2 H), 3.28, (t, J = 5.5 Hz, 2 H); IR ($CHCl_3$) 3440, 3305, 3020, 2940, 2355, 1640, 1560, 1465, 1350, 1260, 1105, 1040 cm^{-1}; CILRMS m/e (relative intensity) 236 (56.9), 219 (17.2), 112 (15.4), 83 (100), CIHRMS calcd for $C_{12}H_{14}O_4N$ (M + H) 236.0923, found 236.0922.

Tricarbonyl 8b. DMP (163 mg, 0.38 mmol), **6b** (70 mg, 0.19 mmol), pyridine (125 μL, 1.55 mmol), and CH_2Cl_2 (1.9 mL) after 1 h at room temperature provided 38 mg (75%) of an inseparable mixture **8b** as a yellow oil: characteristic ^1H NMR data of the tricarbonyl form ($CDCl_3$, 250 MHz) δ 3.58–3.65 (m, 2 H), 3.20–3.29 (m, 2 H), 2.84 (t, J = 7.3 Hz, 2 H), 1.16–1.78 (m, 16 H), 0.84–0.91 (m, 3 H); characteristic ^1H NMR data for the hydrated form δ 5.60 (br s, 2 H), 3.58–3.65 (m, 2 H), 3.20–3.29 (m, 2 H), 2.52 (t, J = 7.4 Hz, 2 H); characteristic ^1H NMR data for the enol form δ 6.01 (br s, 1 H), 5.64 (t, J = 7.6 Hz, 1 H), 3.58–3.65 (m, 2 H), 3.20–3.29 (m, 2 H), 2.35 (dt, J = 7.4, 7.2 Hz, 2 H); IR ($CHCl_3$) 3440, 3310, 3000, 2905, 2840, 1715, 1645, 1450, 1120; CILRMS m/e (relative intensity) 268 (55.0), 142 (25.0), 112 (25.0), 91 (25.0), 79 (55.0), 69 (100); CIHRMS (M + H) calcd for $C_{15}H_{26}O_3N$ 268.1913, found 268.1915.

Tricarbonyl 8c. DMP (122 mg, 0.28 mmol), **6c** (50.0 mg, 0.14 mmol), pyridine (93 μL, 1.15 mmol), and CH_2Cl_2 (1.4 mL) provided 26 mg (73%) of an inseparable mixture **8c** as a yellow oil: characteristic ^1H NMR data of the tricarbonyl form ($CDCl_3$, 250 Mz) δ 3.57–3.61 (m, 2 H), 3.27–3.31 (m, 2 H), 3.06–3.13 (m, 1 H), 1.20–1.95 (m, 16 H); characteristic ^1H NMR data the hydrated form δ 5.68 (br s, 2 H), 3.57–3.61 (m, 2 H), 3.27–3.31 (m, 2 H), 2.60–2.76 (m, 1 H); IR 3410, 3020, 2950, 2870, 1715, 1650, 1460, 1290, 970 cm^{-1}; CILRMS m/e (relative intensity) 252 (100), 223 (20.5), 129 (8.0), 112 (20.5), 83 (11.5); CIHRMS calcd for $C_{14}H_{22}O_3N$ (M + H) 252.1600, found 252.1610.

Tricarbonyl 11. DMP (85 mg, 0.2 mmol), **10** (44 mg, 0.1 mmol), and pyridine (65 μL, 0.8 mmol) in CH_2Cl_2 (1.6 mL) after 1.5 h gave 23 mg (66%) of a yellow oil: ^1H NMR ($CDCL_3$, 490 MHz) 8.0–8.08, 7.66–7.70, 7.58–7.64, 7.48–7.55, 7.42–7.48 (5 m, 5 H), 5.80–5.96 (m, 0.5 H), 5.14–5.22 (m, 0.5 H), 4.40–4.60 (m, 0.5 H), 3.76–3.80 (br d, 0.5 H), 3.43–3.58 (m, 0.5 H), 2.98–3.13 (m, 0.5 H), 2.05–2.38 (m, 1 H), [1.28–1.88 (m), 1.52 (s), 1.50 (s), 14 H]; IR 3005, 2970, 2940, 1725, 1675, 1645, 1450, 1370, 1160 cm^{-1}; CILRMS m/e (relative intensity) 346 (6.2), 330 (14.1), 290 (100), 272 (35.8), 244 (28.8), 216 (30.5), 156 (52.8), 128 (68.1), 105 (83.1); CIHRMS calcd for $C_{19}H_{24}O_5N$ (M + H) 346.1655, found 2346.1659.

Tricarbonyl 14. DMP (68 mg, 0.16 mmol), **13** (55 mg, 0.08 mmol), and pyridine (50 μL, 0.64 mmol) in CH_2Cl_2 (1.0 mL) after 12 h gave 53 mg (77%) of a yellow oil: ^1H NMR ($CDCl_3$, 250 MHz) δ 7.11–7.39 (m, 5 H), 5.12 (br dd, J = 4.7, 4.3 Hz, 1 H), 3.67 (ddd, J = 7.3, 2.5, and 1.6 Hz, 1 H), 3.22–3.35 (m, 2 H), 2.92 (t, J = 7.2 Hz, 1 H), [2.26–2.32 (m), 1.58 (s), 1.51 (s), 1.50 (s), 1.49 (s), 1.25 (d, J = 6.9 Hz), 1.10 (d, J = 7.1 Hz), 0.92 (s), 0.88–1.92 (m), 37 H], −0.09 to 0.02 (m, 6 H); IR 3400, 2945, 2930, 1720, 1715, 1645, 1640, 1460, 1455, 1260, 1160 cm^{-1}; FABLRMS m/e (relative intensity) 610 (4.0), 588 (2.2), 577 (2.3), 530 (14.3), 492 (13.9), 474 (19.7), 456 (11.0), 401 (28.1), 400 (100), 382 (15.1), 347 (23.9), 294 (23.6), 249 (27.3), 185 (6.9); FABHRMS calcd for $C_{33}H_{53}O_6NSiNa$ (M + Na) 610.3542, found 610.3478.

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Supplementary Material Available: ^1H NMR spectra for compounds **4**, **6a–c**, **8a–c**, **9–11**, **13**, and **14** (15 pages). Ordering information is given on any current masthead page.

Preparation and Some Reactions of Allylic Indium Reagents

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A variety of allylic indium sesquihalides were readily prepared by the reaction of indium powder with allylic halides in DMF at room temperature. Protonation of the allylindium reagents proceeded regiospecifically at the γ-position of the allylic group to give 1-propenes. A facile transformation of α-pinene to β-pinene was achieved via a myrtenylindium intermediate. Oxygenation of the allylic indium reagents gave mixtures of allylic alcohol isomers in moderate yields. The coupling of the allylindium reagents with cyclic imides gave diverse products depending on the structures of the substrates and the reagents. Stannylation with tributylchlorostannane occurred exclusively at the α-carbon, yielding allyltributylstannanes; *E*, *Z* isomerization of the allylic double bond depended largely upon the substitution pattern on the allylic moiety.

Despite the intensive use of boron, aluminum, and thallium reagents in synthetic chemistry, the other group XIII elements, gallium and indium, have received little attention. Although reaction of triphenylindium toward electrophiles was described as early as 1940,[1] few investigations on the synthetic use of organoindium compounds have been done until recently.[2] In 1988, we reported that indium metal is effective for the allylation of carbonyl compounds[3] and for the Reformatsky reaction,[4] and since then several interesting transformations of organic compounds have been carried out with indium metal[5] and indium(I) iodide.[6]

Here we describe the preparation of allylic indium reagents and their reactions, i.e., protolysis and oxygenation as well as couplings with imides and chlorostannanes.

Results and Discussion

Preparation. When indium powder was stirred with allylic iodides or bromides **1** in DMF at room temperature,

(1) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1940**, *62*, 2353.
(2) For synthetic uses of indium metal and organoindium compounds, see: (a) Chao, L.-C.; Rieke, R. D. *J. Org. Chem.* **1975**, *40*, 2253. (b) Maeda, T.; Tada, H.; Yasuda, K.; Okawara, R. *J. Organomet. Chem.* **1971**, *27*, 13.
(3) Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831.
(4) Araki, S.; Ito, H.; Butsugan, Y. *Synth. Commun.* **1989**, *18*, 453.
(5) (a) Araki, S.; Katsumura, N.; Ito, H.; Butsugan, Y. *Tetrahedron Lett.* **1989**, *30*, 1581. (b) Araki, S.; Butsugan, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1286.
(6) Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291.

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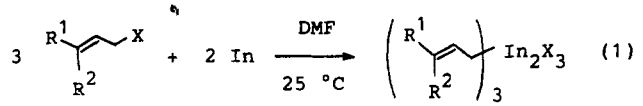
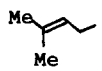
Table I. Protolysis of Allylic Indium Reagents (Eq 3)

2	product	yield, %
2e	$PhCH_2CH{=}CH_2$ (3e)	60
2f	$Ph_2CHCH{=}CH_2$ (3f)	40
2g	$Me_2C{=}CH(CH_2)_2CH(Me)CH{=}CH_2$ (3g)	73
2h	3g	67

exothermic reactions occurred smoothly and allylic indium reagents 2 were formed as colorless solutions within 1 h almost quantitatively (eq 1). Other polar solvents such

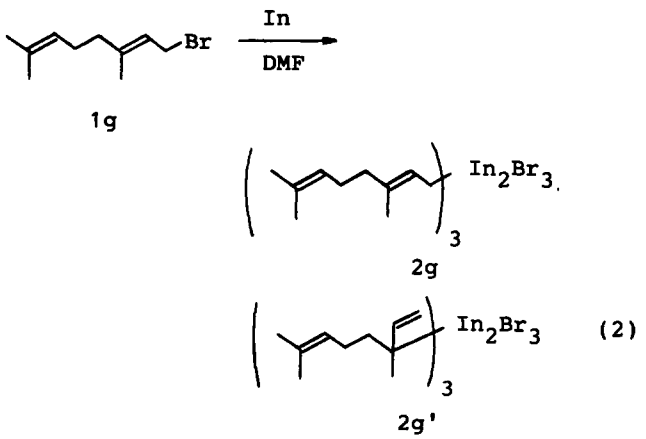


(1)

1, 2	R^1	R^2	X
a	H	H	I
b	Me	H	Br
c	Me	Me	Br
d	n-Pr	H	Br
e	Ph	H	Br
f	Ph	Ph	Br
g		Me	Br
h	Me		Br
i			Br

as tetrahydrofuran (THF) and acetonitrile can be used, but the reactions did not occur in less polar solvents such as benzene, dichloromethane, and hexane. The reactions were sluggish when allylic chlorides were used.

The structure of the resulting allylindium species is considered to be indium sesquihalide 2.[3] The regioselectivity of the oxidative addition of indium to allylic halides was examined by using geranyl bromide (1g). ^1H NMR analysis revealed that the addition occurred exclusively at the α-carbon, giving geranylindium (2g); formation of linalylindium (2g′) (γ-addition) was not detected (eq 2).



(2)

In contrast to allylic magnesium and lithium reagents, the allylic indium reagents 2 do not react with allylic halides under the reaction conditions employed; this makes 2 free from the contamination of 1,5-dienes, the Wurtz-type side products that are often formed in the preparation of allylic magnesium and lithium reagents.[7]

Scheme I

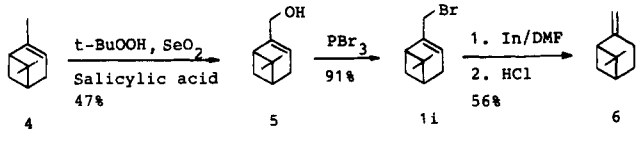
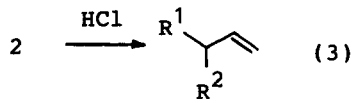


Table II. Oxygenation of Allylic Indium Reagents (Eq 4)

2	product (7[a] and 7′)	7:7′	yield, %
2a	$CH_2{=}CHCH_2OH$ (7a)		42[b]
2b	$MeCH{=}CHCH_2OH$ (7b) $CH_2{=}CHCH(Me)OH$ (7b′)	27:73	48[b]
2c	$Me_2C{=}CHCH_2OH$ (7c) $CH_2{=}CHC(Me)_2OH$ (7c′)	46:54	62[b]
2d	n-$PrCH{=}CHCH_2OH$ (7d) $CH_2{=}CHCH(n\text{-}Pr)OH$ (7d′)	55:45	50
2e	$PhCH{=}CHCH_2OH$ (7e) $CH_2{=}CHCH(Ph)OH$ (7e′)	68:32	57
2g	$Me_2C{=}CH(CH_2)_2C(Me){=}CHCH_2OH$ (7g) $Me_2C{=}CH(CH_2)_2C(Me)(CH{=}CH_2)OH$ (7g′)	43:57	33[b]

[a] E to Z ratio of 7 was not determined. [b] GC yield.

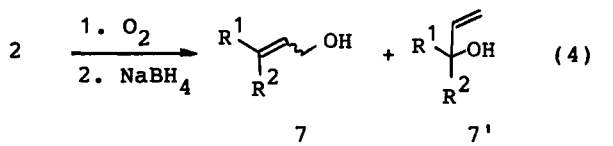
Protolysis. On treatment with dilute hydrochloric acid, the allylic indium reagents 2 were protonated, yielding the corresponding hydrocarbons. Table I summarizes the results on the protolysis of four allylic indium reagents. The protonation is highly regiospecific; only γ-protonated alkenes 3 were formed exclusively (with >99% selectivity) (eq 3). This procedure provides a general method for the



(3)

conversion of allylic halides 1 to 1-propenes 3 with a transposition of the allylic double bond.[8] The high γ-selectivity of the protolysis of the allylindium reagents allows a facile transformation of α-pinene (4) to β-pinene (6) via myrtenylindium sesquibromide (2i) in three steps in a 24% overall yield[9] (Scheme I).

Oxygenation. The allylic indium reagents 2 are air-sensitive. They rapidly absorb oxygen, and after a reductive workup to destroy hydroperoxide intermediates, allylic alcohols were obtained (eq 4). Table II lists some



(4)

representative results. In all cases, the regioselectivity was poor; mixtures of the corresponding allylic alcohol 7 and its regional isomer 7′ were formed in moderate combined yields. Oxygenation of allylmetal species is generally an unselective process giving complex reaction mixtures.[10] Attempts to improve the selectivity and yields of this allylindium oxygenation by changing the solvent and the temperature failed.

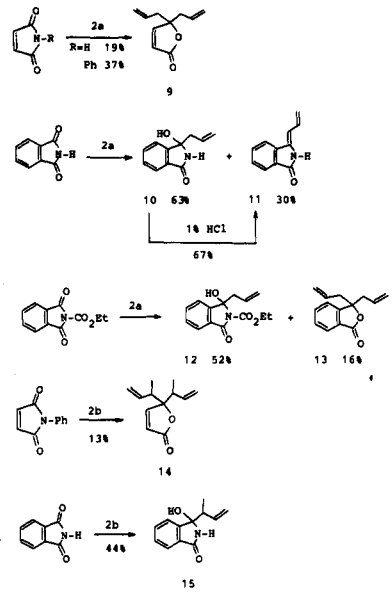
(7) Negishi, E.-I. *Organometallics in Organic Synthesis*; J. Wiley and Sons: New York, 1980; Vol. 1, pp 30–59.

(8) For a recent development of such transformations, see: (a) Tsuji, J.; Shimizu, I.; Minami, I. *Chem. Lett.* **1984**, 1017. (b) Araki, S.; Hatano, M.; Butsugan, Y. *J. Org. Chem.* **1986**, *51*, 2126 and references cited therein.

(9) For the selective conversion of α-pinene to β-pinene, see: Andrianome, M.; Delmond, B. *J. Chem. Soc., Chem. Commun.* **1985**, 1203 and references cited therein. See also ref 8b.

(10) Wakefield, B. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 7, pp 63–65.

Scheme II



Reaction with Imides. Allylic indium reagents have been reported by us to react readily with carbonyl compounds: aldehydes and ketones give homoallylic alcohols,[3] and cyclic anhydrides result in the formation of mono- and diallylation products depending on the degree of substitution of the allylic indium reagents used.[5a] Here, we describe the reaction with cyclic imides (Scheme II). The reaction of allylindium sesquiiodide **2a** with maleimide gave a complex product mixture from which only one product could be isolated. The structure was deduced from the spectroscopic and analytical data as diallylbutenolide (**9**). *N*-Phenylmaleimide gave the same product, but the yields in both reactions were low (19–37%). The reaction of **2a** with phthalimide gave two products, **10** and **11**. Diene **11** is a secondary product formed from **10** during an acidic workup. This was confirmed by treatment of alcohol **10** with dilute hydrochloric acid, resulting in smooth dehydration to provide diene **11**. No trace of diallylation product could be found in the allylation mixture. On the other hand, *N*-(ethoxycarbonyl)phthalimide gave alcohol **12** and diallylphthalide (**13**) in 52 and 16% yields, respectively. Crotylation of *N*-phenylmaleimide gave butenolide **14** in low yield (13%), whereas phthalimide gave a diastereomeric mixture of alcohols **15** in 44% yield. The reaction behavior of cyclic imides toward allylic indium is thus rather complicated compared with that of acid anhydrides,[5a] depending upon the structures of both imides and allylic indium reagents.

Grignard[11] and Reformatsky reagents[12] have been reported to react with cyclic imides yielding various types of C-alkylation products depending on the reaction conditions and the reagents used, whereas the reaction of trialkyltin oxide with imides gives N-stannylation products.[13] Although the yields are low, nitrogen-free compounds **9**, **13**, and **14** were obtained for the first time from the reaction of imides and the organoindium reagents **2**.

(11) (a) Heidenbluth, K.; Scheffler, R. *J. Prakt. Chem.* **1964**, *23*, 59. (b) Heidenbluth, K.; Toenjes, H.; Scheffler, R. Ibid. **1965**, *30*, 204. (c) Qeen, A.; Reipas, A. *J. Chem. Soc. C* **1967**, 245. (d) Flitsch, W. *Chem. Ber.* **1970**, *103*, 3205.

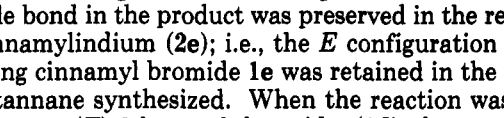
(12) (a) Michel, F.; Flitsch, W. *Chem. Ber.* **1961**, *94*, 1749. (b) Vidic, V.; Bogavac, M.; Arsenijevic, L.; Arsenijevic, V. *Arh. Farm.* **1978**, *28*, 49. *Chem. Abstr.* **1979**, *90*, 120734x.

(13) Razuvaev, G. A.; Shcherbakov, V. I.; Stolyarova, N. E. *Synth. React. Inorg. Met. Org. Chem.* **1983**, *13*, 59. *Chem. Abstr.* **1983**, *99*, 5720p.

Table III. Stannylation of Allylic Indium Reagents (Eq 5)

2	product	*E*:*Z*	yield, %
2a	CH_2=$CHCH_2SnBu_3$ (**16a**)		49
2d	*n*-PrCH=$CHCH_2SnBu_3$ (**16d**)	5:5	83
2e	PhCH=$CHCH_2SnBu_3$ (**16e**)	10:0	59
2g	Me_2C=$CH(CH_2)_2C(Me)$=$CHCH_2SnBu_3$ (**16g**)	9:1	66
2f	**16g**	9:1	61

Reaction with a Chlorostannane. On treatment with tributylchlorostannane, the allylic indium reagents **2** were readily stannylated to give allylic tributylstannanes **16**[14] (eq 5, Table III). In contrast to other electrophiles,



(5)

16

chlorostannane coupled exclusively at the α-carbon of the allylindium reagents. The configuration of the allylic double bond in the product was preserved in the reaction of cinnamylindium (**2e**); i.e., the *E* configuration of the starting cinnamyl bromide **1e** was retained in the cinnamylstannane synthesized. When the reaction was done with pure (*E*)-2-hexenyl bromide (**1d**), however, the product was a partially isomerized mixture of (*E*)- and (*Z*)-tributyl-2-hexenylstannanes (ca. 1:1). Geranyl **1g** and neryl bromides **1h** gave the corresponding α-stannylated products with the same *E* to *Z* ratio of 9:1.

The regio and stereochemistry of the coupling reactions of the allylic indium reagents **2** with electrophiles largely depend on the nature of the electrophiles. Thus, hard electrophiles such as proton and carbonyl compounds attack at the γ-carbon of the allylic indium reagents, whereas soft electrophiles such as a chlorostannane couple at the α-carbon. In the latter reaction, the stereochemistry (*E* and *Z* configuration) of the allylic double bond of the products is determined by the substitution pattern of the allylic systems.

The ease of preparation and the unique reaction behavior of the allylic indium reagents **2** should increase the importance of organoindium chemistry in organic synthesis.

Experimental Section

General. Mass spectra (MS) were recorded by electron impact ionization. GC analyses were carried out on a gas chromatograph having a TCD detector. Indium powder, stabilized by 0.5% MgO, was obtained from Nacalai Tesque Co., Ltd. Allylic halides were commercially obtained or prepared by the reaction of the corresponding allylic alcohols with PBr_3. *N*,*N*-Dimethylformamide (DMF) was distilled from CaH_2 under vacuum and stored over CaH_2. All reactions were conducted under Ar.

Preparation of Allylic Indium Sesquihalides 2. General Procedure. An allylic halide **1** (1.5 mmol) was added to a suspension of In powder (115 mg, 1 mmol) in DMF (1 mL) at room temperature. An exothermic reaction occurred immediately, and the mixture was stirred at room temperature for 0.5–1 h. The In powder was almost consumed, and a colorless clear solution of the allylic indium sesquihalide **2** was obtained in nearly quantitative yield. For ^1H NMR analysis, DMF-d_7 was used as a solvent.

Geranylindium sesquibromide (2g): ^1H NMR (200 MHz, DMF-d_7) δ 1.60 (s, 3 H, Me), 1.62 (s, 3 H, Me), 1.66 (s, 3 H, Me), 1.88–2.12 (m, 6 H, CH_2), 5.17 (m, 1 H, olefinic), 5.48 (m, 1 H, olefinic). For the ^1H NMR of **2a**, see ref 3.

(14) For the synthesis of allylstannanes by the coupling of allylmetals and stannyl halide, see: (a) Abel, E.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199. (b) Andrianome, M.; Delmond, B. *Tetrahedron Lett.* **1985**, *26*, 6341.

Protolysis. General Procedure. Hydrochloric acid (3%, 15 mL) was added to an allylic indium reagent **2** prepared as above, and the mixture was stirred for 1 min. The product was extracted with pentane (20 mL × 3). The extracts were washed with brine and dried (Na_2SO_4). After evaporation, the residue was purified by passing through a short silica gel column (pentane), yielding the pure hydrocarbon. The purity was checked by GC and ^1H NMR.

Allylbenzene (3e): ^1H NMR (90 MHz, $CDCl_3$) δ 3.39 (d, J = 7 Hz, 2 H, CH_2), 4.98 (m, 1 H, olefinic), 5.13 (m, 1 H, olefinic), 5.75–6.40 (m, 1 H, olefinic), 7.22 (m, 5 H, Ph).

3,3-Diphenylpropene (3f):[15] ^1H NMR (90 MHz, $CDCl_3$) δ 4.68 (b d, J = 7 Hz, 1 H, CH), 4.96 (b d, J = 17 Hz, 1 H, olefinic), 5.18 (b d, J = 10 Hz, 1 H, olefinic), 6.28 (ddd, J = 17, 10, 7 Hz, 1 H, olefinic), 7.22 (m, 10 H, Ph).

3,7-Dimethyl-1,6-octadiene (3g):[8b] ^1H NMR (90 MHz, $CDCl_3$) δ 0.98 (d, J = 7 Hz, 3 H, Me), 1.34 (m, 2 H, CH_2), 1.59 (s, 3 H, Me), 1.68 (s, 3 H, Me), 2.00 (m, 3 H, CH and CH_2), 4.70–5.20 (m, 3 H, olefinic), 5.70 (ddd, J = 17, 10, 7 Hz, 1 H, olefinic).

Myrtenol (5). The compound was synthesized by the oxidation of α-pinene (4) according to Sharpless's method[16] in 47% yield.

Myrtenyl Bromide (1i).[17] To a solution of myrtenol (5) (760 mg, 5 mmol) in anhydrous ether (7 mL) was added PBr_3 (0.30 mL, 1.65 mmol) at 0 °C, and the mixture was stirred for 1.5 h. Saturated aqueous $NaHCO_3$ was added and the product extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and evaporated. The residue (980 mg, 91%) was sufficiently pure and used for the next step without purification: ^1H NMR (90 MHz, $CDCl_3$) δ 0.82 (s, 3 H, Me), 1.30 (s, 3 H, Me), 2.25 (m, 6 H, CH_2 and CH), 3.93 (s, 2 H, CH_2), 5.66 (m, 1 H, olefinic).

β-Pinene (6). To a suspension of In powder (144 mg, 1.25 mmol) in DMF (2 mL) was added myrtenyl bromide (1i) (296 mg, 1.72 mmol), and the mixture was stirred at room temperature for 1 h. Hydrochloric acid (3%, 15 mL) was added to the resulting myrtenylindium reagent. Workup as described in the General Procedure gave β-pinene (6) (132 mg, 56%). The product was free from α-pinene and other isomers: ^1H NMR (90 MHz, $CDCl_3$) δ 0.73 (s, 3 H, Me), 1.27 (s, 3 H, Me), 1.93 (m, 4 H, CH_2 and CH), 2.40 (m, 4 H, CH_2 and CH), 4.63 (m, 2 H, olefinic).

Oxygenation of Allylic Indium Reagents (2). The following oxygenation of cinnamylindium reagent represents the general procedure. Cinnamylindium sesquibromide (2e) was prepared from In (164 mg, 1.43 mmol) and cinnamyl bromide (434 mg, 2.20 mmol) in DMF (5 mL) under Ar. Dry O_2 was bubbled into the cinnamylindium solution at room temperature for 3 h. $NaBH_4$ (32 mg, 0.86 mmol) was added and stirred for 1 h. After the addition of hydrochloric acid (3%, 10 mL), the products were extracted with ether and the extracts washed with saturated aqueous $NaHCO_3$ and brine. After the extracts were dried (Na_2SO_4), the solvent was evaporated and the residue was column chromatographed on silica gel (CH_2Cl_2) to give cinnamyl alcohol (7e; 116 mg, 39%) and 1-phenyl-2-propen-1-ol (7e'; 54 mg, 18%).

Oxygenation of other allylic indium reagents **2** was similarly carried out, and the structures of the products were confirmed by the direct comparison with commercially obtained authentic samples.

Reaction of Maleimide with Allylindium Sesquiiodide (2a). Maleimide (194 mg, 2 mmol) in DMF (1 mL) was added to a solution of **2a**, prepared from In metal (575 mg, 5 mmol) and allyl iodide (1.26 g, 7.5 mmol) in DMF (1 mL), and the mixture was stirred at 70–75 °C for 5 h. The reaction was quenched by the addition of hydrochloric acid (1%, 20 mL). NaCl (7 g) was dissolved, and the products were extracted with CH_2Cl_2 (15 mL × 2). The extracts were washed with brine and dried (Na_2SO_4). The solvent was removed, and the residue was distilled in a Kugelrohr apparatus at 110–125 °C (3 Torr) to give 3,3-diallylbutenolide (9)[5a] (62 mg, 19%) as a colorless oil: ^1H NMR (90 MHz, $CDCl_3$) δ 2.52 (d, J = 5 Hz, 4 H, CH_2), 4.9–5.3 (m, 4 H, olefinic), 5.4–5.9 (m, 2 H, olefinic), 6.06 (d, J = 4 Hz, 1 H, COC*H*=CH), 7.31 (d, J = 4 Hz, 1 H, COCH=C*H*); IR (neat) 1740, 920, 810 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.43; H, 7.53.

Reaction of *N*-Phenylmaleimide with Allylindium (2a). The reaction was similarly carried out and the same compound (9) was obtained in 37% yield.

Reaction of Phthalimide with Allylindium (2a). Phthalimide (147 mg, 1 mmol) in DMF (0.9 mL) was added to a solution of **2a**, prepared from In (230 mg, 2 mmol) and allyl iodide (504 mg, 3 mmol) in DMF (0.8 mL), and the mixture was stirred at room temperature for 17 h. The solvent was removed under reduced pressure, and the residue was added into hydrochloric acid (1%, 8 mL). NaCl (3 g) was dissolved in the mixture, and the products were extracted with CH_2Cl_2 (15 mL × 3). The extracts were washed with a 1% Na_2CO_3 solution (saturated with NaCl) and brine and dried (Na_2SO_4). The crude products showed two spots on TLC that were separated by preparative TLC (silica gel, 10–50% AcOEt in hexane) to give **10** (120 mg, 64%) and **11** (50 mg, 29%).

3-Allyl-3-hydroxyphthalimidine (10): mp 129 °C (lit.[11d] mp 123–125 °C); IR (KBr) 3310, 3250, 1700, 1660, 1610, 920 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 2.62 (dd, J = 10, 6 Hz, 1 H, CH_2), 2.90 (dd, J = 10, 4 Hz, 1 H, CH_2), 3.7 (b s, 1 H, OH), 5.1 (m, 2 H, olefinic), 5.5–6.02 (m, 1 H, olefinic), 6.75 (b s, 1 H, NH), 7.54 (m, 4 H, Ar).

3-(2-Propenylidene)phthalimidine (11): mp >260 °C dec; IR (KBr) 3400, 1700, 890, 755 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$ + DMSO-d_6) δ 5.3 (dd, J = 5, 1 Hz, 1 H, olefinic), 5.4 (dd, J = 9, 1 Hz, 1 H, olefinic), 6.2 (d, J = 7 Hz, 1 H, olefinic), 6.9 (ddd, J = 9, 7, 5 Hz, 1 H, olefinic), 7.4–7.9 (m, 4 H, Ar), 10.2 (NH); MS (70 eV) m/z 171 (M^+).

The compound **10** (60 mg) was dissolved in acetone (5 mL), and hydrochloric acid (1%, 10 mL) was added. The mixture was kept at room temperature for 20 h. Fine needles were deposited and filtered (36 mg, 67%). The IR and ^1H NMR were identical with those of **11**.

Reaction of *N*-(Ethoxycarbonyl)phthalimide with Allylindium Sesquiiodide (2a). *N*-(Ethoxycarbonyl)phthalimide (438 mg, 2 mmol) in DMF (1.5 mL) was added to a solution of **2a** prepared from In metal (460 mg, 4 mmol) and allyl iodide (1.0 g, 6 mmol) in DMF (1 mL), and the mixture was stirred at room temperature for 1.5 h. Hydrochloric acid (1%, 16 mL) was added to the reaction mixture, and NaCl (7 g) was dissolved in it. The products were extracted with CH_2Cl_2 (30 mL × 2). The extracts were washed with brine and dried (Na_2SO_4). The crude products showed two spots on TLC that were separated by preparative TLC (silica gel, 30% AcOEt in hexane) to give **12** (262 mg, 52%) and **13** (68 mg, 16%).

2-(Ethoxycarbonyl)-3-allyl-3-hydroxyphthalimidine (12): mp 91 °C; IR (KBr) 3400, 1760, 1675, 1610, 930 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.43 (t, J = 5 Hz, 3 H, Me), 2.8–3.4 (m, 2 H, CH_2), 4.44 (q, J = 5 Hz, 2 H, OCH_2), 4.67 (s, 1 H, OH), 4.72–5.5 (m, 3 H, olefinic), 7.4–7.9 (m, 4 H, Ar); MS (70 eV) m/z 243 ($M^+ - H_2O$). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79; N, 5.36. Found: C, 64.32; H, 5.72; N, 5.36.

3,3-Diallylphthalide (13):[5a] colorless oil; IR (neat) 1760, 1610, 920 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 2.7 (d, J = 5 Hz, 4 H, CH_2), 4.8–5.2 (m, 4 H, olefinic), 5.23–5.8 (m, 2 H, olefinic), 7.23–7.95 (m, 4 H, Ar); MS (70 eV) m/z 173 (M^+ - allyl). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.35; H, 6.63.

Reaction of *N*-Phenylmaleimide with Crotylindium Sesquibromide (2b). To a solution of crotylindium sesquibromide (**2b**) prepared from In (575 mg, 5 mmol) and crotyl bromide (1.09 g, 8 mmol) in DMF (1.5 mL) was added *N*-phenylmaleimide (346 mg, 2 mmol) in DMF (1 mL), and the mixture was stirred at room temperature for 16 h. Hydrochloric acid (1%, 16 mL) was added to the reaction mixture, and NaCl (7 g) was dissolved in it. The product was extracted with CH_2Cl_2 (10 mL × 3). The extracts were washed with aqueous Na_2CO_3 (1%, saturated with NaCl) and brine and dried (Na_2SO_4). Since the residue showed many spots on TLC, it was subjected to distillation in a Kugelrohr apparatus at 120–200 °C (3 Torr). The distillate was further purified by preparative TLC (silica gel, 0.5% AcOEt in hexane) to furnish **14** (60 mg, 13%).

3,3-Di(3-buten-2-yl)butenolide (14): colorless oil; IR (neat) 1760, 1640, 1600, 920, 820 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.95 (m, 3 H, Me), 2.85 (m, 1 H, CH), 5.10 (m, 2 H, olefinic), 5.62 (m,

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1 H, olefinic), 6.1 (m, 1 H, COCH=CH), 7.2 (m, 1 H, COCH=CH). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.42; H, 8.34.

Reaction of Phthalimide with Crotylindium (2b). The reaction was similarly carried out at room temperature for 16 h. Aqueous workup and purification on preparative TLC (silica gel, 30% AcOEt in hexane) gave a diastereomeric mixture of **15** in 44% yield.

3-(3-Buten-2-yl)-3-hydroxyphthalimidine (15): mp 110–120 °C; IR (KBr) 3275, 1700, 1660, 1610, 920 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.85 and 1.2 (each d, J = 4 Hz, total 3 H, Me), 2.6–3.1 (m, 1 H, CH), 3.2 (b s, 1 H, OH), 4.9–5.25 (m, 2 H, olefinic), 5.3 (b s, 1 H, NH), 5.5–6.3 (m, 1 H, olefinic), 7.3–7.8 (m, 4 H, Ar); MS (70 eV) m/z 185 ($M^+ - H_2O$). Anal. Calcd for $C_{12}H_{13}NO$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.45; H, 6.46; N, 6.82.

Reaction of Chlorotributylstannane with Allylic Indium Reagents 2. General Procedure. To an allylic indium reagent **2** prepared from In (1 mmol) and an allylic halide (1.5 mmol) in DMF (1 mL) was added chlorotributylstannane (1 mmol) at room temperature. After the reaction was complete (1–7 h), hydrochloric acid (1%, 10 mL) was added and the product extracted with ether. The extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane–CH_2Cl_2 gradient) to give the allylic tributylstannane **16**. The structure was confirmed on the basis of the spectral data. The isomeric ratio was estimated by ^1H and ^{13}C NMR spectroscopy. Results are summarized in Table III.

Allyltributylstannane (16a):[18] ^1H NMR (200 MHz, $CDCl_3$) δ 0.70–1.08 (m, 15 H, Me and CH_2), 1.15–1.72 (m, 12 H, CH_2), 1.79 (d, J = 8 Hz, 2 H, CH_2), 4.59–5.00 (m, 2 H, olefinic), 5.81–6.18 (m, 1 H, olefinic).

(*E*)- and (*Z*)-2-hexenyltributylstannane (16d):[19] ^1H NMR (200 MHz, $CDCl_3$) δ 0.76–1.04 (m, 18 H, Me and CH_2), 1.15–1.61 (m, 14 H, CH_2), 1.71 (m, 2 H, CH_2), 1.97 (m, 2 H, CH_2), 5.00–5.68 (m, 2 H, olefinic); ^{13}C NMR ($CDCl_3$) 124.3, 125.7, 128.2, 129.2 (olefinic).

(*E*)-Cinnamyltributylstannane (16e):[18] ^1H NMR (200 MHz, $CDCl_3$) δ 0.70–1.02 (m, 15 H, Me and CH_2), 1.17–1.69 (m, 12 H, CH_2), 1.97 (d, J = 8 Hz, 2 H, CH_2), 6.21 (d, J = 15 Hz, 1 H, olefinic), 6.40 (dt, J = 15, 8 Hz, 1 H, olefinic), 7.06–7.44 (m, 5 H, Ph).

(*E*)- and (*Z*)-3,7-dimethyl-2,6-octadienyltributylstannane (16g):[19] ^1H NMR (200 MHz, $CDCl_3$) δ 0.78–1.00 (m, 15 H, Me and CH_2), 1.20–1.70 (m, 14 H, CH_2), 1.57 (s, 3 H, Me), 1.61 (s, 3 H, Me), 1.69 (s, 3 H, Me), 2.02 (m, 4 H, CH_2), 5.12 (m, 1 H, olefinic), 5.34 (b t, J = 8 Hz, 1 H, olefinic); ^{13}C NMR ($CDCl_3$) 122.8, 123.2, 124.6, 129.0, 129.4, 131.0, 131.2 (olefinic).

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Facial Differentiation in Diels–Alder Reactions to Dissymmetric Cyclohexa-1,3-dienes

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Reactions of **2a–c** with maleic anhydride (MA) and benzoquinone (BQ) show strong preference for addition to the "carbonyl" face of the diene. For dimethyl acetylenedicarboxylate (DMAD), attack from this face decreases with successive methylidene substitution while for *N*-phenyl-1,2,4-triazolinedione (PTAD) the reverse occurs. The consequence of orbital tilting and transition-state steric and torsional interactions cannot alone account for the facial selectivity for the reactions with DMAD and PTAD. Unfavorable orbital interaction of the closed shells of the carbonyl(s) and methylidene(s) syn to the incoming orthogonal π orbital of DMAD is considered to be important.

Introduction

The pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCUD, 1) framework has proved to be both of theoretical interest,[1] because of the strain contained in the pentacyclic ring system and the stereochemical relationship of the cofacial carbonyl groups, and of synthetic value as a route for the preparation of linearly fused tricyclopentanoids.[2] The diene analogue, hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (**2a**) is of interest for similar reasons but in addition offers an attractive framework for the study of π-facial selectivity that complements the results for the well-studied diene, isodicyclopentadiene.[3] X-ray crystal structure analyses of this diketone[4] and a hemiacetal derivative[5] show the diene component to be in a planar arrangement in both compounds. The diene **2a**[5] showed a marked preference for alkene addition from the carbonyl face of the diene. A selection of these addition reactions was independently reported somewhat later[6] where it was concluded that the carbonyl groups were not in any way responsible for influencing the facial selectivity since the diol resulting from $NaBH_4$ reduction of the carbonyl groups in **2a** also underwent addition of acrylonitrile from the carbonyl face. This is despite the fact that we had previously reported additions[5] of azo and alkyne dienophiles to **2a** which show variation in facial selectivity inconsistent with the conclusions of Pandey et al.[6]

We have been interested in examining in detail the effect of the carbonyl substituents on the facial selectivity of the Diels–Alder reactions. To this end we now report a series

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