

## Reaction of 1-Substituted Indenes with Diborane or *N*-Bromoacetamide in Protic Solvents. The Effect of the Substituent on the Stereochemistry of Addition

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The reaction of 1-substituted indenenes with diborane or *N*-bromoacetamide (NBA) in protic solvents has been investigated to determine the effect of an increase of steric bulk of the substituent on the stereochemical course of addition. In the hydroboration reaction the proportion of the products *via* attack by diborane from the less hindered side increases, as the steric bulk of the substituent at C-1 increases. The reaction with NBA in aqueous dioxan, followed by acetylation, gave a mixture of 3-substituted-1-acetoxy-2-bromoindans with *trans,trans* and *trans,cis*-configuration: 1-phenylindene gave mainly *trans,trans*-1-acetoxy-2-bromo-3-phenylindan, while *trans,cis*-1-acetoxy-2-bromo-3-methylindan was the major product in the case of 1-methylindene.

MANY studies have been conducted on the stereochemical and conformational problems in the cyclohexyl, cyclopentyl, and norbornyl systems. In the indene system, however, relatively few studies have been reported.<sup>1-4</sup> To provide further information, the stereochemical course of addition of diborane or 'BrX' (X = OH or OMe) to 1-substituted indenenes has been investigated. Data on the stereochemistry of the products from bromination of alkenes are limited.<sup>5</sup> In addition, the  $\alpha$ -substituent effect of alkenes on the stereochemistry of the addition, in our knowledge, has not, as far as we know, been undertaken.

### RESULTS AND DISCUSSION

**Hydroboration.**—The reaction of indenenes (1a—k) with diborane generated *in situ* was performed at 20 °C, which was followed by oxidation with hydrogen peroxide to give a mixture of alcohols. The crude alcohols were converted into the corresponding acetates, which were isolated by column chromatography on silica gel. The acetate composition was determined by <sup>1</sup>H n.m.r. spectroscopy. 2,3-Diphenylindene and 1-methyl-2,3-diphenylindene, however, did not react with diborane (Table I).

TABLE I  
Reaction with diborane <sup>a</sup>

Substrate	Product and % yield <sup>b</sup>
(1a)	95 [(6a) : (8a) = 72 : 28]
(1b)	90 [(6b) : (7b) : (8b + 9b) = 45 : 18 : 37] <sup>c</sup>
(1c)	85 [(6c) : (7c) = 78 : 22]
(1d)	85 [(6d) : (7d) = 75 : 25]
(1e)	85 [(6e) : (7e) = 75 : 25]
(1f)	95 [(6f) : (7f) : (8f + 9f) = 55 : 19 : 26] <sup>c</sup>
(1g)	80 [(6g) : (7g) = 88 : 12]
(1h)	80 [(6h) : (7h) = 81 : 19]
(1i)	(6i) 85
(1j)	(6j) 90
(1k)	(6k) 90

<sup>a</sup> The reaction of (1a) (10 mmol) with 2 mol. equiv. of diborane was performed at 20 °C for 15 min, which was followed by oxidation with aqueous hydrogen peroxide. The crude products were converted into the acetates. <sup>b</sup> Isolated yield. The ratio was determined by <sup>1</sup>H n.m.r. spectroscopy. <sup>c</sup> The (8) : (9) ratio could not be determined.

(a) **Stereochemical Course of Addition.** The hydroboration of indenenes (1c—e, g, or i—k), followed by

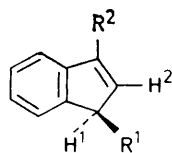
acetylation, gave a mixture of the corresponding 2-acetoxyindans.<sup>6</sup> From (1a) a mixture of (6a) and (8a) was obtained in a ratio of 72 : 28. In the cases of (1b), (1f), and (1h) the ratios of 2-acetoxyindans to 1-acetoxyindans were 63 : 37, 74 : 26, and 81 : 19, respectively.<sup>†</sup>

The data in Table I demonstrate that the ratio of (6) to (7) increases, as the bulk of 1-substituent increases. In the cases of (1b), (1f), and (1h) the (6) : (7) ratios were 71 : 29, 74 : 26, and 100 : 0, respectively. The substituent at C-3 in indenenes seems to accelerate the attack by diborane from the less hindered side; the (6g) : (7g) ratio was 88 : 12, while the (6f) : (7f) ratio was 74 : 26. It is remarkable that boron attacks even the C-3 of (1h) only from the less hindered side to give only one isomeric product (8h), together with (6h).

(b) **Conformations of 1,2-disubstituted and 1,2,3-trisubstituted indans.** The *cis*- and *trans*-1,2-disubstituted indans differed significantly in the spin-spin coupling patterns of the hydrogens at C-3 (Table 2). The same spin-spin coupling patterns have been observed for other 1,2-disubstituted indans;<sup>1</sup> one of the coupling constants between H<sup>2</sup> and the C-3 hydrogens in a *cis*-1,2-disubstituted indan is small, while other coupling constants are considerably larger. By contrast, in a *trans*-1,2-disubstituted indan all coupling constants are large. Molecular models and the spin-spin coupling patterns suggest that the most probable conformation of *trans*-1-phenyl-2-acetoxyindan (6h) is represented as structure (A), in which both the phenyl and acetoxy-groups occupy the pseudo-equatorial positions. Structure (B) is most probable for *cis*-1-phenyl-2-acetoxyindan (7h), in which C-2 of the indan ring is distorted to relieve the steric hindrance of eclipsed functional groups. In *trans,trans*-1-methyl-2-acetoxy-3-phenylindan (6d) all substituents are expected to occupy the pseudo-equatorial positions [structure (C)], with  $J(H^1, H^2)$  and  $J(H^2, H^3)$  being as large as 6.6 Hz. The <sup>1</sup>H n.m.r. spectrum of (7d) is also in good agreement with the conformation (D); both  $J(H^1, H^2)$  and  $J(H^2, H^4)$  are 6.3 Hz.

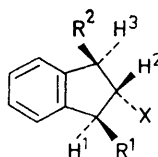
**Reaction with *N*-Bromoacetamide in Protic Solvents.**—

<sup>†</sup> The reaction of 1,3-dimethylindene (1c) with the bulkier 9-borabicyclo[3.3.1]nonane gives exclusively *trans,trans*-1,3-dimethylindan-2-ol (2c).<sup>7</sup>



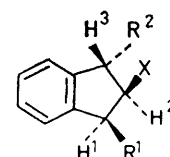
(1)

- a ; R<sup>1</sup> = R<sup>2</sup> = H  
 b ; R<sup>1</sup> = Me, R<sup>2</sup> = H  
 c ; R<sup>1</sup> = R<sup>2</sup> = Me  
 d ; R<sup>1</sup> = Me, R<sup>2</sup> = Ph  
 e ; R<sup>1</sup> = Me, R<sup>2</sup> = C<sub>6</sub>H<sub>4</sub>Me - *p*  
 f ; R<sup>1</sup> = Et, R<sup>2</sup> = H  
 g ; R<sup>1</sup> = Et, R<sup>2</sup> = Ph  
 h ; R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 i ; R<sup>1</sup> = R<sup>2</sup> = Ph  
 j ; R<sup>1</sup> = H, R<sup>2</sup> = Me  
 k ; R<sup>1</sup> = H, R<sup>2</sup> = Ph



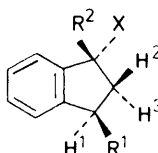
(2); X = OH, (6); X = OAc

- a ; R<sup>1</sup> = R<sup>2</sup> = H  
 b ; R<sup>1</sup> = Me, R<sup>2</sup> = H  
 c ; R<sup>1</sup> = R<sup>2</sup> = Me  
 d ; R<sup>1</sup> = Me, R<sup>2</sup> = Ph  
 e ; R<sup>1</sup> = Me, R<sup>2</sup> = C<sub>6</sub>H<sub>4</sub>Me - *p*  
 f ; R<sup>1</sup> = Et, R<sup>2</sup> = H  
 g ; R<sup>1</sup> = Et, R<sup>2</sup> = Ph  
 h ; R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 i ; R<sup>1</sup> = R<sup>2</sup> = Ph



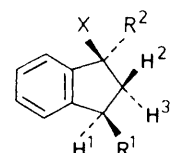
(3); X = OH, (7); X = OAc

- b ; R<sup>1</sup> = Me, R<sup>2</sup> = H  
 c ; R<sup>1</sup> = R<sup>2</sup> = Me  
 d ; R<sup>1</sup> = Me, R<sup>2</sup> = Ph  
 e ; R<sup>1</sup> = Me, R<sup>2</sup> = C<sub>6</sub>H<sub>4</sub>Me - *p*  
 f ; R<sup>1</sup> = Et, R<sup>2</sup> = H  
 g ; R<sup>1</sup> = Et, R<sup>2</sup> = Ph  
 h ; R<sup>1</sup> = Ph, R<sup>2</sup> = H



(4); X = OH, (8); X = OAc

- a ; R<sup>1</sup> = R<sup>2</sup> = H  
 b ; R<sup>1</sup> = Me, R<sup>2</sup> = H  
 f ; R<sup>1</sup> = Et, R<sup>2</sup> = H  
 h ; R<sup>1</sup> = Ph, R<sup>2</sup> = H



(5); X = OH, (9); X = OAc

- b ; R<sup>1</sup> = Me, R<sup>2</sup> = H  
 f ; R<sup>1</sup> = Et, R<sup>2</sup> = H  
 h ; R<sup>1</sup> = Ph, R<sup>2</sup> = H

TABLE 2

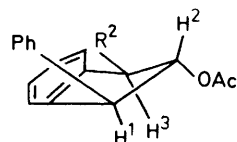
Chemical shifts and coupling constants for indan derivatives ( $\delta$  from SiMe<sub>4</sub>, J/Hz)

Indan	H <sup>1</sup>	H <sup>2</sup>	H <sup>3</sup>	R
(6h)	4.49 (d, 5.4)	5.40 (td, 5.4, 6.3)	3.54 (dd, 18.0, 6.3)	2.95 (dd, 18.0, 5.4)
(7h)	4.57 (d, 6.0)	5.71 (td, 6.0, 3.6)	3.04 (dd, 15.9, 3.6)	3.29 (dd, 15.9, 6.0)
(8h)	4.30 (t, 8.1)	1.88—2.24 (m)	3.12 (dt, 13.5, 8.1)	6.27 (t, 8.1)
(6e)	3.27 (q, 6.6)	5.26 (t, 6.6)	4.33 (d, 6.6)	
(7e)	3.62 (q, 6.6)	5.37 (t, 6.3)	4.44 (d, 6.3)	

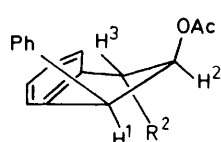
s = Singlet, d = doublet, t = triplet, q = quintet, m = multiplet.

The reaction of the indenenes (1b, f, g, i, and k) with *N*-bromoacetamide (NBA) in aqueous dioxan or methanol gave a mixture of 2-bromoindanols or 1-methoxy-2-

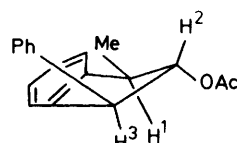
bromoindans, respectively (Table 3).<sup>3</sup> 2-Bromoindan-1-ols were converted into the corresponding 1-acetoxy-2-bromoindans. The position of attachment of the



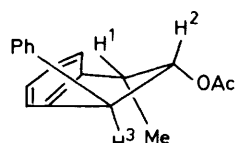
(A)



(B)



(C)



(D)

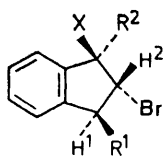
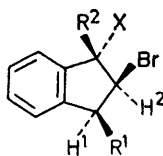
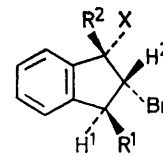
TABLE 3

Reaction with *N*-bromoacetamide<sup>a</sup>

Substrate	Solvent	Product and yield (%) <sup>b</sup>
(1a)	Aqueous dioxan	(13a) 90
(1b)	Aqueous dioxan	78 [(13b) : (14b) = 35 : 65]
(1f)	Aqueous dioxan	69 [(13f) : (14f) = 49 : 51]
(1h)	Aqueous dioxan	86 [(13h) : (14h) = 75 : 25]
(1i)	Aqueous dioxan	(12i) 95
(1k)	Aqueous dioxan	(12k) 95
(1b)	Methanol	89 [(15b) : (16b) = 33 : 67]
(1f)	Methanol	95 [(15f) : (16f) = 44 : 55]
(1h)	Methanol	91 [(15h) : (16h) = 70 : 30]
(1i)	Methanol	(17i) 95

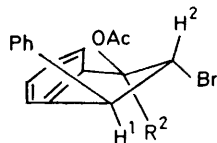
<sup>a</sup> The reaction of (1) with 1 mol. equiv. of NBA was performed at 70 °C. <sup>b</sup> The isolated yield. The ratio of the products was determined by <sup>1</sup>H n.m.r. spectroscopy.

bromine in (13b) or (14b) has been unambiguously determined to be C-2 on the basis of the chemical shift

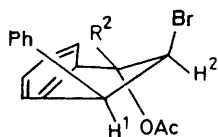
(10a)  $R^1 = R^2 = H, X = OH$ (10b)  $R^1 = Me, R^2 = H, X = OH$ (10f)  $R^1 = Et, R^2 = H, X = OH$ (10h)  $R^1 = Ph, R^2 = H, X = OH$ (10i)  $R^1 = R^2 = Ph, X = OH$ (10k)  $R^1 = H, R^2 = Ph, X = OH$ (13a)  $R^1 = R^2 = H, X = OAc$ (13b)  $R^1 = Me, R^2 = H, X = OAc$ (13f)  $R^1 = Et, R^2 = H, X = OAc$ (13h)  $R^1 = Ph, R^2 = H, X = OAc$ (15b)  $R^1 = Me, R^2 = H, X = OMe$ (15f)  $R^1 = Et, R^2 = H, X = OMe$ (15h)  $R^1 = Ph, R^2 = H, X = OMe$ (11b)  $R^1 = Me, R^2 = H, X = OH$ (11f)  $R^1 = Et, R^2 = H, X = OH$ (11h)  $R^1 = Ph, R^2 = H, X = OH$ (14b)  $R^1 = Me, R^2 = H, X = OAc$ (14f)  $R^1 = Et, R^2 = H, X = OAc$ (14h)  $R^1 = Ph, R^2 = H, X = OAc$ (16b)  $R^1 = Me, R^2 = H, X = OMe$ (16f)  $R^1 = Et, R^2 = H, X = OMe$ (16h)  $R^1 = Ph, R^2 = H, X = OMe$ (12i)  $R^1 = R^2 = Ph, X = OH$ (12k)  $R^1 = H, R^2 = Ph, X = OH$ (17i)  $R^1 = R^2 = Ph, X = OMe$ 

of the C-1 hydrogen: this hydrogen, attached to the same carbon as the acetoxy-group, appears at  $\delta$  ca. 6.4.

(a) *Products and their configurations.* The reaction of 1-phenylindene (1h) with NBA in aqueous dioxan gave two alcohols, which were converted into the corresponding acetates. One isomer with a larger  $J(R^2, H^2)$  (6.6 Hz) value and another one with a smaller  $J(R^2, H^2)$  (3.3 Hz) value were assigned as (13h) (the product by attack of the bromine cation from the less hindered side) and (14h) (attack by the bromine cation from the more hindered side), respectively, on the basis of the relation between conformation and coupling constant. The best conformations of (13h) and (14h) are represented as (E) and (F), respectively. In (F) the dihedral angle between  $R^2$  and  $H^2$  is ca.  $100^\circ$ , with the coupling constant thus being small. The (13h):(14h) ratio was found to be 75:25, indicating that the attack by the bromine cation occurred mainly from the less hindered side. In the case of (1f) the (13f):(14f) ratio was 49:51. It is



(E)

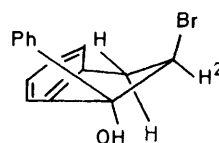


(F)

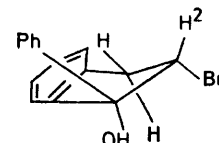
striking that the reaction of (1b) gave a 78% yield of a mixture of 35% (13b) and 65% (14b), the bromine cation attacking mainly from the more hindered side. The same trend for the substituent effect on the product composition was observed in the reaction in methanol.

The reaction of 1,3-diphenylindene (1i) gave only one alcohol [ $J(H^1, H^2)$  9.2 Hz]. This product is expected to be either (12i) by a *cis*-addition of 'BrOH' or (10i) by a *trans*-addition, when it is considered that the bromine cation attacks (1h) from the less hindered side predominantly. The following fact may be helpful in

elucidating the configuration; indene (1k) also gave one product, which was either a *trans*-addition product (10k) or a *cis*-addition product (12k). The large coupling constants (8.3 Hz) between  $H^2$  and two C-3 hydrogens seem to fit the conformation (H) rather than (G),



(G)



(H)

*i.e.*, the product is (12k). At a reasonable extrapolation the product from (1i) may be (12i).

#### EXPERIMENTAL

$^1H$  N.m.r. spectra were obtained with a JEOL 1UM 4P 100 instrument, mass spectra with a Hitachi RMU-6H spectrometer, and i.r. spectra with a Hitachi 215 spectrometer.

The indenenes (1b),<sup>8</sup> (1c),<sup>9</sup> (1d),<sup>10</sup> (1e),<sup>10</sup> (1f),<sup>11</sup> (1g),<sup>12</sup> (1h),<sup>8</sup> (1i),<sup>13</sup> (1j),<sup>8</sup> and (1k)<sup>8</sup> were prepared according to the reported methods.

*Hydroboration.*—The hydroboration of the indenenes was performed according to the method of Brown *et al.*<sup>14</sup> The crude alcohols were treated with a mixture of acetyl chloride (3 mol. equiv.) and pyridine (3 mol. equiv.) in ether (15 ml) at  $0^\circ C$  for 12 h to give the acetates, which were isolated by column chromatography on silica gel.

The alcohol (2b) was an oil;  $\delta$  1.30 (3 H, d,  $J$  6.6 Hz), 1.95 (1 H, br s), 2.81 (1 H, dd,  $J$  14.2 and 6.6 Hz), 3.06 (1 H, m), 3.26 (1 H, dd,  $J$  14.2 and 6.6 Hz), and 4.15 (1 H, q,  $J$  6.6 Hz);  $\nu_{max}$  3 300—3 400 and 1 060  $cm^{-1}$ : the *p*-nitrobenzoate of (2b) was a solid, m.p. 105—106  $^\circ C$  (from benzene-light petroleum) (Found: C, 68.5; H, 4.95.  $C_{17}H_{15}NO_4$  requires C, 68.67; H, 5.09%);  $\nu_{max}$  1 720  $cm^{-1}$ : the *p*-nitrobenzoate of (2c) was a solid, m.p. 118—119  $^\circ C$  (from benzene-light petroleum) (Found: C, 69.55; H, 5.35.  $C_{18}H_{17}NO_4$  requires C, 69.44; H, 5.50%);  $\delta$  1.42

(6 H, d,  $J$  7.2 Hz), 3.33 (2 H, quintet,  $J$  7.2 Hz), 5.11 (1 H, t,  $J$  7.2 Hz), 7.06–7.34 (4 H, m), and 8.20–8.34 (4 H, m);  $\nu_{\max}$  1 720, 1 520, 1 340, 1 270, 1 115, 1 100, and 985  $\text{cm}^{-1}$ : (2e) was a solid, m.p. 135–136 °C (from benzene–light petroleum) (Found: C, 85.6; H, 7.6.  $\text{C}_{17}\text{H}_{18}\text{O}$  requires C, 85.67; H, 7.61%);  $\delta$  1.42 (3 H, d,  $J$  6.6 Hz), 2.05 (1 H, br s), 2.35 (3 H, s), 3.11 (1 H, quintet,  $J$  6.6 Hz), 3.91 (1 H, t,  $J$  6.6 Hz), and 4.06 (1 H, d,  $J$  6.6 Hz);  $\nu_{\max}$  3 150–3 450, 1 100, and 1 065  $\text{cm}^{-1}$ : (2h) was an oil;  $\delta$  2.15 (1 H, br s), 2.92 (1 H, dd,  $J$  16.5 and 6.6 Hz), 3.31 (1 H, dd,  $J$  16.5 and 6.6 Hz), 4.16 (1 H, d,  $J$  6.6 Hz), and 4.46 (1 H, q,  $J$  6.6 Hz);  $\nu_{\max}$  3 150–3 400, 1 080, and 740  $\text{cm}^{-1}$ : the *p*-nitrobenzoate of (2h) was a solid, m.p. 156 °C (from benzene–light petroleum) (Found: C, 73.75; H, 4.7; N, 3.75.  $\text{C}_{22}\text{H}_{17}\text{NO}_4$  requires C, 73.57; H, 4.77; N, 3.90%);  $\delta$  3.11 (1 H, dd,  $J$  17.1 and 5.4 Hz), 3.66 (1 H, dd,  $J$  17.1 and 6.3 Hz), 4.63 (1 H, d,  $J$  6.3 Hz), and 5.63 (1 H, td,  $J$  6.3 and 5.4 Hz);  $\nu_{\max}$  1 725  $\text{cm}^{-1}$ : the *p*-nitrobenzoate of (2g) was a solid, m.p. 66–68 °C (from benzene–light petroleum) (Found: C, 74.8; H, 5.85; N, 3.4.  $\text{C}_{24}\text{H}_{21}\text{NO}_4$  requires C, 74.40; H, 5.46; N, 3.62): (3e) was a solid; m.p. 127–128 °C (from benzene–light petroleum) (Found: C, 85.5; H, 7.5.  $\text{C}_{17}\text{H}_{18}\text{O}$  requires C, 85.67; H, 7.61%);  $\delta$  1.27 (3 H, d,  $J$  6.3 Hz), 1.80 (1 H, br s), 2.34 (3 H, s), 3.39 (1 H, quintet,  $J$  6.3 Hz), and 4.41 (1 H, t,  $J$  6.3 Hz);  $\nu_{\max}$  3 150–3 450, 1 100, and 1 065  $\text{cm}^{-1}$ : the *p*-nitrobenzoate of (4h) was a solid, m.p. 118–119 °C (from benzene–light petroleum) (Found: C, 73.65; H, 4.75; N, 3.7.  $\text{C}_{22}\text{H}_{16}\text{NO}_4$  requires C, 73.57; H, 4.77; N, 3.90%);  $\nu_{\max}$  1 715 and 1 270  $\text{cm}^{-1}$ : (5b) was a solid, m.p. 67–69 °C (from benzene–light petroleum);  $\delta$  1.34 (3 H, d,  $J$  6.3 Hz), 1.30–1.60 (1 H, m), 1.79 (1 H, br s), 2.74 (1 H, dt,  $J$  12.6 and 6.3 Hz), 3.07 (1 H, sextet,  $J$  6.3 Hz), and 5.16 (1 H, t,  $J$  6.3 Hz);  $\nu_{\max}$  3 150–3 350 and 1 055  $\text{cm}^{-1}$ : (2i) was a solid, m.p. 165–166 °C (from benzene–light petroleum) (Found: C, 88.0; H, 6.65.  $\text{C}_{21}\text{H}_{18}\text{O}$  requires C, 88.08; H, 5.58%);  $\delta$  2.12 (1 H, br s);  $\nu_{\max}$  3 300–3 400  $\text{cm}^{-1}$ .

The acetate (6b) was an oil;  $\delta$  1.48 (3 H, d,  $J$  6.9 Hz), 1.98 (3 H, s), 2.77 (1 H, dd,  $J$  16.2 and 5.4 Hz), 3.05–3.34 (1 H, m), 3.37 (1 H, dd,  $J$  16.2 and 6.3 Hz), and 4.96 (1 H, td,  $J$  6.3 and 5.4 Hz);  $\nu_{\max}$  1 730, 1 245, and 1 040  $\text{cm}^{-1}$ : (7b) was an oil;  $\delta$  1.39 (3 H, d,  $J$  6.3 Hz), 1.95 (3 H, s), 2.90 (1 H, dd,  $J$  17.7 and 3.9 Hz), 3.20 (1 H, dd,  $J$  17.7 and 6.3 Hz), 3.36 (1 H, quintet,  $J$  6.3 Hz), and 5.46 (1 H, td,  $J$  6.3 and 3.9 Hz);  $\nu_{\max}$  1 730, 1 245, and 1 040  $\text{cm}^{-1}$ : (9b) was an oil;  $\delta$  1.35 (3 H, d,  $J$  6.3 Hz), 1.62 (1 H, dt,  $J$  12.6 and 6.3 Hz), 2.10 (3 H, s), 2.78 (1 H, dt,  $J$  12.6 and 6.3 Hz), 3.18 (1 H, sextet,  $J$  6.3 Hz), and 6.13 (1 H, t,  $J$  6.3 Hz);  $\nu_{\max}$  1 730, 1 240, and 1 040  $\text{cm}^{-1}$ : (6c) was an oil;  $\delta$  1.32 (6 H, d,  $J$  7.2 Hz), 2.04 (3 H, s), 3.09 (2 H, quintet,  $J$  7.2 Hz), and 4.08 (1 H, t,  $J$  7.2 Hz): (7c) was an oil;  $\delta$  1.14 (3 H, d,  $J$  6.3 Hz), 1.27 (3 H, d,  $J$  6.3 Hz), 3.01–3.67 (2 H, m), and 5.08 (1 H, t,  $J$  6.0 Hz): (6d) was a solid, m.p. 98–99 °C (from benzene–light petroleum) (Found: C, 81.05; H, 6.8.  $\text{C}_{16}\text{H}_{18}\text{O}_2$  requires C, 81.17; H, 6.81%);  $\delta$  1.34 (3 H, d,  $J$  6.6 Hz), 1.96 (3 H, s), 3.17 (1 H, quintet,  $J$  6.6 Hz), 4.25 (1 H, d,  $J$  6.6 Hz), and 5.15 (1 H, t,  $J$  6.6 Hz): (6e) was an oil;  $\delta$  1.38 (3 H, d,  $J$  6.6 Hz), 2.04 (3 H, s), 2.34 (3 H, s), 3.27 (1 H, quintet,  $J$  6.6 Hz), 4.33 (1 H, d,  $J$  6.6 Hz), and 5.26 (1 H, t,  $J$  6.6 Hz): (7e) was an oil;  $\delta$  1.21 (3 H, d,  $J$  6.3 Hz), 2.08 (3 H, s), 2.36 (3 H, s), 3.62 (1 H, quintet,  $J$  6.3 Hz), 4.44 (1 H, d,  $J$  6.3 Hz), and 5.37 (1 H, t,  $J$  6.3 Hz): (6g) was an oil;  $\delta$  0.99 (3 H, t,  $J$  6.3 Hz), 2.02 (3 H, s), 3.16 (1 H, q,  $J$  6.0 Hz), 4.31 (1 H, d,  $J$  6.0 Hz), and 5.36 (1 H, t,  $J$  6.0 Hz): (6h) was an oil;  $\delta$  2.04 (1 H, s), 2.95 (1 H, dd,

$J$  18.0 and 5.4 Hz), 3.54 (1 H, dd,  $J$  18.0 and 6.3 Hz), 4.49 (1 H, d,  $J$  5.4 Hz), and 5.40 (1 H, td,  $J$  5.4 and 6.3 Hz): (7h) was a solid, m.p. 59–60 °C (from benzene–light petroleum);  $\delta$  1.59 (3 H, s), 3.04 (1 H, dd,  $J$  15.9 and 3.6 Hz), 3.29 (1 H, dd,  $J$  15.9 and 6.0 Hz), 4.57 (1 H, d,  $J$  6.0 Hz), and 5.71 (1 H, td,  $J$  6.0 and 3.6 Hz): (6a) was an oil;  $\delta$  2.00 (3 H, s), 2.99 (2 H, dd,  $J$  18.0 and 3.3 Hz), 3.35 (2 H, dd,  $J$  18.0 and 6.0 Hz), and 5.42–5.62 (1 H, m): (8a) was an oil;  $\delta$  2.05 (3 H, s), 2.27–2.82 (2 H, m), 2.82–3.34 (2 H, m), and 6.20 (1 H, dd,  $J$  6.3 and 3.6 Hz): (6i) was an oil;  $\delta$  1.91 (3 H, s), 4.43 (2 H, d,  $J$  7.5 Hz), and 5.74 (1 H, t,  $J$  7.5 Hz).

The physical properties of (5h) and (9h) have been reported in the literature.<sup>15</sup>

*Reaction with N-Bromoacetamide (NBA) in Aqueous Dioxan.*—To a solution of the indene (10 mmol) in aqueous dioxan (28 ml, 4:1 v/v), was added a solution of NBA (1.2 mol. equiv.) in aqueous dioxan (18 ml, 1:1 v/v) in one portion. Then the mixture was kept with stirring at 70 °C for 20 min. After conventional work-up the crude alcohols were converted to the acetates as above. The alcohol (10b) was a solid, m.p. 109–110 °C (from benzene–light petroleum) (Found: C, 52.9; H, 4.85; Br, 35.85.  $\text{C}_{10}\text{H}_{11}\text{BrO}$  requires C, 52.89; H, 4.88; Br, 35.18%);  $\delta$  1.40 (3 H, d,  $J$  6.3 Hz), 2.63 (1 H, br s), 3.03–3.34 (1 H, m), 3.67 (1 H, dd,  $J$  8.1 and 6.9 Hz), and 5.26 (1 H, d,  $J$  8.1 Hz);  $\nu_{\max}$  3 250–3 400  $\text{cm}^{-1}$ : (11b) was a solid, m.p. 50.5–51.5 °C (from benzene–light petroleum) (Found: C, 52.85; H, 4.85; Br, 35.15.  $\text{C}_{10}\text{H}_{11}\text{BrO}$  requires C, 52.89; H, 4.88; Br, 35.18%);  $\delta$  1.38 (3 H, d,  $J$  6.3 Hz), 2.49 (1 H, br s), 3.49 (1 H, quintet,  $J$  6.3 Hz), 4.23 (1 H, t,  $J$  6.3 Hz), and 5.30 (1 H, d,  $J$  6.3 Hz);  $\nu_{\max}$  3 250–3 400  $\text{cm}^{-1}$ : (10h) was a solid, m.p. 130–132 °C (from benzene–light petroleum) (Found: C, 62.1; H, 4.35; Br, 27.7.  $\text{C}_{15}\text{H}_{13}\text{BrO}$  requires C, 62.31; H, 4.53; Br, 27.63%);  $\delta$  2.55 (1 H, br s), 4.05 (1 H, dd,  $J$  9.0 and 7.5 Hz), 4.32 (1 H, d,  $J$  9.0 Hz), and 5.34 (1 H, d,  $J$  7.5 Hz);  $\nu_{\max}$  3 300–3 450  $\text{cm}^{-1}$ : (12i) was an oil;  $\delta$  2.95 (1 H, s) and 4.57–4.66 (2 H, m): (12k) was a solid; m.p. 62–63 °C (from benzene–light petroleum);  $\delta$  2.56 (1 H, br s), 3.13 (1 H, dd,  $J$  15.0 and 8.4 Hz), 3.53 (1 H, dd,  $J$  15.0 and 8.4 Hz), and 4.62 (1 H, t,  $J$  8.4 Hz);  $\nu_{\max}$  3 250–3 300  $\text{cm}^{-1}$ .

The acetate (13a) was an oil;  $\delta$  2.03 (1 H, s), 3.18 (1 H, dd,  $J$  16.8 and 4.2 Hz), 3.65 (1 H, dd,  $J$  16.8 and 6.3 Hz), 4.34–4.62 (1 H, m), and 6.27 (1 H, d,  $J$  3.6 Hz);  $\nu_{\max}$  1 740 and 1 230  $\text{cm}^{-1}$ : (13b) was an oil;  $\delta$  1.42 (3 H, d,  $J$  7.2 Hz), 2.16 (3 H, s), 3.34 (1 H, quintet,  $J$  7.2 Hz), 3.93 (1 H, t,  $J$  7.2 Hz), and 6.43 (1 H, d,  $J$  7.2 Hz);  $\nu_{\max}$  1 740 and 1 230  $\text{cm}^{-1}$ : (14b) was an oil;  $\delta$  1.41 (3 H, d,  $J$  6.3 Hz), 2.05 (3 H, s), 3.60 (1 H, quintet,  $J$  6.3 Hz), 4.67 (1 H, dd,  $J$  6.3 and 2.7 Hz), and 6.32 (1 H, d,  $J$  2.7 Hz);  $\nu_{\max}$  1 740 and 1 230  $\text{cm}^{-1}$ : (13f) was an oil;  $\delta$  1.03 (3 H, t,  $J$  6.6 Hz), 1.86 (2 H, quintet,  $J$  6.6 Hz), 2.11 (3 H, s), 3.35 (1 H, q,  $J$  6.6 Hz), and 4.44 (1 H, dd,  $J$  6.6 and 6.0 Hz): (14f) was an oil;  $\delta$  1.04 (3 H, t,  $J$  6.6 Hz), 1.58–2.00 (2 H, m), 2.02 (3 H, s), 3.23–3.49 (1 H, m), 4.69 (1 H, dd,  $J$  6.0 and 2.4 Hz), and 6.28 (1 H, d,  $J$  2.4 Hz): (13h) was a solid;  $\delta$  2.18 (3 H, s), 4.25 (1 H, dd,  $J$  9.0 and 6.6 Hz), 4.48 (1 H, d,  $J$  9.0 Hz), and 6.54 (1 H, d,  $J$  6.6 Hz).

The physical properties of (10a) have been already reported.<sup>3</sup>

*Reaction with NBA in Methanol.*—To a solution of the indene (10 mmol) in methanol (30 ml) was added a solution of NBA (1.2 mol. equiv.) in methanol (20 ml) in one portion. The mixture was then refluxed for 20 min. After work-up

the products were isolated by column chromatography on silica gel.

The ether (15b) was an oil;  $\delta$  1.37 (3 H, d,  $J$  7.2 Hz), 3.23 (1 H, quintet,  $J$  7.2 Hz), 3.68 (1 H, s), 3.81 (1 H, dd,  $J$  7.2 and 6.3 Hz), and 4.93 (1 H, d,  $J$  6.3 Hz);  $\nu_{\max}$  1 080  $\text{cm}^{-1}$ : (16b) was an oil;  $\delta$  1.35 (3 H, d,  $J$  6.3 Hz), 3.47 (3 H, s), 3.44–3.69 (1 H, m), 4.65 (1 H, dd,  $J$  6.3 and 3.0 Hz), and 4.89 (1 H, d,  $J$  3.0 Hz);  $\nu_{\max}$  1 080  $\text{cm}^{-1}$ : (15f) was an oil;  $\delta$  0.99 (3 H, t,  $J$  6.0 Hz), 1.83 (2 H, quintet,  $J$  6.0 Hz), 3.27 (1 H, q,  $J$  6.0 Hz), 3.63 (1 H, s), 4.08 (1 H, t,  $J$  6.0 Hz), and 4.94 (1 H, d,  $J$  6.0 Hz);  $\nu_{\max}$  1 090  $\text{cm}^{-1}$ : (16f) was an oil;  $\delta$  1.01 (3 H, t,  $J$  6.0 Hz), 1.50–2.10 (2 H, m), 3.23–3.40 (1 H, m), 3.42 (1 H, s), 4.68 (1 H, dd,  $J$  6.0 and 3.0 Hz), and 4.86 (1 H, d,  $J$  3.0 Hz);  $\nu_{\max}$  1 090  $\text{cm}^{-1}$ : (15h) was an oil;  $\delta$  3.66 (3 H, s), 4.07–4.22 (1 H, m), 4.14 (1 H, d,  $J$  8.7 Hz), and 5.06 (1 H, d,  $J$  6.3 Hz): (16h) was an oil;  $\delta$  3.56 (3 H, s), 4.67–4.79 (1 H, m), 4.87 (1 H, d,  $J$  6.3 Hz), and 5.07 (1 H, d,  $J$  3.6 Hz): (17i) was a solid;  $\delta$  3.14 (3 H, s), 4.20 (1 H, d,  $J$  9.3 Hz), and 4.73 (1 H, d,  $J$  9.3 Hz).

*Lithium Aluminium Hydride Reduction of Indanones.*—The alcohols (3h), (5a), (5f), and (5h) were obtained by treating the corresponding indanones with lithium aluminium hydride (2 mol. equiv.) in ether under reflux for 1 h (for the physical properties see the section on hydroboration).

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