 (*dt*, *J*=5.8, 4.8, 1H, CH), 4.29 (*d*, 1H, *J*=4.8, PhCOC*H*), 7.46 - 7.69 (*m*, 3H, Ph), 7.99 - 8.08 (*m*, 2H, Ph); the PhCOC*H* signal of the *trans*-isomer appeared at δ 4.03 (*d*, *J*=1.9); HRMS: calcd for $C_{16}H_{22}O_2$: 246.1615, found: 246.1620.

Indium-mediated coupling of α,α-dibromoacetophenone. A mixture of α,α-dibromoacetophenone (0.28 g, 1.0 mmol) and indium powder (0.11 g, 1.0 mmol) in DMF (3.0 cm^3) was ultrasonicated for 3 h at room temperature. Usual aqueous workup and column chromatography on silica gel (dichloromethane : hexane = 2 : 1) gave *cis*-2-bromomethyl-2-phenyl-3-benzoyloxirane (*cis*-**13**) (5.0 mg, 3%), *trans*-2-bromomethyl-2-phenyl-3-benzoyloxirane (*trans*-**13**) (71 mg, 45%), α,α-dibromoacetophenone (9%), and α-bromoacetophenone (4%).

cis-*2-Bromomethyl-2-phenyl-3-benzoyloxirane* (cis-*13*). Pale yellow oil (*lit.*[26] mp 133-134 °C); ^1H NMR (200 MHz): 3.70 (*d*, *J*=11.7, 1H, CHBr), 3.84 (*d*, *J*=11.7, 1H, CHBr), 4.44 (*s*, 1H, CH), 7.32-7.68 (*m*, 8H, Ph), 7.85-8.10 (*m*, 2H, Ph).

trans-*2-Bromomethyl-2-phenyl-3-benzoyloxirane* (trans-***13***). Colourless needles; mp 160-162 °C (*lit.*[26] mp 159-160 °C); ^{1}H NMR (200 MHz): 3.86 (*d*, *J*=11.2, 1H, CHBr), 3.99 (*d*, *J*=11.2, 1H, CHBr), 4.63 (*s*, 1H, CH), 7.18-7.63 (*m*, 8H, Ph), 7.86-7.94 (*m*, 2H, Ph).

Experiments with deuterium-labelled α,α-dibromoacetophenone. α,α-Dibromo-α-deuterioacetophenone was obtained by stirring α,α-dibromoacetophenone (0.28 g, 1.0 mmol) with sodium carbonate (0.32 g, 3.0 mmol) in acetonitrile (3.0 cm^3) containing D_2O (0.60 cm^3) (overnight, room temperature). Purification by column chromatography (silica gel, dichloromethane) gave the product (96% D) in 97% yield. Reaction of the deuterium-labelled compound with indium metal was carried out and the deuterium-content of the product was determined by MS and ^{1}H NMR spectroscopy.

Indium-mediated reaction of 3,3-dichloropropene with aldehydes. The following reaction with benzaldehyde represents the general procedure. A mixture of indium powder (0.23 g, 2.0 mmol), lithium iodide (0.54 g, 4.0 mmol), 3,3-dichloropropene (0.22 g, 2.0 mmol), and benzaldehyde (0.10 cm^3, 1.0 mmol) in DMF (6.0 cm^3) was ultrasonicated for 3 h at room temperature. Usual aqueous workup and column chromatography on silica gel (dichloromethane) gave 2-chloro-1-phenyl-1-buten-1-ol (**14a**)[27] (0.17 g, 93%). ^{1}H NMR analysis revealed that the product was a mixture of the diastereomers (78 : 22). Reactions with other aldehydes were similarly carried out. The results are summarized in Table 2.

*2-Chloro-1-(*p*-methoxyphenyl)-3-buten-1-ol* (***14b***). IR (neat, cm^{-1}): 3450, 2950, 1675, 1605, 1509, 1453, 1300, 1245, 1175, 1030, 930, 830, 780, 730; ^{1}H NMR (200 MHz): 2.52 and 2.79 (each *d*, *J*=3.5, 3.3, 1H, OH), 3.80 (*s*, 3H, OMe), 4.52 (*bt*, *J*=7.8, 1H, CHCl), 4.68 (*dd*, *J*=7.7, 3.3, 0.84H, C*H*OH), 4.89 (*dd*, *J*=4.9, 3.5, 0.16H, C*H*OH), 5.09 - 5.35 (*m*, 2H, =CH_2), 5.69 - 5.87 (*m*, 1H, =CH-), 6.88 (*d*, *J*=8.4, 2H, Ar), 7.26 (*d*, *J*=8.4, 2H, Ar); MS: *m/z* (rel. intensity) 212 (M$^+$, 5), 137 (100); Anal: calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16. Found: C, 61.82; H, 6.16.

4-Chloro-1-phenyl-1,5-hexadien-3-ol (***14c***). IR (neat, cm^{-1}): 3400, 3025, 1658, 1492, 1446, 1417, 1068, 1023, 965, 930, 827, 747, 789; ^{1}H NMR (200 MHz): 2.32 and 2.42 (each *d*, *J*=5.0, 1H, OH), 4.37 - 4.58 (*m*, 2H, CHCl and C*H*OH), 5.31 (*d*, *J*=10.0, 1H, *cis* HC=C*H*$_2$), 5.42 (*d*, *J*=16.0, 1H, *trans* HC=C*H*$_2$), 5.99 (*m*, 1H, -CH=), 6.24 (*dd*, *J*=16.0, 5.6 1H, PhCH=C*H*-), 6.70 and 6.72 (each *d*, *J*=16.0, 1H, PhC*H*=CH), 7.21 - 7.44 (*m*, 5H, Ph); MS: *m/z* (rel. intensity) 209 (M$^+$, 0.5), 133 (100); Anal: calcd for $C_{12}H_{13}ClO$: C, 69.07; H, 6.28. Found: C, 69.37; H, 6.48.

3-Chloro-1,5-nonadien-4-ol (***14d***). IR (neat, cm^{-1}): 3455, 3005, 2975, 2920, 1694, 1464, 1438, 1388, 977, 936; ^{1}H NMR (200 MHz): 0.90 and 0.94 (each *t*, *J*=7.2, total 3H, Me), 1.32 - 1.64 (*m*, 2H, CH_2), 1.97 - 2.12 (*m*, 2H, CH_2), 2.29 (*d*, *J*=5.3, 1H, OH), 4.11 - 4.47 (*m*, 2H, CHCl and C*H*OH), 5.22 - 6.00 (*m*, 5H, =CH_2 and =CH x 3); MS: *m/z* (rel. intensity) 157 (M$^+$-H_2O, 17), 57 (100); Anal: calcd for $C_9H_{15}ClO$: C, 61.89; H, 8.66. Found: C, 62.00; H, 8.87.

3-Chloro-1-undecen-4-ol (***14e***). IR (neat, cm^{-1}): 3400, 2925, 2855, 1634, 1458, 1417, 1373, 1120, 1065, 983, 922, 757, 714; ^{1}H NMR (200 MHz): 0.88 (*t*, *J*=6.3, 3H, Me), 1.16 - 1.63 (*m*, 12H, CH_2), 2.09 and 2.12 (each *d*, *J*=4.9, 6.1 total 1H, OH), 3.59 - 3.73 (*m*, 0.5H, CHCl), 3.73 - 3.85 (*m*, 0.5H, CHCl), 4.28 - 4.43 (*m*, 1H, C*H*OH), 5.24 - 5.40 (*m*, 2H, =CH_2), 5.86 - 6.06 (*m*, 1H, -CH=); MS: *m/z* (rel. intensity) 169 (M$^+$-Cl, 1), 69 (100); Anal: calcd for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34. Found: C, 64.25; H, 10.60.

Indium-mediated reactions of 1-substituted 3,3-dichloropropene with aldehydes. These reactions were done in a way similar to the 3,3-dichloropropene case described above, except that the reaction temperature in entries *g* to *j* in Table 3 was 100 - 120 °C. The results are summarized in Table 3.

*2-Phenyl-3-buten-ol (**15a**).*[28] IR (neat, cm^{-1}): 3375, 2930, 2875, 1638, 1599, 1493, 1447, 1052, 1022, 915, 754, 697; ^1H NMR (200 MHz): 1.54 (*bs*, 1H, OH), 3.54 (*dt, J*=7.7, 7.1, 1H, PhCH), 3.83 (*d, J*=7.1, 1H, CH_2), 5.20 (*dd, J*=16.8, 1.4, 1H, *trans* HC=C*H*$_2$), 5.22 (*dd, J*=10.7, 1.4, 1H, *cis* HC=C*H*$_2$), 6.02 (*ddd, J*=16.8, 10.7, 7.7, 1H, C*H*=CH), 7.19 - 7.62 (*m*, 5H, Ph).

*4-Phenyl-5-hexen-3-ol (**15b**).*[29] IR (neat, cm^{-1}): 3440, 2960, 1638, 1598, 1492, 1450, 1108, 970, 916, 758, 698; ^1H NMR (200 MHz): 0.93 and 1.00 (each *t, J*=7.3, total 3H, Me), 1.20 - 1.54 (*m*, 2H, CH_2), 1.80 (*d, J*=4.0, 1H, OH), 3.22 - 3.37 (*m*, 1H, PhC*H*), 3.68 - 3.86 (*m*, 1H, C*H*OH), 5.21 (*dd, J*=17.2, 1.7, 1H, *trans* HC=C*H*$_2$), 5.23 (*dd, J*=9.8, 1.7, 1H, *cis* HC=C*H*$_2$), 5.97 - 6.22 (*m*, 1H, HC=C), 7.16 - 7.40 (*m*, 5H, Ph).

*3-Phenyl-hepten-4-ol (**15c**).*[30] IR (neat, cm^{-1}): 3300, 2950, 1638, 1600, 1493, 1450, 1065, 918, 850, 740, 700; ^1H NMR (200 MHz): 0.78 - 0.98 (*m*, 3H, Me), 1.16 - 1.65 (*m*, 4H, CH_2 x 2), 1.78 (*d, J*=2.5, 1H, OH), 3.20 - 3.35 (*m*, 1H, PhC*H*), 3.73 - 3.96 (*m*, 1H, C*H*OH), 5.04 - 5.26 (*m*, 2H, CH=C*H*$_2$), 5.86 - 6.22 (*m*, 1H, C*H*=CH_2), 7.13 - 7.42 (*m*, 5H, Ph).

*3-Phenyl-1-undecen-4-ol (**15d**).*[31] IR (neat, cm^{-1}): 3420, 2925, 2855, 1636, 1600, 1493, 1452, 1067, 991, 913, 756, 699; ^1H NMR (200 MHz) : 0.86 (*t, J*=6.6, 3H, Me), 1.10 - 1.50 (*m*, 12H, CH_2), 1.78 (*d, J*=4.2, 1H, OH), 3.42 (*dd, J*=7.2, 8.4, 1H, C*H*Ph), 3.72 - 3.87 (*m*, 1H, C*H*OH), 5.20 (*d, J*=16.2, 1H, *trans* HC=C*H*$_2$), 5.22 (*d, J*=10.2, 1H, *cis* HC=C*H*$_2$), 6.15 (*m*, 1H, =CH-), 7.16 - 7.40 (*m*, Ph, 5H), MS: *m/z* (rel. intensity) 152 (18), 129 (0.5), 118 (100).

*1,2-Diphenyl-3-buten-1-ol (**15e**).*[32] IR (neat, cm^{-1}): 3420, 3035, 1630, 1599, 1493, 1448, 1383, 1294, 1183, 1016, 914, 846, 754, 694; ^1H NMR (200 MHz): 2.06 (*d, J*=2.5, 0.1H, OH), 2.30 (*d, J*=2.5, 0.9H, OH), 3.55 (*bt, J*=8.2, 1H, C*H*Ph), 4.85 (*dd, J*=7.7, 2.5, 1H, C*H*OH), 5.22 (*d, J*=18.2, 1H, *trans* =CH_2), 5.26 (*d, J*=9.5, 1H, *cis* =CH_2), 6.16 - 6.35 (*m*, 1H, =CH-), 7.00 - 7.20 (*m*, 10H, Ph x 2); MS: *m/z* (rel. intensity) 115 (100).

*3-Phenyl-1,5-nonadien-4-ol (**15f**).* IR (neat, cm^{-1}): 3410, 2955, 2925, 1663, 1627, 1598, 1492, 1449, 1377, 1298, 1016, 964, 911, 752, 697; ^1H NMR (200 MHz): 0.76 and 0.88 (each *t, J*=7.5, total 3H, Me), 1.17 - 1.43 (*m*, 2H), 1.75 (*s*, 1H, OH), 1.80 - 2.06 (*m*, 2H, CH_2), 3.35 and 3.39 (each *t, J*=8.4, 1H, C*H*Ph), 4.20 - 4.37 (*m*, 1H, C*H*OH), 5.02 - 5.77 (*m*, 4H, =CH_2 and =CH- x 2), 6.13 - 6.24 (*m*, 1H, =CH-), 7.16 - 7.41 (*m*, 5H, Ph); Anal: calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.15; H, 9.38.

*2-Methyl-1-phenyl-3-buten-1-ol (**15g**).*[33] IR (neat, cm^{-1}): 3400, 2950, 1700, 1638, 1600, 1490, 1445, 1368, 1190, 1015, 905, 785, 785, 695; ^1H NMR (200 MHz): 0.87 (*d, J*=6.8, 1.5H, Me), 1.01 (*d, J*=6.8, 1.5H, Me), 1.95 (*bs*, 0.5H, OH), 2.15 (*bs*, 0.5H, OH), 2.40 - 2.64 (*m*, 1H, C*H*Me), 4.36 (*d, J*=7.9, 0.5H, C*H*OH), 4.62 (*d, J*=5.5, 0.5H, C*H*OH), 5.00 - 5.25 (*m*, 2H, =CH_2), 5.67 - 5.91 (*m*, 1H, -CH=), 7.20 - 7.40 (*m*, 5H, Ph).

*1-Phenyl-2-propyl-3-buten-1-ol (**15h**).*[34] IR (neat, cm^{-1}): 3390, 2950, 1638, 1490, 1445, 1415, 1375, 1190, 1022, 990, 758, 795; ^1H NMR (200 MHz): 0.78 and 0.87 (each *t, J*=6.0, total 3H, Me), 1.03 - 1.59 (*m*, 4H, CH_2 x 2), 2.07 (*bs*, 1H, OH), 2.22 - 2.50 (*m*, 1H, CHPr), 4.39 (*d, J*=7.9, 0.6H, C*H*OH), 4.61 (*d, J*=5.8, 0.4H, C*H*OH), 4.96 - 5.29 (*m*, 2H, =CH_2), 5.42 - 5.68 (*m*, 1H, -CH=), 7.21 - 7.40 (*m*, 5H, Ph).

*3-Methyl-1-undecen-4-ol (**15i**).*[35] IR (neat, cm^{-1}): 3350, 2920, 1638, 1450, 1372, 992, 908, 720; ^1H NMR (200 MHz): 0.88 (*bt, J*=7.6, 3H, Me), 1.01 (*d, J*=2.0, 1.5H, Me), 1.05 (*d, J*=2.0, 1.5H, Me), 1.18 - 1.62 (*m*, 13H, CH_2 x 6 and OH), 2.16 - 2.30 (*m*, 1H, C*H*Me), 3.37 - 3.51 (*m*, 1H, C*H*OH), 5.03 - 5.15 (*m*, 2H, $=CH_2$), 5.68 - 5.89 (*m*, 1H, -CH=).

*3-Propyl-1-undecen-4-ol (**15j**).* IR (neat, cm^{-1}): 3350, 2920, 1710, 1638, 1450, 1418, 1375, 1040, 995, 905, 795; ^1H NMR (200 MHz): 0.86 - 0.92 (*m*, 6H, Me x 2), 1.10 - 1.60 (*m*, 16H, CH_2 x 8), 1.70 (*bs*, 1H, OH), 1.94 - 2.18 (*m*, 1H, C*H*Pr), 3.39 - 3.52 (*m*, 1H, C*H*OH), 5.01 - 5.20 (m, 2H, $=CH_2$), 5.51 - 5.73 (m, 1H, -CH=); Anal: calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.26; H, 13.51.

*2-Chloro-4-phenyl-3-buten-1-ol (**16a**).* IR (neat, cm^{-1}): 3350, 3090, 3040, 2940, 2875, 1625, 2598, 1492, 1448, 1347, 1325, 1297, 1180, 1053, 1020, 730, 713, 695; ^1H NMR (200 MHz): 1.49 (*bs,* 1H, OH), 3.86 (*d, J*=6.4, 2H, CH_2), 4.16 (*dt, J*=9.3, 6.4, 1H, CHCl), 6.05 (*dd, J*=9.3, 7.2, 1H, PhCH=C*H*), 6.24 (*d, J*=7.2, 1H, PhC*H*=CH), 7.20 - 7.44 (*m,* 5H, Ph); Anal: calcd for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07. Found: C, 65.69; H, 5.87.

*4-Chloro-6-phenyl-5-hexen-3-ol (**16b**).* IR (neat, cm^{-1}): 3430, 2960, 1684, 1621, 1597, 1490, 1448, 1316, 1118, 1027, 968, 860, 735, 694; ^1H NMR (200 MHz): 0.98 (*t, J*=7.4, 3H, Me), 1.37 - 1.60 (*m,* 2H, CH_2), 1.58 (*bs*, 1H, OH), 3.80 (*dt, J*=7.4, 5.1, 1H, C*H*OH), 3.90 - 4.06 (*m,* 1H, CHCl), 6.19 - 6.30 (*m,* 2H, CH=CH), 7.19 - 7.46 (*m,* 5H, Ph); Anal: calcd for $C_{12}H_{15}ClO$: C, 68.41; H, 7.18. Found: C, 68.66; H, 6.97.

*3-Chloro-1-phenyl-1-hepten-4-ol (**16c**).* IR (neat, cm^{-1}): 3460, 2960, 1672, 1623, 1492, 1450, 1120, 970, 742, 695; ^1H NMR (200 MHz): 0.91 (*t,* J=7.1, 3H, Me), 1.42 (*m*, 4H, CH2 x 2), 1.58 (*bs*, 1H, OH), 3.83 - 4.04 (*m*, 2H, CHCl and CHOH), 6.20 - 6.29 (*m*, 2H, CH=CH), 7.19 - 7.62 (*m*, 5H, Ph); Anal: calcd for $C_{13}H_{17}ClO$: C, 69.48; H, 7.62. Found: C, 69.50; H, 7.64.

Experiments with deuterium-labelled 1-phenyl-3,3-dichloropropene. 1-Phenyl-3,3-dichloro-3-deuteriopropene was synthesized from cinnamaldehyde-*d* prepared from pyridinium dichromate oxidation of cinnamyl alcohol-d_2, which in turn obtained by $LiAlD_4$ reduction of ethyl cinnamate. Reaction with the deuterium-labelled compound was carried out and the deuterium-contents of the products were determined by MS and ^1H NMR spectroscopy.

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